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Pesticide spray drift monitoring in the evaluation of air dispersion models: A South African atrazine case study

By

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Submitted in partial fulfilment of the requirements for the degree

Master of Science (Chemistry)

In the Department of Chemistry, Faculty of Natural and Agricultural Sciences

University of Pretoria

July 2015

Declaration of Authorship

I, Sifiso Albert Nsibande, declare that this dissertation, which I hereby submit for the degree Masters in Science at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signed: _____   Date: _____

Acknowledgements

I would like to express my sincere gratitude to Dr Patricia Forbes, my study leader, for expertly guiding and supporting me as I was doing this exciting project. I truly appreciate her patience and motivation, and for inspiring confidence in me as a person.

My appreciation also extends to Etienne van der Walt for all his insightful comments and advice. Dr James Dabrowski is thanked for all his contributions from sample collection and to reviewing my work for conference and journal publications. I am grateful to Anette Venter for her valuable assistance with laboratory analysis. Justinus Shadung and Ernst Bekker assisted me with sample collection for which I am grateful. The farm owners in Standerton are deeply thanked for kindly allowing me to use their farm for this study.

Gratitude goes to the following institutions: the Water Research Commission (WRC) for financially supporting this project as well as my studies at Tuks; the Agricultural Research Council Plant Protection Research Institute (ARC-PPRI) for their assistance with my sample collection and analysis; the National Association for Clean Air (NACA) for offering me a bursary as well as funding my attendance of the IUAPPA 2013 conference in Cape Town; PerkinElmer® for being kind to allow me to analyse some of my samples in their labs; and finally Anatech for sponsoring me to attend the Analitika 2014 conference in Parys.

I would also like to thank all my colleagues in the students' office for being there to talk to, for asking how I was doing, and for your kindness. Thanks to Leandri van der Wat for occasionally lifting my mood with cake, coffee, and snacks in the office; and Neil Milan for basically being my search engine.

Finally I thank my beautiful family for their love, support, and words of encouragement which kept me going.

Abstract

Air dispersion software models that evaluate pesticide spray drift during application have been developed. These models can potentially serve as a cheaper and more 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 project, a pesticide active ingredient, namely atrazine, was used as a tracer to monitor spray drift up to 400 m downwind for comparison and validation of the AGricultural DISPersal (AGDISP) model outputs. Airborne drift samples were collected using high volume air sampling onto polyurethane foam (PUF) at six downwind locations while ground deposition drift was captured with chromatography fallout paper samplers. Additional data, including meteorological information and some application parameters required to simulate spray drift with AGDISP, was collected.

Airborne samples were extracted with a plunger method using a hexane:acetone solvent mixture and analysed by Gas Chromatography coupled to a Nitrogen Phosphorus Detector (GC-NPD) which performed well (94.5% recovery, 3.3% RSD and LOD 8.7 pg). Atrazine airborne concentrations ranged from 4.55 ng L^{-1} adjacent to the field to 186 pg L^{-1} at 400 m downwind. The experimental results correlated favourably with the modelled output, suggesting that the AGDISP model can be used to provide a good estimate for airborne drift in risk assessment studies or for regulatory purposes.

A simple and rapid screening method using a Direct Sample Analyser coupled to a Time-of-Flight Mass Spectrometer (DSA-TOFMS) was employed for semi-quantitation of atrazine deposition. This method was shown to be quick (30 min extraction and 25 s analysis) and useful for the large sample set that was collected. The deposition sample extracts were also analysed by GC-NPD using a method similar to that used for airborne samples. Compared to the AGDISP-simulated deposition output, the model under-predicted the deposition by up to one order of magnitude compared to the GC-NPD results and even more compared to the DSA-TOFMS results. This suggested that the model should be used cautiously for predicting pesticide deposition.

For the first time this project has shown the use of a pesticide active ingredient to validate the AGDISP ground application model under local South African conditions up to 400 m downwind of the application area.

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List of Abbreviations

AERMOD	American Environmental Regulatory Model
AGDISP	AGricultural DISpersal
AgDRIFT®	Agricultural Drift Model
ANOVA	Analysis of Variance
APCI	Atmospheric Pressure Chemical Ionization
APVMA	Australian Pesticides and Veterinary Medicines Authority
ARC-PPRI	Agricultural Research Commission – Plant Protection Research Institute
ASAE	American Society of Agricultural Engineers
ASE	Accelerated Solvent Extraction
BLM	Bureau of Land Management
BSF	Brilliant Sulfo Flavin
CFD	Computational Fluid Dynamics
DAFF	Department of Agriculture, Forestry and Fisheries
DCM	Dichloromethane
DOE	Design of Experiments
DRTs	Drift Reduction Technologies
DSA-TOFMS	Direct Sample Analyser coupled to Time-of-Flight Mass Spectrometer
DSD	Droplet Size Distribution
EDTA	Ethylenediaminetetraacetic acid
FDM	Fugitive Dust Model
FM	Fortified Matrix
FSCBG	Forest Service Cramer-Barry-Grimm
FSCBG	US Forest Service Cramer-Barry-Grimm model
GC-NPD	Gas Chromatography coupled to Nitrogen Phosphorus Detector
GDM	Gaussian Diffusion Model

GFF	Glass Fiber Filter
GUI	Graphical User Interface
HBC	Hexachlorobenzene
IDEFICS	IMAG program for drift Evaluation from Field sprayers by Computer Simulation
ISCST3	Industrial Source Complex Dispersion model
LIDAR	Light Detection and Ranging
LOD	Limit of Detection
LOQ	Limit of Quantification
MAE	Microwave Assisted Extraction
NEMAQA	National Environmental Management Air Quality Act
OCs	Organochlorine
OPs	Organophosphorus
PAN	Pesticide Action Network
PCBs	Polychlorinated Biphenyls
PFBBR	Pentafluorobenzyl Bromide
PFE	Pressurized Fluid Extraction
PGG	Polymer-Coated Glass
PLE	Pressurized Liquid Extraction
POPs	Persistent Organic Pollutants
PUF	Polyurethane Foam
QFF	Quartz Fiber Filter
RSD	Relative Standard Deviation
SFE	Supercritical Fluid Extraction
SIM	Selected Ion Monitoring
SPE	Solid Phase Extraction
SPMDS	Semi-Permeable Membrane Devices
STDF	Spray Drift Task Force
TSD	Thermionic Specific Detector

USEPA	United States Environmental Protection Agency
VMD	Volume Median Diameter
WRC	Water Research Commission
WTDISP	Wind Tunnel Dispersion
XAD	Hydrophobic cross-linked polystyrene copolymer resin
HPLC-UV	High Pressure Liquid Chromatography with Ultra-Violent detection

Chapter 1   Background to the Study

1.1   Pesticides

According to van der Hoff and van Zoonen (1999) pesticides can be described as substances or mixtures of substances intended for preventing, destroying, repelling, or mitigating any pest. These pests can be insects, mice and other animals, unwanted plants (weeds), fungi, or microorganisms like bacteria and viruses. Pesticides are normally grouped and named according to the type of pest they control, for example herbicides, algaecides and insecticides are used to control herb, algae and insects respectively. They may also be grouped according to their chemical structure, for example organochlorides and triazines (USEPA, 2014a).

Although pesticides are important in agriculture to ensure high crop yields, and therefore food security, their extensive use in agricultural areas can cause serious contamination of air, water, soil and other natural resources through various pathways. The persistent nature of some of these compounds in the environment may also pose serious health effects whose reversibility is not known (Patterton, 2013).

Maybank *et al.* (1978) stated that some 30 – 40% of an initially deposited agricultural chemical (agrichemical) can evaporate and drift downwind as vapour in just 2 hrs after application. Salyani and Cromwell (1992) highlighted that 10 – 60% of applied chemicals can drift more than 300 m off the targeted crop, and a similar assertion was made by van den Berg *et al.* (1999) who suggested that during application up to 30 – 50% of the amount applied can be lost to the air. This shows some of the inefficiencies of the application process and a loss to the farmer, but most importantly it shows that a significant amount of pesticides can be introduced to the atmosphere during application. Although most pesticides are specifically designed to have low persistence in the environment, they still undergo atmospheric transport at regional or global scales. For example, triazines, acetanilides and phenoxyacids are sufficiently stable to undergo atmospheric transport over 100 – 1000 km (van Dijk & Guicherit, 1999).

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1.2   Effects of Pesticide Contamination of the Environment

Pesticide use can potentially lead to contamination of surrounding natural resources thereby causing direct or indirect exposure to humans and other organisms in the ecosystem through different pathways. Even though they may occur at low concentrations, the continuous exposure to these compounds can lead to serious long-term effects (Patterton, 2013).

Aquatic systems are susceptible to direct effects of pesticides because after application pesticides can easily enter water systems through runoff, spray drift deposition, or erosion. For example, pesticides have been shown to have an impact on the invertebrate community composition in aquatic systems (Liess & Ohe, 2005). Also, a number of pesticides have been shown to have endocrine disrupting effects in some animals (Hass *et al.*, 2012; Hrouzková & Matisová, 2012; Kojima *et al.*, 2004). This may affect sex hormones thereby affecting the reproduction of the affected organism. It has also been shown that pesticide mixtures can also interact synergistically thereby causing enhanced toxicity in some aquatic species (Norgaard & Cedergreen, 2010).

Another environmental problem associated with pesticides is that they tend to bioaccumulate in aquatic organisms (Bussolaro *et al.*, 2012; Zhang *et al.*, 2014; Zhao *et al.*, 2014b). This phenomenon can serve as a vehicle for exposure to humans or any other higher organisms in the food chain.

According to Bedos *et al.* (2002), pesticides can occur in the atmosphere either in the particulate, gaseous or liquid phase and they can easily enter the atmosphere during application through wind effects (drift) or evaporation (Sanusi *et al.*, 1999; Sauret *et al.*, 2008; Schummer *et al.*, 2010). Even after application, pesticides can still enter the atmosphere through volatization from crops or the soil surface as well as through wind erosion. In the atmosphere they can undergo transformations via different degradation pathways (hydrolysis in water and soils, and photolysis and reaction with ·OH radicals in the atmosphere) (De Rossi, 2010). Once they enter the atmosphere, pesticides can undergo both regional (Muir *et al.*, 2004) and long range (Oehme, 1991) transport. A study by Murray and Vaughan (1970) measured pesticide drift up to over 6 km away from the application site. Air currents can transport pesticides over thousands of km to areas as remote as the polar regions (Unsworth *et al.*, 1999). Pesticides in the gas phase can be removed from the atmosphere through dissolution into precipitation and surface water and

sorption onto soil and vegetation. Those that are particle-bound can be washed out of the atmosphere by precipitation or removed by dry particle deposition to surface water, soil, or vegetation (Foreman *et al.*, 2000). A summary of possible routes of pesticide circulation in the atmosphere is shown in Figure 1.1.
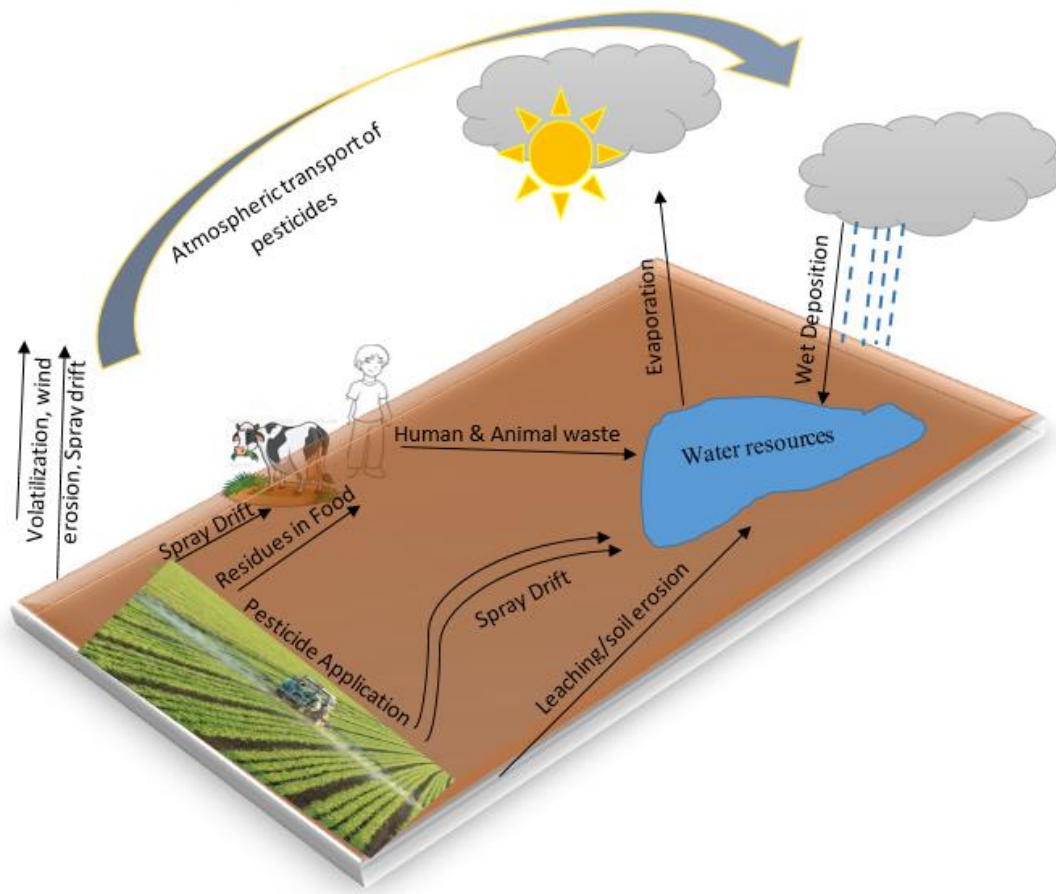
Figure 1.1 Schematic diagram showing the possible route routes of pesticide circulation in the environment (adapted from Kosikowska and Biziuk (2010))

1.3   Pesticide Spray drift

Pesticides are usually applied to crops by means of spraying. During this process, some of the spray material may drift away from the target area. Pesticide spray drift can simply be defined as the spray material which unintentionally reaches areas outside the target area either as droplets, dry particles or vapour, during or after application on the target area (Carlsen *et al.*, 2006a). The United States Environmental Protection Agency (USEPA) defines spray drift as the movement of a pesticide through the air off the target site during or immediately after application or use,

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where an off- target site can mean deposition on immediately adjacent areas or 'extended airborne displacement' (Miller & Stoughton, 2000).

The growing concern about pesticide spray drift is that it can cause serious environmental contamination and a potential hazard (Murray & Vaughan, 1970). A number of studies have suggested that spray drift is one of the important routes for pesticide contamination of natural surface waters and off-crop habitats (Dabrowski & Schulz, 2003; Wang & Rautmann, 2008). Environmental contamination by pesticides may result in adverse effects to humans, plants and animals that utilize these contaminated resources. The effects of pesticides on aquatic life are well documented as discussed in section 1.2.

The factors that affect the extent of spray drift are discussed in detail in Chapter 2. In broad terms spray drift is largely influenced by meteorological factors, application factors, and the type and composition of the pesticide formulation being applied (Miller *et al.*, 2011). Although there are some ways that have been developed to reduce drift during application, it still remains an environmental concern.

1.4   Pesticide Use and Management in South Africa

South Africa is the highest user of pesticides in sub-Saharan Africa (Dalvie *et al.*, 2009) and this can be related to the country's intensive agricultural activity. A recent report states that there are over 3 000 approved pesticide products for use in South Africa (DAFF, 2010). South Africa is also one of the largest importers of pesticides (Osibanjo *et al.*, 2002; Quinn *et al.*, 2011).

In an effort to protect the environment against these substances, the country has a number of laws in place and they are regulated by different government departments. Relevant South African laws include the National Water Act no. 36 of 1998, the Environment Conservation Act no. 73 of 1989 and the Fertilizers, Farm Feeds, Agricultural Remedies and Stock Remedies Act of 1947 (Naidoo & Buckley, 2003). Due to the growing concern on air quality, the National Environmental Management Air Quality Act no. 20 of 2014 was introduced to amend the National Environmental Management Air Quality Act no. 39 of 2004 (NEMAQA, 2014).

A Pesticide Management Policy has recently been adopted by the Department of Agriculture, Forestry and Fisheries (DAFF, 2010) which seeks to ensure that pesticides are used in ways that

lead to the minimization of significant adverse effects on human health and the environment. It also seeks to encourage the development of alternative techniques to reduce the dependence on pesticides.

1.5 Pesticide Modeling

Pesticide regulators in some developed countries are using mathematical model software programmes to simulate pesticide drift. In the USA for example, the government, through the US Environmental Protection Agency, has adopted a number of different models to assess possible risks of pesticide exposure to human health or the environment, via aquatic, terrestrial, atmospheric and health effects assessments (USEPA, 2014b).   Among the atmospheric dispersion models, the AGricultural DISPersal (AGDISP) and AgDrift models are of particular interest to this study. Governments in some developed countries like Australia, Canada and New Zealand, are also using these models for pesticide spray drift risk assessments (APVMA, 2010).

In South Africa pesticide regulators have not yet used these models for simulating pesticide spray drift during application. Caution needs to be taken when employing these models because although they are very useful, they could generate different results from real field data because of differing interactions of pesticides with different crops, as well as temporal and spatial variation in environmental conditions (Gil & Sinfort, 2005). There is therefore ongoing research that is aimed at validating and improving the prediction power of these models under different conditions.

1.6 Aims and Objectives of this Study

This project formed part of a broader research study that was commissioned by the Water Research Commission (WRC) entitled "Investigation of the contamination of water resources by agricultural chemicals and the impact on human health" (WRC, 2013). The aim of this particular work was to validate an air dispersion model which could be used to predict spray drift for human exposure risk assessment studies.

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The specific objectives were therefore to:

1. Monitor pesticide spray drift during pesticide application at a large scale agricultural farm. This required that a method to sample and quantify the spray drift of the active pesticide be developed.

2. Use the data collected during the sampling campaign as input data to the AGricultural DISPersal (AGDISP) model and then to compare the model output with the monitoring data for model validation purposes. In addition necessary recommendations in terms of model uncertainties for using the model under local conditions were to be determined.

1.7 Justification for this Study

Given the high usage of pesticides in South Africa and the harmful effects they can pose to both humans and the environment, as highlighted in section 1.2, there is a crucial need for studies to be conducted to investigate possible environmental effects of the usage of these agrichemicals. Spray drift during application is a route of pesticide entry to the environment, therefore it is vital to evaluate drift in order to assess the possible impact thereof on sensitive surrounding areas. The high costs of field monitoring campaigns and the variation in environmental conditions during monitoring warrants the need to evaluate the alternative of using computer models to simulate drift. Atrazine is a pesticide which is used in large quantities in South Africa (Dabrowski *et al*, 2014); it is also stable in the atmosphere, therefore it was suitable for use as a tracer in the validation of such an air dispersion model.

1.8 Structure of the Thesis

Following this introduction, Chapter 2 of this thesis provides a review of both pesticide spray drift and analytical approaches for determining pesticides in the atmosphere. Chapter 3 gives a review of air dispersion models which are used to simulate spray drift during pesticide application, focusing on the AGDISP model. Chapter 4 details the experimental methods employed and the results are presented in Chapter 5. Lastly, an overall conclusion of the study is given in Chapter 6.

Chapter 2   Literature Review

2.1   Atrazine

Atrazine (6-chloro-4-N-ethyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine) is a widely used herbicide for controlling annual broad-leaved weeds and grasses in pre- or post-emergent crops like maize, sorghum and sugar cane. It kills weeds by inhibiting the photosynthetic electron transport, but the target crop is tolerant to atrazine because of rapid detoxification (MacBean, 2012). The chemical structure of atrazine is shown in Figure 2.1 while Table 2-1 provides some of its physicochemical properties. These properties are important in determining the fate and lifetime of the compound in the environment. The Henry's constant, for example, describes the tendency to volatilize from aqueous to gas phase and atrazine is considered to be moderately volatile (Ratola *et al.*, 2014).   The solubility describes the ability to mix with aqueous particles or droplets and therefore determines the dry or wet deposition of the compound (Hodzic *et al.*, 2013). According to a scoring scheme by Ratola *et al.* (2014), atrazine is considered to have a low deposition potential and in soil it can be highly mobile because it does not adsorb strongly to the soil particles (Log $K_{SA} < 8$).
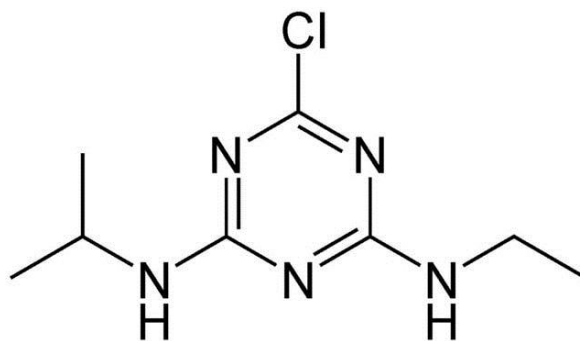
Figure 2.1 Chemical structure of atrazine

Table 2-1 Physicochemical properties of atrazine

Property	Value
Molecular Weight[1]	215.7 g mol^{-1}
Molecular formula[1]	$C_8H_{14}ClN_5$
Form[1]	Colourless powder
Melting point[1]	175.8 °C
Boiling point[1] (at 101 kPa)	205.0 °C
Vapour pressure[1] (at 25 °C)	3.85×10^{-2} mPa
K_{ow} log P[1]	2.5 (25 °C)
Henry's constant[1]	1.5×10^{-4} Pa m^3 mol^{-1}
Density[1] (at 22 °C)	1.23 g cm^{-3}
Solubility[1]:	
in water (at 22 °C, pH 7)	33 mg L^{-1}
in acetone (25 °C)	31 g L^{-1}
in n-hexane (at 25°C)	0.11 g L^{-1}
Volatilization potential[2]	
Water-air:	
Soil-air:	
k_d	2.60
Log K_{SA}	7.18
Deposition potential[2], Φ (%)	17.60

K_{SA} – volatilization potential from soil to air

k_d – distribution coefficient from soil and soil-water partitioning

K_{ow} – octanol-water partition coefficient

[1]MacBean (2012)

[2]Ratola et al. (2014)

Because of its high annual use in agriculture, atrazine has been one of the most frequently detected pesticides in freshwater systems in many parts of the world. For example, Gilliom (2007) showed it to be the most frequently detected pesticide in USA surface and ground water systems. A similar assertion has been made for European ground water (Gavrilescu *et al.*, 2014). In South Africa, atrazine has also been shown to have the largest number of seasonal occurrences (Patterton, 2013). A recent study by Dabrowski *et al.* (2014) dealing with the prioritization of pesticides that are used in South Africa, featured atrazine as the highest ranked pesticide among

25 priority pesticides. Their ranking and prioritization was based on a weighted hazard potential (WHP) – a prioritization index which is directly proportional to the pesticide's toxicity potential (TP) and total quantity of use.

Several studies have found atrazine in South African freshwater systems (Dabrowski *et al.*, 2013; Du Preez *et al.*, 2005; Pick *et al.*, 1992) which is due in part to the high usage of this pesticide, as shown in Table 2-2.

Table 2-2 Use of atrazine in South Africa for the year 2009 (Dabrowski & Schadung, 2011)

Crop	Crop area (10^3 ha)	Base Area (10^3 ha)	Area treated (10^3 ha)	Dose rate (kg or L ha^{-1})	Volume (10^3 kg or L)
Sorghum	87.00	87.00	20.42	2.106	43.015
Corn	2750.00	2750.00	915.89	0.936	890.981

Once in water systems, atrazine can have harmful effects on aquatic life, such as endocrine disrupting activity (Giusi *et al.*, 2006; Hayes *et al.*, 2010; Hrouzková & Matisová, 2012). Alarmingly, some studies have shown atrazine to be an endocrine disruptor in human cells (Fan *et al.*, 2007; Sanderson *et al.*, 2000). Atrazine can be quite persistent in water as a study by (Thurman & Cromwell, 2000) in Lake Superior in Canada, suggested that the half-life of atrazine in lakes was over 10 years.

In the atmosphere, atrazine is fairly stable and has been shown to be capable of undergoing regional atmospheric transport up to over 1 000 km (Muir *et al.*, 2004). The degradation pathway of atrazine in the atmosphere is through ·OH radical attack. If this attack occurs with a rate constant of 1.4×10^{-11} cm^3 s^{-1}, and if the ·OH concentration is between $5 - 10 \times 10^{-5}$ cm^3 then the average lifetime of atrazine is approximately 1 day. Also, if the mean wind speeds are $3 - 5$ m s^{-1}, then it can travel $250 - 500$ km within a day before any significant degradation can occur (De Rossi, 2010). Thus the atmosphere is also a potential exposure route especially for humans and animals through inhalation.

The stability of atrazine in the atmosphere makes it suitable for use as a spray drift tracer during application. A study by Ravier *et al.* (2005) successfully used atrazine to monitor atmospheric spray drift up to 134 m downwind. It can be easily trapped onto sampling media such as filter paper or polyurethane foam (PUF) and the analysis does not require any derivatization.

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Analytical techniques such as gas chromatography coupled with mass spectrometry (GC-MS) or nitrogen phosphorus detector (GC-NPD) are normally used for quantitation.

Atrazine can undergo transformations in the environment to dealkylated, hydroxylated, and chlorinated products (Qiao *et al.*, 1996). It is also persistent in soil where it has a half-life of between 77 – 101 days in surface soil and over 900 days in subsurface soil (Blume *et al.*, 2004).

2.2 Spray Drift

2.2.1 Factors affecting spray drift

A lot of research has been done to try and understand the different factors that could possibly affect spray drift during application. Some researchers have used computer simulation methods (Hobson *et al.*, 1993; Holterman *et al.*, 1997), while others have utilised wind tunnel experiments to investigate these factors. Miller *et al.* (2011) stated that spray drift is largely influenced by the droplet size distribution (DSD) that the nozzles produce, the height at which the spray liquid is released, and the wind speed at the time of spraying. Using both experimental data and the computational fluid dynamic (CFD), Nuyttens *et al.* (2013) reached a similar conclusion and stated that the most influential factors are the fraction of small droplets and spray boom height. In a different study, Holterman *et al.* (1997) concluded that wind speed, boom height, and nozzle size were the major factors affecting spray drift. Most of the factors described below indirectly affect spray drift because of their effect on droplet size.

2.2.1.1 Meteorological conditions

The effects of meteorological factors on spray drift is well documented (Nuyttens *et al.*, 2006b). Meteorological parameters mainly affect the rate at with droplets evaporate upon being released through nozzles, thereby decreasing the droplet size. Differences in meteorological conditions make it difficult to compare previously reported information with recent studies due to an inability to isolate and correct for weather differences (Nuyttens *et al.*, 2008).

Wind Speed

From studies conducted by the Spray Drift Task Force (SDTF) Bird *et al.* (1996) noted that wind speed and atmospheric stability were the only meteorological parameters that correlated with off-target deposition. They noted that higher wind speeds increased both near- and far- field ground

deposition and increasing atmospheric stability correlated with higher far field deposition. Studies by Phillips and Miller (1999) showed that the downwind airborne spray volume in the air from a single stationary nozzle increased linearly with wind speed in the near-field during neutral conditions.

In a wind tunnel experiment to compare droplet size effects, Fritz *et al.* (2010) found that the volume median diameter (the droplet diameter size marking where 50% of the spray volume is reached – denoted VMD or $D_{V0.5}$) decreased by 30% to 50%, as the wind speed in high-speed airstreams increased from 45 to 63 m s^{-1} When they performed air dispersion modelling (using the AGDISP model, which will be discussed in Chapter 3), they found increased downwind deposition for higher wind speeds, an observation they attributed to the increased number of finer droplets in the spray. Hoffmann (2006a) found that when actual weather conditions during application were used as input for the AGDISP model, a 1.5 m s^{-1} increase in wind speed resulted in a 100% increase in the spray flux at 50 m from the application site.

Relative Humidity

Relative humidity is the second most important meteorological factor, after wind speed, that significantly affects spray drift (Huang *et al.*, 2010; Miller *et al.*, 2000). This is because of the relationship between relative humidity and droplet size, where relative humidity affects droplet evaporation in the atmosphere which in turn determines how long an aerosol remains suspended in the atmosphere. Water is also commonly used as a pesticide carrier. Relative humidity is said to be the primary meteorological factor that affects droplet evaporation (Miller *et al.*, 2000) and thus droplet size. The droplet size in turn determines how long an aerosol remains suspended in the atmosphere.

Temperature

Temperature affects the evaporation rate of the droplets produced during spray applications. At higher temperatures the droplets evaporate very quickly and become smaller and therefore can drift further prior to deposition (Enz *et al.*, 2014; Hanna & Schaefer, 2009). A study by Zhu *et al.* (1994) showed that the effect of temperature is more pronounced on smaller droplets because they have greater surface area to volume ratios and longer flight times compared to larger

droplets. They also showed that temperatures between 10 and 30 ˚C have little influence on 200 μm diameter or larger water droplets.

According Miller *et al.* (2000) the term "atmospheric stability" includes both static stability and dynamic stability processes. Static stability refers to the atmosphere's capability for buoyant convection. Air that is positively buoyant and less dense than surrounding air will tend to rise, whilst air that is negatively buoyant and denser than surrounding air tends to subside, such as during atmospheric inversion conditions. Dynamic stability refers to the effects of wind shear generated (mechanical) turbulence on the static stability condition. High mechanical turbulence causes mixing and reduces the buoyancy effects. Therefore higher wind speeds act to decrease the intensity of the thermal stability by reducing the relative buoyancy.

Spray drift studies conducted by Miller *et al.* (2003a) after application of malathion on an 11 m high pecan orchard with an air-blast orchard sprayer, showed atmospheric stability to be the primary factor affecting spray drift measured on and above an adjacent field. They found the amount of spray drift collected under very stable conditions to be more than 2 times the amount collected under unstable conditions. A different study by Miller and Stoughton (2000) in which they tracked the drift plume of small suspended droplets after application of a biological pesticide with an elastic-backscatter lidar, also confirmed this observation.

2.2.1.2   Application Technique

Application parameters such as the nozzle type and size, sprayer driving speed, boom height, and the spray pressure have been shown to have an effect on spray drift for ground applications (Nuyttens *et al.*, 2006a). In most cases these parameters can be controlled by the operator and can therefore be manipulated to achieve minimal spray drift. While some studies were looking at these factors separately, a study by Hassen *et al.* (2013) showed that a combination of the nozzle type, nozzle angle, and nozzle pressure can have an influence on spray drift. They found that flat fan nozzle type TPE with a nozzle angle of 80° and nozzle pressure of 300 kPa gave the best spray distribution.

Nozzle type

The nozzle type, size, and pressure that is used during pesticide application can have a significant influence on the droplet size distribution (DSD) that is produced by the sprayer. It has been found that the larger the nozzle size, the larger the droplet size spectrum produced (Nuyttens *et al.*, 2007). A study by Jones *et al.* (2002) showed that air induction type nozzles produce the largest droplet size and smallest volume of very fine droplets. This is desirable because large droplets are less susceptible to drift and thus improve the application efficiency. Hassen *et al.* (2014) investigated the effect of different spray fan angles, namely 65°, 80° and 95°, on spray drift. They found that the nozzle angle had a significant effect on the total spray drift and an angle of 65° resulted in the highest reduction of spray drift compared to the other angles.

Application height

A study by Huang and Thomson (2012) where an adjuvant (Syl-Tac[®]) and a rubidium chloride tracer were sprayed, showed that aerial application at different altitudes (3.7 m, 4.9 m, and 6.1 m) had a significant effect on downwind spray deposition. Even for ground applications the release height has been shown to have significant effects on spray drift. Nuyttens *et al.* (2006a) showed that lowering the spray boom height from 0.50 m to 0.35 m reduced spray drift by 52%.

Crop canopy

Hoffmann (2006b) observed that when crop height inputs into the AGDISP (version 8.08) air dispersion model were changed from 0.3 m to 1.3 m, the spray flux decreased by 20-fold, suggesting the dramatic filtering effect that a canopy can have on a spray cloud. Having made this observation, in the following year Hoffmann *et al.* (2007) carried out some sensitivity studies in cotton fields to quantify the effects of different crop canopy characteristics, such as height and canopy closure, on spray deposition and drift upon aerial application of a solution with a dye tracer. They kept the application height at 3 m above canopy for all simulations they investigated canopy heights (CH) from 0, 0.7 and 1 m. Their results showed a higher deposition where there was no canopy (Figure 2.2).
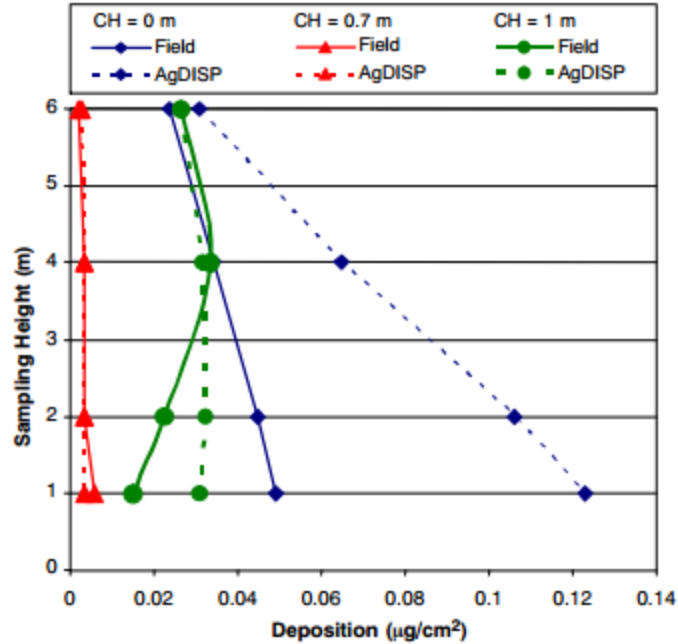
Figure 2.2 Comparison of field and AGDISP vertical deposition for different canopy heights (Hoffmann *et al.*, 2007).

2.2.1.3   Spray Material

The dependence of spray drift on the nature of the spray material can be explained in terms of the evaporation rates of the different materials. The rate of evaporation of the tank mix diluent influences the eventual downwind pesticide spray drift (Teske *et al.*, 1998). In turn, the evaporation rate directly influences the droplet sizes, with smaller droplets being capable of drifting further downwind compared to larger droplets.

Fritz *et al.* (2010) studied the effects of spray mixtures on droplet size, and hence spray drift, under aerial application conditions. From the AGDISP air dispersion model predictions they found differing amounts of downwind deposition at similar air speeds for different formulations. They concluded that while mimic and simulated sprays can give similar atomization results and follow similar trends with respect to effects on droplet size from changes in wind speeds, active ingredients *can* have a significant effect on the atomization of spray solutions.

(Hewitt *et al.*, 2009) performed a wind tunnel study which showed that the droplet size distribution is dependent on the composition of the spray material. For a tank mix of 44%

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glyphosate they found a volume median diameter (VMD) of 158 μm, whilst for a tank mix of 4.9% glyphosate the $D_{v0.5}$ was 140 μm. They found the droplet size distribution for tank mixes containing glyphosate to be considerably finer than those containing water, as glyphosate has surfactant properties which lower the surface tension. The droplet size became finer with increasing aircraft speed.

Miller and Ellis (2000) looked at the effect of formulation on nozzle performance for ground applications. They deduced that water-soluble formulations are likely to increase spray drift compared to formulations which form emulsions. This is because emulsions give sprays that are coarser than those from water-soluble formulations. They also concluded that changes in the physical characteristics of the spray liquid will mostly affect air induction nozzle systems as opposed to conventional hydraulic pressure nozzles.

De Schampheleire *et al.* (2009) found that the dynamic surface tension of spray formulations is the major property of the spray material that affects drift. They also found that the addition of a polymer drift-retardant increased the viscosity of the spray liquid, thus forming coarser droplets, which subsequently reduced drift significantly. This was also supported in a study by Celen (2010) conducted with an airblast sprayer on vineyards, where it was shown that treating the spray material with three different adjuvants had an impact on the downwind deposition of the applied formulation.

2.2.2   Means of Spray Drift Mitigation

Finding ways of minimizing spray drift can result in a commensurate increase in application efficiency and cost reduction due to off-site losses. Drift reduction is also important for minimizing possible non-target environmental contamination.

According to Carlsen *et al.* (2006b), spray drift can generally be reduced significantly by spraying under conditions where there is low wind speed, low temperature, low turbulence, low radiation from the sun, and high relative humidity. Drift can also be reduced by avoiding fine droplets (achieved by adding additives to the spray material, for example), by minimizing spraying boom height, and by minimizing the release pressure at the nozzles.

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Means of reducing spray drift have been investigated in a number of studies in the past (Hoffmann *et al.*, 2010; Vischetti *et al.*, 2008). According to Hoffmann *et al.*, the ways of reducing spray drift – drift reduction technologies (DRTs) – involve modification of spray nozzles, sprayer modifications, spray delivery assistance, spray property modifiers, and/or land scape modifications with the intent of minimizing spray drift. Therefore ways of reducing spray drift include the use of low drift nozzles, air-assist sprayers, drift control additives and sprayer shields (Pepper *et al.*, 2001).

Miller *et al.* (2011) showed that the use of nozzles having spray fan angles of less than 110° can reduce the risk of drift when releasing spray material at heights that are greater than 0.5 m. They showed that using the minimum possible release height is very crucial for any drift control strategy especially when medium or fine spray qualities are required for an application.

Fritz *et al.* (2011) conducted a study where they evaluated performance of some drift reduction technologies (DRTs) that were proposed by the United States Environmental Protection Agency (USEPA). They judged the performance of each DRT by measuring the downwind deposition on horizontal fallout collectors. They found that the use of different adjuvants and/or surfactants can affect the recoveries of pesticides from the fallout collectors, therefore correcting for recovery is important where relevant comparisons between DRTs are to be made.

2.2.3   Techniques for field monitoring pesticide spray drift

There are a number of ways to monitor spray drift during pesticide application (Donkersley & Nuyttens, 2011). Two of the most useful and widely used techniques are based on (i) sedimentation of the pesticide aerosol onto horizontal surfaces and (ii) measurement of airborne pesticide concentrations at defined downwind locations from the application site by either actively drawing air onto adsorbent surfaces or by passively intercepting the airborne flux with suitable adsorbent materials (Wolters *et al.*, 2008). Both of these sets of data are commonly collected in spray drift studies. Information on deposition is mainly useful in assessing the risks of pesticides settling into nearby surface water systems (Schulz, 2001), non-target crops and soil, while airborne concentrations are important for bystander exposure and inhalation assessments (Butler Ellis *et al.*, 2010; De Schampheleire *et al.*, 2007; Tupper *et al.*, 2012).

When measuring spray drift, it is important to consider the nature of the exposed environment nearby in order to make meaningful interpretations of the results. Measurement and predictions of the effective spray drift dose received by horizontal surfaces (like surface waters and ground-based vegetation) can be very different from those received by vertical taller surfaces (like human bystanders and buildings) which can intercept and collect more airborne spray. Butler Ellis and Miller (2010) showed, using both measurements and computer simulations (Silsoe Spray Drift Model developed by the same authors), that there are indeed significant differences between airborne and ground-deposited spray drift (Figure 2.3) and these should therefore be interpreted differently.
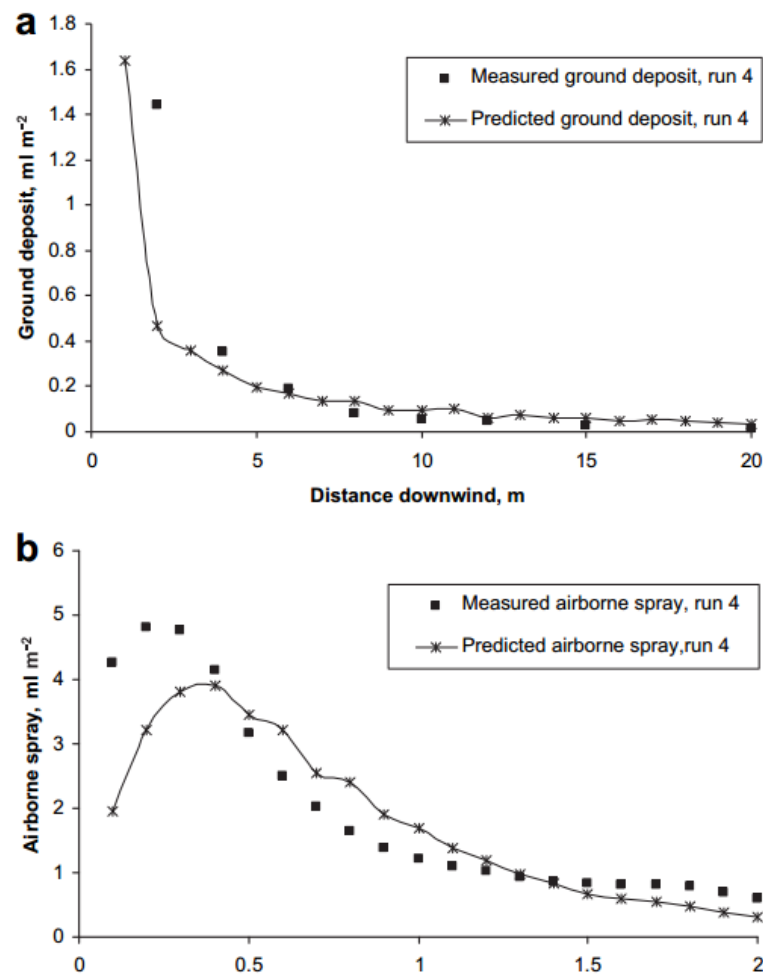
Figure 2.3 Comparison between predicted and measured (a) ground deposition and (b) airborne pesticide spray profile at 2.0 m downwind for a single experimental run (Butler Ellis & Miller, 2010).

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It is therefore common practice in pesticide spray drift studies to measure both airborne flux and ground-deposited spray in order to make meaningful exposure assessments.

Different types of collector materials can be used to sample and quantify the drift tracer material (Table 2-3). A study by (Bui *et al.*, 1998) compared different types of samplers that can be used to monitor spray drift. These included (i) high-volume sampler with glass fiber filter (ii) horizontal alpha cellulose fallout sheets, (iii) high volume air samplers, (iv) sampling trains of rotary disk impactors, (v) rotating rod strings (vi) vertical string samplers, and (vii) polyurethane foam (PUF) plugs with glass fiber filter in-series. As expected, they found the passive type of samplers to collect less of the drift material (malathion). With the active samplers they found that samplers using high-volume sampling with either glass fiber filter only (at 400 L min^{-1}) or with the filter coupled to a PUF plugs (at 200 L min^{-1}) collected similar amounts of airborne malathion, 836 ng m^{-3} and 728 ng m^{-3} respectively. Their study also showed that these materials have good collection efficiency of the active ingredient, and they reported recoveries of 96, 75, and 93% for the fallout sheets, glass fiber filters, and PUF respectively.

A study by Hewitt *et al.* (2010) also looked at a number of collector systems that were used in a spray drift monitoring campaign by the Spray Drift Task Force (SDTF). To monitor spray drift deposition they used 1 m^{2} alpha cellulose cards that were placed horizontally to represent flat terrestrial and aquatic surfaces. The campaign also monitored passive airborne flux using 0.8 mm cotton string, 2 mm Teflon lines, alpha cellulose strips, and polythene cords. Amongst these they found cotton strings to be most suitable for passive flux sampling because of their high collecting efficiency (above 85%). Additionally they also used low-volume air samplers (at 2 L min^{-1}) which had filter paper (2.5 cm diameter) as the adsorbing material.

Cooper *et al.* (1996) conducted a wind tunnel experiment where they compared two samplers for monitoring spray drift, a passive sampler made of synthetic wool yarn and a battery-powered rotary sampler. They found the wool sampler to have a collection efficiency of between 40 and 100%, whilst the rotary sampler collection efficiency was between 1 and 70%. They noted that volatile compounds may be underestimated with the wool sampler. They concluded that the two samplers are complementary because they provide different information.

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Most of these pesticide spray drift samplers are point-collectors, meaning they give information on the concentration of the pesticide at that point. Although they are widely used, Gregorio *et al.* (2011) highlighted some of the limitations of using this approach. They include the following:

- The pesticide cloud is not time resolved. This makes is difficult to fully understand the evolution of the spray cloud during the application period.
- The collectors do not provide an overall picture of the pesticide plume. They only provide specific sample points of it.
- The results are strongly influenced by meteorological conditions during the trial.
- It requires a lot of personnel and time to carry out the monitoring, thereby limiting the number of trials that can be done.

To overcome these challenges the authors then suggested the use of an optical remote sensing technique. However this requires specialized equipment which may not be readily available. The three most commonly used monitoring techniques for assessing pesticide spray drift are discussed below, and studies which have utilized them are summarized in Table 2-3.

2.2.3.1 Tracer Techniques

The use of tracers generally involves addition of a different substance (the tracer) into the spray solution mix that will be transported together with the spray material in the atmosphere during application. The air samples that are collected are then analysed for that particular substance. The concentration of the tracer is then related to the concentration of the pesticide. The choice of a suitable tracer is usually based on ease of analysis and its stability in the atmosphere.

A number of different types of tracers have been used to simulate transport of pesticides in the air and analysis methods depend on the tracer that is used. Commonly used tracers are fluorescent dyes which can be sampled and analysed by fluorometry. The low cost of this method has contributed to its wide usage but one drawback is that some dyes can undergo both aqueous photolysis and degradation under humid conditions which may occur in some field study locations (Hewitt *et al.*, 2010). Another disadvantage is that different florescent tracers may be influenced differently by the pH of the pesticide formulation. A study by (Zhu *et al.*, 2005), for example, showed that a Fluorescein tracer at pH >8.43 had 124 times greater fluorescence intensity than a solution containing the same amount of Acid Yellow 7 tracer.

Despite this, the method is still widely used in drift monitoring studies and it has been stated that the accuracy of the fluorescent tracer method is within ±5% agreement with chemical analyses of chemically stable active ingredients (Arvidsson *et al.*, 2011).

Where dyes are used as tracers, a non-ionic surfactant is normally added to the spray material to simulate the physicochemical characteristics of the pesticide solution. The different dyes that have previously been used as tracers include Rhodamine, Brilliant Sulfo Flavin (BSF), Acid Yellow, Eosin, Pyramine, Tinopal, Fluorescein, and Caracid Brilliant Flavine. Among the dyes, BSF is considered to the best due to its low degradation in sunlight (11% degrades after 8 hrs) (Cai & Stark, 1997). This method has been widely used in different studies to monitor spray drift from both aerial and ground applications (Fritz *et al.*, 2011; Kasiotis *et al.*, 2014; Miller *et al.*, 2011) and, in some cases, with the aim of validating drift prediction models (Butler Ellis & Miller, 2010; Hoffmann, 2006b).

Metal ions have also been used as tracers in a number of studies (Brusselman *et al.*, 2004; Cross *et al.*, 2001; Thistle *et al.*, 2007; Zabkiewicz *et al.*, 2008). The study by Cross *et al.* (2001) for example, used ethylenediaminetetraacetic acid (EDTA) chelates of manganese, zinc, strontium, and copper to assess spray deposits and off-target contamination upon application in different sized apple tree orchards from an axial fan orchard sprayer. In this study they used atomic absorption spectroscopy to analyse their samples.

Studies by Woodward *et al.* (2008) and Zabkiewicz *et al.* (2009) used a metal cation salt to assess deposition of spray drift to validate the AGDISP ground spray model. Using this technique, they found that the AGDISP model over predicted downwind deposition by a factor of 3.5 – 100 times. It is important to mention that this research project sought to carry-out a similar validation study but using the active ingredient approach.

2.2.3.2   Laser Measurements

Another way of monitoring spray drift is through optical techniques which have been developed to assess the transport and dispersion of spray clouds from aerial sprayers. These make use of a laser beam and allow for measurement of relative spray concentration and particle speed along the beam at each sample point (Gil & Sinfort, 2005). Light detection and ranging (LIDAR) systems have been developed to monitor spray drift and they make use of interactions between

the aerosol or molecular atmospheric constituents with electromagnetic radiation at optical wavelengths. A number of studies have made use of this technique to monitor pesticide spray drift during application (Gil *et al.*, 2013; Gregorio *et al.*, 2014; Gregorio *et al.*, 2011; Gregorio López, 2012; Miller *et al.*, 2003b; Stoughton *et al.*, 1997). A recent study has shown good correlation ($R^2 \approx 0.90$) between LIDAR spray drift measurements and analytical concentrations from passive collectors (Gregorio *et al.*, 2014).

2.2.3.3 Active Ingredient Techniques

This technique involves chemical analysis of the actual active ingredient(s) in the spray material. Hewitt *et al.* (2010) noted that although the use of active ingredients in assessing spray drift is relatively expensive, it remains an optimum technique for field studies because it offers possible advantages of high stability and low levels of detection, and most importantly it is truly representative of the drift cloud or plume.

This method has been used in a number of spray drift monitoring studies from both aerial and ground pesticide applications (Frank *et al.*, 1994). A study by Ravier *et al.* (2005) used alachlor and atrazine to evaluate pesticide spray drift during ground application to a maize crop. They used Petri dishes containing fiber filters soaked in ethyl acetate for deposition sampling, and for airborne drift they sampled at 1.5 m using air samplers that were equipped with Tenax adsorbent and operating at about 2 L min^{-1}. They monitored drift up to 134 m downwind and found that alachlor was more easily diluted in space that atrazine since it is more volatile. Their study showed that in addition to droplet transport, the evaporation of the spray liquid and the volatility of the pesticides involved have to be considered when monitoring spray drift using pesticides as tracers.

In model evaluation studies, however, this technique has only been used to validate models that simulate aerial applications, such as studies by (Hewitt *et al.*, 2002a; Teske *et al.*, 2002) which used the active pesticide ingredient (diazinon & malathion) to validate AGDISP and AgDRIFT$^{®}$ aerial models. A study by Tsai *et al.* (2005) used methamidophos as a drift tracer to validate two models, the AgDRIFT model and the Fugitive Dust Model (FDM).

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Table 2-3 Collectors and tracers used in spray drift deposition monitoring studies, including the means of application and maximum downwind distance studied.

Deposition Collector	Drift Tracer	Application	Maximum Downwind Distance (m)	Study
Filter paper	Dye: Univex LV concentrate	Ground	50	Arvidsson *et al.* (2011)
Horizontal cellulose fallout sheets (20 cm^2)	Malathion	Ground	30	Bui *et al.* (1998)
Strips of paper (0.05 x 0.5 m)	Dye	Ground	20	Butler Ellis and Miller (2010)
Filter paper	Tartrazine	Ground (orchard)	24	Celen (2010)
Non-sterile polythene tubing (1.98 mm diameter)	EDTA chelates of Zn, Mn, Strontium, & Cu + Tartrazine	Ground (orchard)	5	Cross *et al.* (2001)
Glass petri dishes with distilled water	Azinphos-methyl (AZP)	Ground (orchard)	5	Dabrowski *et al.* (2005)
Filter paper (0.25 m × 0.25 m)	Dye: Brilliant Sulfo Flavine (BSF)	Ground	20	De Schampheleire *et al.* (2008)
Filter paper (5.7 cm × 2.6 cm)	Mineral chelates [Fe, Co, Cu, Mn, Mo, & Zn, Chelal®]	Ground	0.225	Foqué *et al.* (2014)
Mylar cards (10 × 10 cm)	SilGuard 309 + Caracid Brilliant Flavine (FFS) dye	Aerial & Ground	100	Fritz *et al.* (2011)
Kimby cards, TFE Teflon, Whatman No. 1 Filter paper (all 1 ft^2)	Malathion and its impurities	Aerial		Brown *et al.* (1993)
Filter papers (glass fiber GFA or cellulose #1) (9 cm diameter)	Chlorpyrifos, diazinon, improdione, pirimiphos-methyl & vinclozolin	Ground (orchard)	120	Holland *et al.* (1997)
Synthetic cloth (0.5 x 0.08 and 1.00 × 0.08 m^2)	Brilliant Sulfo Flavin	Ground (grass field)	5	Holterman *et al.* (1997)
Mylar sheets Water-sensitive paper	Rubidium Chloride (RbCl)	Aerial	40	Huang and Thomson (2012)
Polypropylene green plastic cards Acetate cards Water-sensitive paper	Fluorescent dye (oil-soluble Yellow, water-soluble Pyramine)	Ground	48	Khot *et al.* (2011)
Petri dishes (15 cm diameter)	2,4-D formulations Brilliant Sulfo Flavine Rhodamine B, (RhB)	Ground & Aerial	150	Maybank *et al.* (1978)
Ground plates (similar to Bui *et al*., 1998) (929 cm^2)	Malathion	Ground (Orchard)	20	Miller *et al.* (2000)
Petri dishes with Glass Fiber filter soaked in ethyl acetate (80 mm diameter).	Atrazine & Alachlor	Ground	134	Ravier *et al.* (2005)

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Mylar plastic sheets (45.7 × 30.35 cm)	Rhodamine-free base fluorescent dye	Ground & Aerial	200	(Salyani & Cromwell, 1992)
Whatman® chromatography paper (50 × 10 cm)	Chlorpyrifos and Metalaxyl	Ground (Orchard)	24	(Vischetti *et al.*, 2008)
Chromatography paper	Endosulfan Fluorescent dye: Uvitex	Aerial	1000	(Woods *et al.*, 2001)
Plastic tapes (10 × 100 cm)	Cation salts: $Co(NO_3)_2$, KCl, $MnCl_2$, & $MgCl_2$	Ground	20	(Woodward *et al.*, 2008; Zabkiewicz *et al.*, 2008)
Cotton fabric (7 × 7 cm)	Malathion	Ground	5	(Yarpuz-Bozdogan & Bozdogan, 2009)
Petri dishes (9 cm diameter)	Imidacloprid	Ground	5	(Zhao *et al.*, 2014a)
Petri dishes with Filter paper Whatman chromatography paper (90 mm x 15 mm diameter)	Food dye: Sunset Yellow FCF	Ground	12	(Kasiotis *et al.*, 2014)

2.3 Sampling and Analysis of Pesticides in the Atmosphere

To fully understand the transport and eventual fate of pesticides in the atmosphere, it is important to consider the environmental pathways and different phases in which they can occur. Pesticides can enter the atmosphere through various processes including spray drift, volatization and evaporation. Regardless of the mechanism by which the pesticide enters the atmosphere, it eventually distributes among aqueous, particulate, and vapour phases as equilibrium conditions are approached (De Rossi, 2010). The extent to which a particular pesticide distributes among these phases is governed by its physical and chemical properties including water solubility, Henry's law constant, and vapour pressure. Different sampling and analytical approaches are typically required for the different phases and these are discussed in this section.

2.3.1 Sampling Pesticides in the Atmosphere

Sample collection is a very important step in any analytical work. For analysis of spray deposition and drift, it is crucial to choose an appropriate method for collecting sedimenting spray droplets or sampling airborne flux (Salyani *et al.*, 2006). Incorrect sampling can compromise the quality of the results and therefore lead to inaccurate interpretation of pesticide

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spray drift and hence poor management of the problem at hand. It is therefore of vital importance that the correct methods and techniques are used to collect samples of a particular analyte.

Since pesticides in the air may occur at very low concentrations, it is important to ensure that the appropriate sampling material (adsorbent) and sampling technique is employed. In addition, pre-concentration of the analytes may be necessary to achieve the analytical sensitivity required Miles *et al.* (1970) noted that sampling of air for pesticide determinations may be complicated by the fact that the pesticide can exist in the aerosol, vapour or particulate form. They noted that the common air sampling techniques for pesticide determination at that time included:

- Collection on packed columns which adsorb the pesticides
- Passing the air through scrubbers fitted with fritted disks or gas dispersion tubes that break up the air stream to promote adsorption of the pesticide by a liquid phase
- Collection in freeze-out traps filled with glass helices maintained at low temperatures
- Drawing large volumes of air through glass-fiber filters or cellulose filter pads
- Trapping in impingers

Briand *et al.* (2002) more recently compared different sampling techniques for the evaluation of airborne pesticide spray drift in a commercial apple orchard. They compared low volume automatic air samplers comprised of a glass tube packed with Supelpak-2, a high volume sampler, an impinger containing cyclohexane and a glass fiber filter, and finally glass cartridges packed with Supelpak-2 and filter paper. A key finding of their study was that the physiochemical properties of the pesticides including vapour pressure, as well as weather conditions, strongly influenced gas and particle distribution in the atmosphere.

Sampling of pesticides in the atmosphere can be broadly categorized as either active or passive sampling, which will be further discussed in the following sections.

2.3.1.1 Passive Air Sampling

Passive samplers are chemical accumulators that can be used to assess ambient air concentrations of target chemicals (Shoeib & Harner, 2002; Waite *et al.*, 2005). They consist of an accumulating medium (or adsorbent) that has a high retention capacity for the target analyte

(Harner *et al.*, 2004) and are operated without the aid of a pump to draw the air into the adsorbent material.

The adsorption of organics from the atmosphere into a passive sampler is dependent on the passive sampler medium air partition coefficient, K_{PSM-A}, which is essentially the ratio of analyte concentration in the adsorbent divided by the concentration in air when the two phases are in equilibrium. This value, together with the sampling rate of the sampler, is important when quantitative assessment of ambient air concentration is to be made (Shoeib & Harner, 2002).

The use of passive air samplers is usually motivated by the fact that they are simple to operate, cheap, and they allow for time-averaged concentrations to be sampled even in locations where the use of active samplers would not be practical because of the required longer sampling periods and/or lack of power supply for the active sampler's pump. In some situations, passive samplers may be the only option, especially when several concurrent samples are required from different locations. Passive samplers are, however, only able to collect the free gaseous phase of air samples and require a longer sampling time than active samplers, ranging from a week to several months (Yusà *et al.*, 2009).

A comprehensive review of the materials that are usually used for passive sampling was done by Yusà *et al.* (2009) and they pointed out that the materials that are commonly used as passive samplers are mainly polyurethane foam (PUF) discs, semi-permeable membrane devices (SPMDs), polymer-coated glass (PCG) samplers, and XAD resins. These adsorbents are said to have a high capacity to retain organics in the atmosphere (Jaward *et al.*, 2003) and they operate as kinetic samplers, where it is necessary to know the uptake rate, rather than as equilibrium samplers. Among these samplers, the PUF disks are particularly attractive samplers because they are cheap, easy to handle, and can be used to sample pesticides over periods of several weeks (Chaemfa *et al.*, 2008; Jaward *et al.*, 2003; Waite *et al.*, 2005).

The use of passive samplers for long term monitoring of pesticides and other compounds in the atmosphere has been explored in a number of studies (Harner *et al.*, 2004; Jaward *et al.*, 2003; Shoeib & Harner, 2002). Chaemfa *et al.* (2008) performed field calibration of PUF disk passive air samplers for organochlorine pesticides (OCs). In their study, they showed that PUF disks with different densities will have different uptake rates of the analytes. This is because less dense

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PUF disks easily allow for the diffusion or movement of air which allows for better analyte uptake compared to denser PUF.

Carlsen *et al.* (2006a) used a simple passive dosimeter as a passive sampling device to monitor the deposition of a number of herbicides. Their dosimeter consisted of four microscope slides placed on plastic lids that were mounted about 20 cm from the ground. The found these samplers to be efficient in for collecting the active ingredients because they do not get saturated with water vapour like filter papers in cases of high water vapour.

Figure 2.4 A passive dosimeter for collecting pesticide spray drift. It consists of four microscope slides placed on a plastic lid which is then mounted about 20 cm above ground (Carlsen *et al.*, 2006a).

Brown *et al.* (1993) monitored malathion spray drift deposition after aerial application using 90 cm^2 horizontal cards. The cards were made of Whatman cellulose filter papers, Teflon cards, and polyethylene paper (Kimby cards). They used these to measure downwind deposition at three different sites that were located over 1 km downwind of the application area and they found no significant difference on the malathion concentration from cards that were placed in the same location. In the same study they also sampled airborne drift using a high-volume sampler (>1300 m^3/day) which had XAD-2 resin as adsorbing material on the cartridge. These allowed them to detect malathion in the air up to 10 days after application.

Williams *et al.* (2001) used alpha cellulose cards for visual observation and measurement of spray drift deposition for pesticide exposure assessment purposes. In their study, they simultaneously collected spray particles on flat alpha-cellulose paper and on a child-like

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mannequin which was covered with aluminum foil. They used Malathion 50 Plus® Insect Spray to spray at the mannequin after which they separately analysed the alpha-cellulose cards, and the mannequin head, torso, arms, hands, legs and feet for malathion. They extracted the malathion using ethyl acetate with shaking. 25 mL aliquots were analysed by Gas Chromatography equipped with a HP-5 column and a flame photometric detector (FPD). Their results showed that the alpha-cellulose cards had significantly greater retention of the pesticide than the mannequin.

2.3.1.2 Active Air Sampling

Active sampling involves the use of a pump operating at a known flow rate to draw air through an adsorbent material (Figure 2.5) for known period of time. When the sampling flow rate is in the order of 25 L min^{-1} or greater it is considered as 'high volume' air sampling (Cessna *et al.*, 2011). The adsorbent materials that are normally used for the sampling of pesticides in the atmosphere are polyurethane foam (PUF) or XAD resins (Muir & Sverko, 2006). Other adsorbent materials include Tenax®, Anasorb, Chromosorb and Amberlite®. PUF plugs have been widely used for pesticide active air sampling because they have a number of advantages which include flexibility of flow rates which can be employed, high adsorption efficiency and capacity, ease of sample changing and storage, convenience of analytical extraction, and they are generally inexpensive (Turner & Glotfelty, 1977). Active air sampling through PUF plugs may, however, result in possible breakthrough especially of the more volatile or low molecular weight pesticides. This breakthrough can be reduced by either using additional PUF plugs in series or addition of a solid sorbent that is sandwiched between two PUF plugs or held by a metal sieve. This results in an improved collection efficiency of the samplers (Raina & Hall, 2010).

A study by Armstrong *et al.* (2013) compared PUF matrices with XAD-2 resins for active air sampling of airborne organophosphorus pesticides in an agricultural community. They found that the PUF matrix was a better sampling medium for organophosphorus pesticides compared to XAD-2 resins. This was because the resins showed significant (up to 32%) artificial transformation of the OPs to oxygen analogs while the PUF showed very little or no transformation.

Jongen *et al.* (1991) used cellulose filters (type SC, pore size 8 μm) for sampling air for the pesticide chlorothalonil with analysis by High Pressure Liquid Chromatography with UV detection (HPLC-UV). During sampling they compared this filter with Teflon and glass fiber

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filters respectively as well as XAD2. Sampling was conducted at a flow rate of 2 L min^{-1} and their sampling time varied between 20 and 60 min. The analyte was extracted using 3 mL of methanol. To validate their method, they determined recoveries by spiking all three types of filters (cellulose, Teflon, and glass fiber) and XAD2 with 20 μL of 10, 100, and 1000 μg mL^{-1} of chlorothalonil in methanol and allowed them to dry for 30 min prior to extraction.
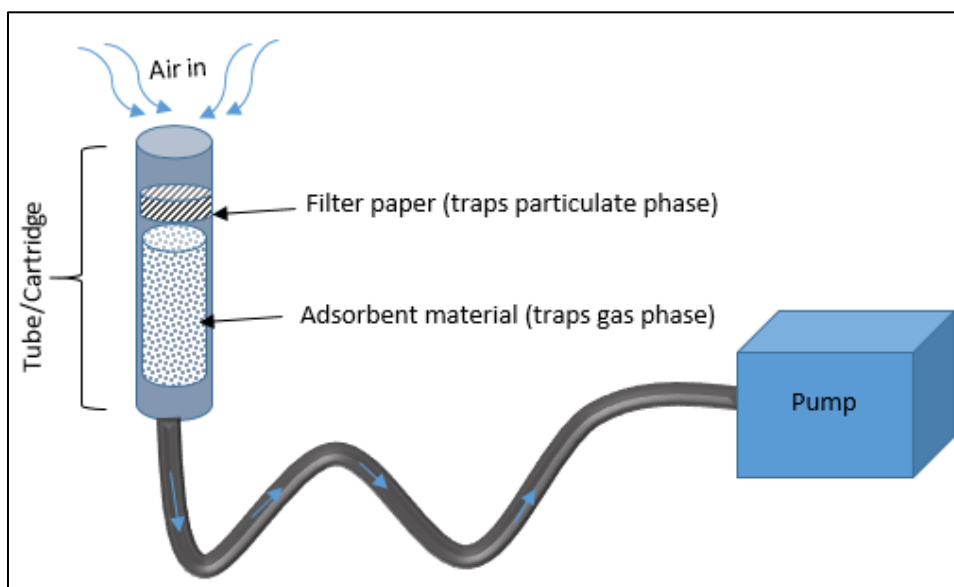
Figure 2.5 Schematic diagram of a typical active air sampler. The adsorbent and filter are analyzed and the concentration is then related to the flow rate of the pump and sampling duration.

2.3.2 Sample Extraction Techniques

Extraction, which is the process of removing analytes from the adsorbent matrix, is a very important step in the analysis of pesticides since it improves the sensitivity of the analytical method. Different extraction methods have been developed to extract pesticides from adsorbent materials. These include Soxhlet extraction, accelerated solvent extraction (ASE), supercritical fluid extraction (SFE) and microwave assisted extraction (MAE).

Soxhlet Extraction

Soxhlet is the traditional method for the extraction of pesticides from air samples. Despite the disadvantages of high solvent consumption, long extraction time (8 to 24 hrs), Soxhlet extraction is still widely used for extraction of pesticides from air samplers because it provides efficient extractions. For example de Castro and Ayuso (2000) and Kuang *et al.* (2003) used this method

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to extract pesticides from PUF plugs after air sampling. They found very good recoveries and for atrazine they reported 101 ± 9% recovery.

Microwave Assisted Extraction (MAE)

Microwave extraction offers a number of advantages over conventional classical extraction techniques. These include shortened extraction times and lower consumption of solvents. Furthermore, stirring is possible in the microwave ovens and this makes the extraction conditions more homogenous (Barriada-Pereira *et al.*, 2003). Numerous studies have employed MAE for the extraction of pesticides from air samples (Coscollà *et al.*, 2011; Coscollà *et al.*, 2009).

Accelerated Solvent Extraction (ASE)

Accelerated solvent extraction (ASE) is also known as pressurized fluid extraction (PFE) or pressurized liquid extraction (PLE) (Kosikowska & Biziuk, 2010). The method makes use of low volumes of solvent heated to high temperatures under pressure to extract organic compounds. By pressurizing the solvent, it can be raised well above its boiling point and remain in the liquid state. This then accelerates the kinetic processes involved in desorbing the analyte from the matrix, making automated extractions possible. Therefore the operating variables that affect analyte recoveries in ASE are temperature, pressure and solvent composition (Alexandrou *et al.*, 2001). The advantages of ASE over traditional methods, like Soxhlet extraction, is that is uses very little solvent and the extraction time is reduced. This method, however, has disadvantages of high initial cost for the instrumentation and the need for a stable power supply to avoid premature instrument shutdown (Muir & Sverko, 2006).

He *et al.* (2009) developed, validated, and applied ASE for quantitative extraction of OCs from quartz and PUF filters after air sampling. During method development they optimized the method with respect to extraction solvent, temperature and extraction time. For all the compounds they studied they found optimal recoveries when using a 3:1 mixture of *n*-hexane:acetone at 100 °C for 20 min. Compared to Soxhlet extraction (8 h) and MAE (20 min), they found ASE (40 min; 2 cycles) to give the best recoveries both from filter and PUF samples (Figure 2.6).
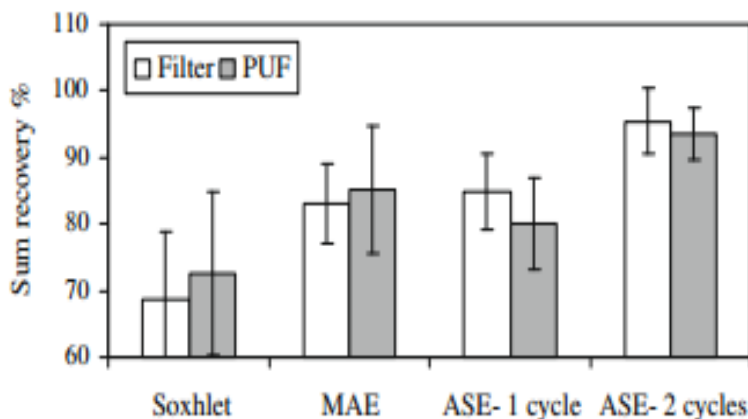
Figure 2.6 Average recovery of target compounds for different extraction techniques (He *et al.*, 2009).

Yao *et al.* (2007) compared Soxhlet extraction (with 30 mL DCM for 24 h) versus ASE (with 30 mL hexane/acetone, 70/30 v/v, for 25 min, at 100 °C, 2000 psi) of atrazine from quartz fiber filters after air sampling. They found the recoveries were 139% and 114% respectively. Coscollà *et al.* (2008) also used this technique to extract pesticides from particulate matter in air samples collected onto filter paper.

Ultrasonic Extraction

In this method the adsorbent material is simply placed in a suitable solvent in an ultrasonic system to desorb the analyte of interest into the solvent. Lammel *et al.* (2007) used ultrasonic extraction with n-hexane for 30 min to extract some pesticides deposited on filter paper. Borras *et al.* (2011) used ultrasonic extraction to extract pesticides air sampled onto quartz fiber filters and XAD resins. When they optimized the solvents employed, they found that isooctane was better than ethylacetate, DCM, methanol, or a 1:1 mixture of acetone:hexane and obtained recoveries greater than 95%.

2.3.3 Extract Clean-up & Derivatization

Extract clean-up involves fractionating the extract using techniques like column chromatography, adsorption chromatography, and gel-permeation chromatography, or simply filtering the extract. In some cases, especially where more selective detectors like GC-MS-MS are used, the clean-up step may be omitted (Kosikowska & Biziuk, 2010). Adsorption

chromatography using SPE cartridges packed with Florisil have been widely used in numerous pesticide studies (Foreman *et al.*, 2000; Harner *et al.*, 2004; Jin *et al.*, 2013; Yao *et al.*, 2007).

Derivatization involves changing the chemical structure of the target analyte, which may be necessary when isolation together with pre-concentration of the target analyte is not successful, as derivatization improves selectivity, sensitivity and separation of sample constituents, although losses of analyte may occur during derivatization. For pesticide analysis by GC, pentafluorobenzyl bromide (PFBBr) is often used as the derivatization agent (Kosikowska & Biziuk, 2010).

2.3.4   Analysis of Pesticides from Air Samples

Gas chromatography (GC) is one of the widely used techniques for the determination of organic compounds in the atmosphere (Gil & Sinfort, 2005; Sipin *et al.*, 2003). It has thus been used in a number of studies to quantify pesticides in the atmosphere during application (Yarpuz-Bozdogan & Bozdogan, 2009). In addition it has been used for post application emission determinations (Ferrari *et al.*, 2003; Majewski, 1999) and for quantifying pesticide concentrations due to long-range transport (Foreman *et al.*, 2000; Scheyer *et al.*, 2007).

In order for pesticides to be analysed by gas chromatography they must be volatile and thermally stable. Injection into the GC column can either be in the split mode (where the gas stream is divided) or splitless mode (where the gas stream is not divided). Split injection is not suitable for trace analysis due to large losses of sample and thermal degradation is much more pronounced due to a longer dwell time in the heated inlet. This makes splitless injection preferred for trace analysis because there the entire sample is introduced into the column (Kosikowska & Biziuk, 2010).

The detection methods that are widely used in pesticide analysis are electron-capture detection (ECD), nitrogen-phosphorus detection (NPD) and mass spectrometry (MS). Among these methods, MS detection is increasingly being used because of its capability to provide quantitative and confirmatory results, and because of its high sensitivity and selectivity. Among the MS detectors that are available, the quadrupole in selected ion monitoring (SIM) mode is the one that is commonly employed because it provides higher sensitivity than full scan mode (Yusà

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et al., 2009). GC-ECD is, however, still widely used as a selective detector for the analysis of selected pesticides, specifically organochlorine and organophosphate pesticides.

Table 2-4 Studies that used PUF to sample atrazine and other pesticides in the atmosphere through active sampling

Cartridge compositions	Flow rate	Sampling time	Pesticide(s) sampled	Extraction solvent	Study
PUF + filter paper	200 L min^{-1}	18 min	Malathion	Hexane + 5% diethyl ether	Bui *et al.* (1998)
QFF & PUF	700 L min^{-1}	24 h	OCs		Jin *et al.* (2013)
PUF-XAD-PUF	14.6 m^3	24 h	Atrazine, Chlorothalonil, Alachlor, Metolachlor, HCB, Endosulfan, Trifluralin, Pendimethalin		Hayward *et al.* (2010)
PUF	3.8 L min^{-1}	4 h	OCs, Atrazine, PCBs, OPs	Hexane + 5% diethyl ether	MacLeod and Lewis (1982)
PUF and QFF	14.6 m^3 h^{-1}	24 h	Atrazine	Hexane	Yao *et al.* (2007)
PUFs/XAD-2	12.5 m^3 h^{-1}	24 h	Atrazine, 2,4-D, Bromoxynil, Triallate, Trifluralin, Dicamba, MCPA, Lindane, Thalfluralin, Metoclachlor, and Alachlor.	Acetone	Waite *et al.* (2005)
GFF + PUF	1.0 m^3 min^{-1}	4 h	Atrazine, Acetochlor, Alachlor, etc		Foreman *et al.* (2000)
PUFs/XAD-2	100 L min^{-1}	24 h	Atrazine, Alachlor, Benfluralin, Butylate, CIAT, Cyanazine, Dacthal	Hexane:Acetone (1:1 v/v)	Majewski *et al.* (1998)

PUF – Polyurethane foam *PCBs – Polychlorinated biphenyls*
QFF – Quartz fiber filter *OCs – Organochlorine pesticides*
GFF – Glass fiber filter *HBC – Hexachlorobenzene*

Gas Chromatography coupled to a Nitrogen Phosphorus Detector (GC-NPD), also known as a Thermionic Specific Detector (TSD), was first described by Burgett *et al.* (1977). It is a technique that is mainly used to analyse nitrogen or phosphorous containing organic compounds. The detector set-up is similar to that of the Flame Ionization Detector (FID). The difference is that the bead through which the carrier gas passes is made of rubidium or cesium chloride which is electrically heated by means of a coil. The heated bead emits electrons by thermionic emission

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and these are collected at the anode to provide a background current. When nitrogen and/or phosphorus-containing compounds elute from the column, they adsorb on the surface of the bead, thereby increasing the emission of electrons and hence the measured current allowing for the detection of those species. Unlike the FID, in NPD the ionization of the compound occurs in a low-temperature plasma rather than a flame. Several studies (Dores *et al.*, 2006; Psathaki *et al.*, 1994; Vryzas & Papadopoulou-Mourkidou, 2002) have used GC-NPD to determine triazine pesticides, including atrazine, in different environmental samples.

An alternative analytical technique for the analysis of pesticides has recently been developed and it uses PerkinElmer's AxION® Direct Sample Analysis coupled a Time-of-flight mass spectrometer (DSA-TOFMS). The DSA is a unique ionization technique that is similar to atmospheric pressure chemical ionization (APCI). Nitrogen gas is passed through a high voltage corona needle to generate reagent ions that are then directed onto a sample on a mesh grid. Upon impacting the surface of the sample, analyte desorption and ionization occurs, producing a stream of molecular ions that are directed to the flight tube of the TOFMS (Daugherty & Crowe, 2013; PerkinElmer, 2012). In time-of-flight mass spectrometry, ions from the ion-source (the DSA in this case) are accelerated through a flight tube before they reach a detector. Ions with larger mass-to-charge (m/z) ratios take longer to reach the detector while the smaller ones reach the detector faster. The time it takes for an analyte to reach the detector is directly proportional to the square root of its mass (Guilhaus, 1995). Overall, this technique provides for separation of molecular ions according to their mass and allows for identification based on library matching.

This chapter has dealt with a review on sampling and analysis of pesticides from the atmosphere. The next chapter will provide a literature review with regard to pesticide spray drift modelling and will look at some studies in which they were used as well as the outcome of those studies.

Chapter 3   Literature review on modelling of pesticide spray drift

3.1   Background

Monitoring environmental exposure during and after spray operations can be difficult because of variations in environmental conditions. Air monitoring of pesticide spray drift, which involves sampling, extraction, and chemical analysis, for the large geographical areas involved can be an exorbitantly expensive and time-consuming exercise. The relatively long sampling period, in the order of hours for most methods, in relation to the relatively short spray event (an hour for a 34 ha crop circle) does not allow the investigator to understand the evolution of a spray event (Tsai *et al.*, 2005).

It therefore becomes necessary to use predictive models to assess the extent to which off-target spray drift may contaminate the environment. As pointed out by the Spray Drift Task Force (SDTF, 1997), "Due to the complexity of evaluating all possible interactions of the numerous application variables, a computer model is the most practical way to conduct spray drift risk assessments." Modelling is an essential component for estimating the spread, deposition concentration, and time evolution of spray drift (Tsai *et al.*, 2005).

To date, a number of pesticide spray drift models have been developed to overcome the aforementioned challenges of air monitoring. In this study two related air dispersion models, namely AGDISP and AgDRIFT® are focused on. At this point it is important to note that this thesis will not discuss the detailed mathematical basis of the models. Instead a review of their working principles and of the outcomes of other validation studies, focusing on deposition and airborne outputs, will be provided and other models available for predicting pesticide spray drift will be reviewed in this chapter.

3.2 The AGDISP Model

The AGDISP model was initially developed to simulate spray drift during aerial application (Bilanin *et al.*, 1989). It is based on Lagrangian equations that describe the motion of droplet trajectories as they are released from spray nozzles. The model also includes simplified equations that describe the effects of the aircraft-wake and ambient turbulence (Huang *et al.*, 2010; Teske *et al.*, 2003). Such equations that describe the motion of a spray material that is released from nozzles on an aircraft were first developed as early as 1953 (Teske & Curbishley, 2012). The AGDISP model calculates the deposition of agrichemicals both in the area being sprayed and, more importantly, downwind on neighbouring environments (Connell *et al.*, 2009).

The AGDISP model was initially developed primarily to focus on defining in-swath deposition patterns or as a near-wake model for forestry or other high-release applications, and it therefore combines Lagrangian calculations with a Gaussian plume algorithm (Teske *et al.*, 2003). Since then there has been ongoing research to modify and refine the model so that it better simulates real field measurements. In the mid-1990s it was modified by the Spray Drift Task Force (SDTF), a consortium of about 40 chemical manufacturing companies, into a regulatory version called AgDRIFT® (discussed in section 3.3) in an effort to have some of their agricultural pesticide products re-registered with the United States Environmental Protection Agency (USEPA) (Teske *et al.*, 2003).

One of the modifications, for example, was to include a set of equations that account for evaporation of the droplets. The model uses a single evaporation constant to account for the evaporation of the active, additive, and carrier components of a spray mix. As the droplet evaporates the active fraction is also programmed to change (Escoffier & Scire, 2013).

In the early 2000s Teske *et al.* started working towards developing AGDISP algorithms for simulating spray drift from ground boom sprayer applications (Teske *et al*., 2000, 2001, 2004). Their work followed that of Holterman *et al.* (1997) who were also modelling pesticide spray drift from boom sprayers using a different model. In doing this a number of modifications had to be made to the initial aircraft-based AGDISP model, for example the wake and turbulence that is found in the aircraft application is not included, instead it includes a more detailed modelling of

the spray droplet behaviour near the nozzles. It assumes the droplets to be spherical and separated, thus drag and gravitational forces act on them when they are released.

Teske's group conducted some preliminary validations of the AGDISP ground model in which they found some promising results, as well as some areas which needed improvement (Teske *et al.*, 2009). Since then, researchers have undertaken studies to validate this ground based model, which will be discussed in more detail in section 3.3 (Connell *et al.*, 2009; 2012; Fritz *et al.*, 2011; Woodward *et al.*, 2008; Zabkiewicz *et al.*, 2009).

The current version of AGDISP (version 8.27) incorporates the following:

- Exact solution of droplet equations of motion
- Computation of horizontal deposition and vertical flux of the spray
- Up to 30 drop size categories and 60 nozzle types
- Deposition smoothing functions
- Improvement of the evaporation model and the helicopter wake model
- Extensive validation based on 180 separate aerial treatments performed during trials by the SDTF.

In order for the AGDISP model to provide accurate predictions of deposition and downwind drift from aerial pesticide applications, a consistent set of inputs that represent the aircraft and its flight conditions, spray nozzles and the droplet size distribution they create, spray material properties, surface features, and ambient meteorology, is all required. These inputs drive the various elements of the model used to approximate the physics within the wake behind the spray aircraft and to the local environmental conditions (Teske *et al.*, 2003).

In general, input parameters that must be provided by the user of the model in order to allow for the calculation of the predicted spray drift, includes information on the sprayer description/operation, nozzle setup, meteorology, spray material as well as on application conditions. The model also requires characterization of the droplet size distribution (DSD) produced by the nozzle. The reader is referred to Table A1 in the appendix section for a full list of the input parameters required for the ground based spray drift model which was employed in this study.

3.3 The AgDRIFT® Model

AgDRIFT® is a product of the Cooperative Research and Development Agreement between the USEPA Office of Research and Development and the SDTF. It was developed for use in regulatory assessments of off-site drift associated with agricultural use of pesticides through aerial, ground, and orchard or airblast applications (BLM, 2005). It is the result of research conducted by the SDTF in the late 1980s and early 1990s involving 180 aerial, 48 ground hydraulic boom, 21 orchard airblast and 6 chemigation field trial treatments as well as >2000 wind tunnel atomization droplet size spectrum measurements and physical chemical property studies for >70 tank mixes of different pesticide types (Hewitt *et al.*, 2010). The AgDRIFT model is essentially a commercial spin-off of the AGDISP model and uses similar algorithms (Stellman & Stellman, 2004).

The graphic user interface of the AgDRIFT® model allows the user to choose between three tiers (Tiers I, II, and III) of increasingly complex evaluations of off-site drift and deposition. Tier I allows the user to modify a small number of variables, and requires little knowledge of the actual application conditions and properties of spray materials. It basically represents a screening level which supports the evaluation of aerial and ground application scenarios. Tiers II and III allow the user to modify a progressively larger set of variables to make the scenario more representative of actual environmental conditions and, unlike Tier I, these are only used for evaluation of aerial application scenarios.

3.4 Validation and Sensitivity studies of the AGDISP and AgDRIFT® Models

Most of the work that has been done on validating the AGDISP or AgDRIFT® models has focused on aerial applications and few studies have validated the ground application features of the models.

Woods *et al.* (2001) monitored the off-target deposition of endosulfan pesticide which was applied to cotton during the 1993 – 1998 period. To measure off-target transport of droplets they used a number of collection surfaces which included chromatography paper placed on horizontal flat plates at 1 m height above ground, vertically oriented pipe cleaners, and cotton string which they suspended from 20 m high towers. To model the spray drift they used AgDRIFT® and the Gaussian Diffusion Model (GDM), which assumes a single line source. Their results for the

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actual and computed off-target deposition of the pesticide at up to 10 km downwind of the field are shown in Figure 3.1, which showed that the field data compared reasonably well with the outputs of both the GDM and AgDRIFT$^®$ models.
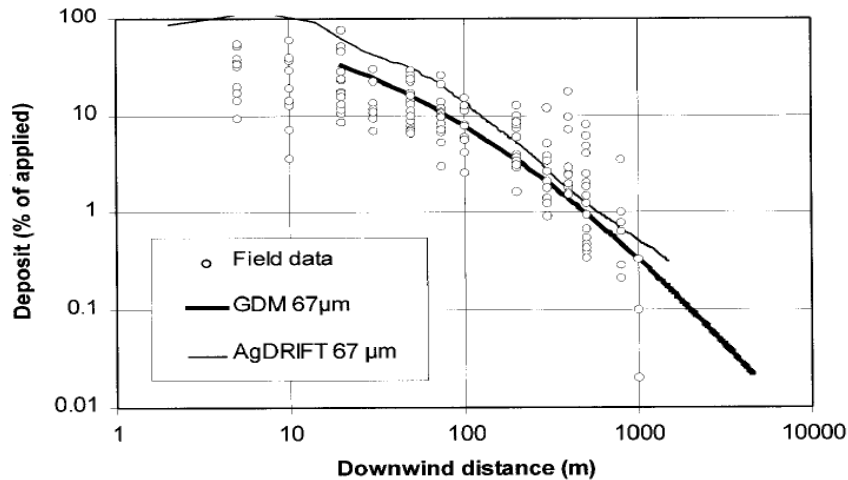
Figure 3.1 Downwind pesticide deposition concentrations obtained on horizontal flat plates. Data compared to Gaussian Diffusion Model and AgDRIFT® model outputs (Woods *et al.*, 2001).

Fritz *et al.* (2011) used AGDISP to evaluate drift reduction technologies (DRTs) for both aerial and ground applications. When conducting the field experiments they used a spray solution that consisted of SilGuard (a surfactant polymer) and a fluorescent dye and they sampled deposition from the edge of the application area up to 100 m downwind and airborne drift at 50 m downwind. Mylar fallout cards (10 x 10 cm) were used to sample deposition, while airborne drift was sampled by means of suspended monofilament lines at three heights (1, 5, and 10 m). A number of challenges were encountered, including low recoveries from the mylar samples (14.4% for ground application and 26.7% for aerial application) and inconsistent replication results due to changes in wind direction. The low recoveries were attributed to the polymer, SilGuard, which they suggest might have resulted in the dye binding to the surfaces of the samplers. Despite this, it was found that the drift reduction between the reference and DRT system measured in aerial trials, was similar to that estimated with AGDISP.

Hewitt *et al.* (2009) used AGDISP to model the spray drift potential of glyphosate in aerial applications. They used input parameters typical of those occurring in Colombia for aerial application of pesticides. The results showed that, despite using a 'very fine to fine' droplet size

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classification as input, the model predicted lower evaporation rates compared to similar sized agricultural sprays. This they attributed to the large non-volatile fraction of the tank mix. Overall it was found that the drift potential would be small because, among other factors, they used high humidity (70%) which is typical for the Colombian fields they were simulating, which reduces the evaporation rate of the droplets. Another reason for the low drift potential could be that an evaporation rate of only 37 μm^2 $°C^{-1}$ s^{-1} was used which was suggested as being typical of glyphosate products. The authors then proposed that only a 50 to 120 m downwind buffer would be required to protect other surrounding areas.

Hoffmann (2006b) measured airborne spray flux after several aerial application scenarios and compared the experimental data with AGDISP simulation outputs. In conducting the experimental part of the study, a spray solution was utilized which contained a fluorescent dye (Caracid Brilliant Flavine FFN) and a sampling station 50 m downwind consisting of a monofilament line suspended at different heights to intercept the spray flux. When comparing the field measured spray flux to AGDISP predictions the model results were found to be 1 – 6 times higher than those found experimentally.

Woodward *et al.* (2008) collected experimental data during ground boom spray applications of a solution of water, wetting adjuvant and a metal cation salt (tracer) and used it to evaluate the AGDISP 2003 ground application model. It was found that AGDISP overestimated off-target deposition by a factor of 3.5 to 100. This was attributed to the fact that the model was originally designed to simulate aerial applications and did not consider factors that could be important for ground applications, although Teske *et al.* (2009) stated that modelling of nozzles release velocities is included for ground applications.

A number of sensitivity studies have been conducted regarding the AGDISP and AGDRIFT models. For aerial applications, Hoffmann (2006b) found that a 1.5 m s^{-1} increase in wind speed corresponded to a 100% increase in spray flux at 50 m and changing crop heights from 0.3 to 1.3 m resulted in a 20-fold decrease in the spray flux (Figure 3.2a). They observed however, that the model's sensitivity to wind speed and canopy height was greater than that seen in experimental data, suggesting a need for further studies. They also investigated the significance of surface roughness on the predicted spray flux and found that by changing surface roughness values

incrementally from 0.003 to 0.015 had no significant effect on the spray flux at heights over 2 m (Figure 3.2), but it did have an impact closer to the surface.
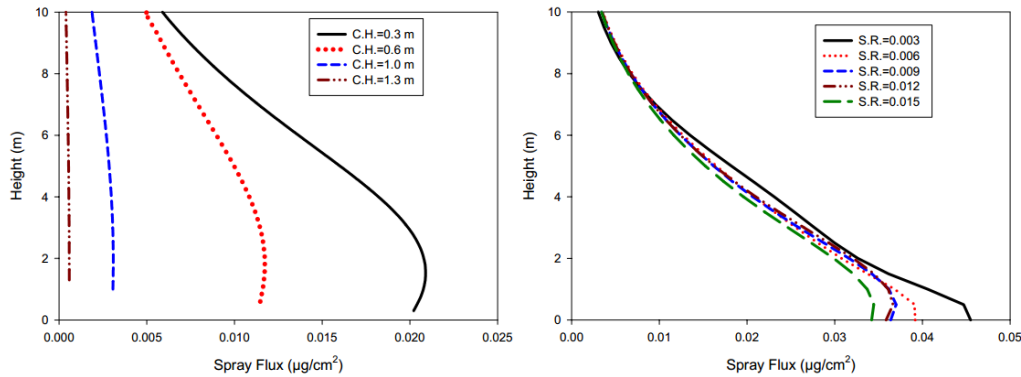
Figure 3.2 Sensitivity of AGDISP model spray flux predictions to (a) crop height (C.H.) and (b) surface roughness (S.R.) (Hoffmann, 2006a).

Huang *et al.* (2010) used AGDISP simulations to study various factors that could affect downwind deposition of aerially applied pesticides. In this study Design of Experiments (DOE) statistics was used to investigate the factors that affect downwind deposition as well as interactions among factors that have more significant impacts than others. The factors investigated were: release height, nozzle extent, droplet size, wind speed, temperature and relative humidity, whilst all other factors (or AGDISP input parameters) were kept the same. It was found that wind speed was the most significant factor followed by relative humidity, whilst the contribution of the other factors on downwind deposition was not that significant (Figure 3.3).

40
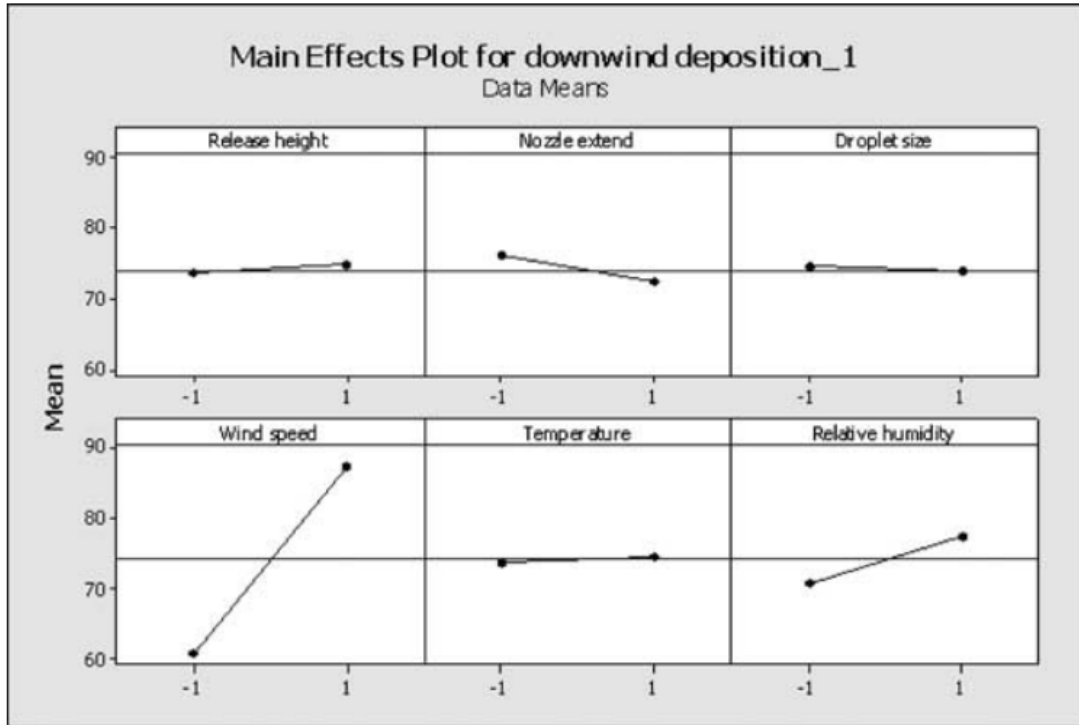
Figure 3.3 Determination of factors that mainly affect downwind spray drift deposition, where the slope represents the sensitivity of the AGDISP model to that factor (Huang *et al.*, 2010).

3.5 Other Models for Predicting Pesticide Spray Drift

3.5.1 Wind Tunnel Dispersion (WTDISP)

The Wind Tunnel Dispersion (WTDISP) model by Connell *et al.* (2009) uses AGDISP type algorithms but with modifications to effectively model the breakup and evaporation of spray droplets over the first few meters. It was developed because the AGDISP ground model was found to under predict the droplet size distribution at those distances. Using field data Connell *et al.* (2009) showed that the WTDISP model predictions were improved compared to those of AGDISP at these distances.

3.5.2 Computational Fluid Dynamics (CFD)

This model calculates individual droplet tracks as a function of atmospheric, field and operating conditions. It consists of two sub-models that are reciprocally coupled – an airflow model and a particle tracking model (Nuyttens *et al.*, 2013). A study by Baetens *et al.* (2007) validated this model in a ground application study where a fluorescent tracer was applied with a 25 m boom

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sprayer equipped with 54 nozzles. They measured spray drift up to 20 m downwind and compared the results with those of the model. The CFD model was able to predict short distance drift satisfactory up to 5 m downwind but there was a small discrepancy from 5 to 20 m. They found that the boom height was the most sensitive parameter for this model, followed by wind direction and wind velocity.

3.5.3 Forest Service Cramer-Barry-Grimm (FSCBG)

Just like AGDISP, this model also uses the Lagrangian approach to track the spray particle movement from the spray equipment under known conditions. It uses AGDISP results from the top of a canopy or near the ground to solve Gaussian diffusion equation that accounts for deposition. It also includes algorithms that take into consideration multiple sources originating in any wind direction, the evaporation of volatile compounds, and canopy penetration (Teske, 1996). This model was validated by Rafferty and Bowers (1993) and they found that it compared well with field data and this was attributed to the model's ability to account for aircraft wake effects. Teske *et al.* (1991) used it evaluate canopy penetration and ground deposition in an orchard treatment and the prediction was within 7.8% of the overall field data.

3.5.4 Atmospheric Dispersion Modelling System (ADMS)

The ADMS model is based on a Gaussian distribution of concentrations in the atmospheric boundary layer that are transported downwind by the prevailing air flow (Butler Ellis *et al.*, 2010). Computational efficiency, particularly when long distances downwind need to be modelled, is the main advantage of this model, while the main drawback is that it is difficult to model effects of changes, for example, in nozzle design, which is important when modelling short-range pesticide drift (Butler Ellis *et al.*, 2010). The ADMS model has been used by Butler Ellis *et al.*, to assess the pesticide vapour exposure risk of bystanders and residents in the United Kingdom. In assessing exposure risk, the ADMS model had to take into account the vapour emission of active ingredients, atmospheric vapour dispersion, and position and height of the bystanders or residents relative to the field that was being sprayed with the pesticide.

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3.5.5 The Silsoe spray drift model

The Silsoe spray drift model was developed by Butler Ellis and Miller (2010) and is based on a modification of an earlier particle-tracking model by Miller and Hadfield (1989) to account for multiple nozzles on a moving boom. The model did, however, not account for droplet evaporation since the initial use of the model was to predict drift relatively close to the edge of the sprayed swath in typical UK conditions where humidity would be high and therefore evaporation would be low. The authors evaluated the model in a number of field trials in predicting airborne spray concentrations and ground deposition for a range of variables including forward speed, boom height, wind speed and nozzle design. The results showed that the Silsoe Spray Drift Model provided reasonably good predictions but under-estimated ground deposits near to the sprayer (at higher drift values) and over-estimated at distances further away from the sprayer, a trend similar to that found by Teske *et al.* (2009) when validating AGDISP and AgDRIFT® models. In addition, the model over-predicted airborne spray at distances away from the sprayer and predictions for standard flat-fan nozzles were better over short grass but were less satisfactory in taller crops.

3.5.6 Gaussian Diffusion model (GDM)

Craig *et al.* (1998) developed the Gaussian Diffusion Model (GMD) model for predicting pesticide spray drift deposition from agricultural aircraft at far wake distances (greater than 50 m). Their model only used a simplified form of a time-dependent Gaussian diffusion equation which was said to give similar results to the FSCBG model at distances >50 m. They intended to use the model to demonstrate effects of wind speed, turbulence intensity, release height, droplet size and uniformity on downwind spray drift deposition. The model was developed for use in preparing guidelines for determining buffer zone distances and best ways of reducing and managing pesticide spray drift. They found that the model compared very well with experimental data obtained from flat plate sampling of aerially applied insecticides.

3.5.7 RTDrift Gaussian advection-diffusion

The RTDrift model is a Gaussian tilted plume type model that describes the transport and dispersion of droplets after their release from nozzles (Lebeau *et al.*, 2009). It considers each nozzle as an instantaneous source that has its own movements and thus requires nozzle input

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such as a global positioning system, ultrasonic anemometer and several sensors to give accurate information on the nozzle position and operation. The authors evaluated the spray drift prediction of this model by measuring ground drift at different distances using fluorimetry analysis. They found that that drift deposition was mainly affected by wind speed and direction which the model correctly accounted for. Overall it was concluded that this model provided realistic maps of drift deposition compared to experimental measurements of up to 30 m downwind. The short-coming of this model was that it over-estimated short distance drift deposition and it also under-estimated long distance drift.

3.5.8   IDEFICS model

IDEFICS (IMAG program for drift Evaluation from Field sprayers by Computer Simulation) is a ground boom sprayer model that describes the trajectories of droplets produced by a single nozzle and can be used to predict downwind distribution of deposited droplets, as well as vertical distribution of airborne droplets (Holterman *et al.*, 1997).

Validation studies of this model were done by collecting deposited droplet samples, using synthetic cloths, and airborne droplet samples, using spherical synthetic cleaning pads tied to a vertical string during application of a fluorescent dye (BSF) solution. Their results showed good correlation between calculated and experimental concentrations of the BSF tracer (Holterman *et al.*, 1997). However the major drawback of this model is that it was only validated for predictions up to 10 m downwind and for a single nozzle spraying above grass. The usability of the model to large downwind distances and above crop canopies is unknown, as it was not validated in this regard.

This chapter has provided a review of the different air dispersion model software programmes that are used to simulate pesticide spray drift as well as the results of field studies which have been conducted to validate them and it is evident that each model has advantages and limitations. The next three chapters of this dissertation will focus specifically on the AGDISP ground model. This model was chosen because it was readily available for use in this project and also because of its capability to predict drift over longer downwind distances (up to 800 m downwind),

making it suitable for human health risk assessments. The predicted spray drift will be compared to experimental data measured under local South African conditions for validation of the model.

Chapter 4 Experimental Methods

4.1 Atrazine Spray Drift Monitoring Campaign

A field monitoring campaign was conducted on a commercial farm during ground application of pesticides in order to validate the AGDISP model under local conditions. During this campaign, both airborne and deposition spray drift were monitored. One of the active ingredients in the pesticide formulation, namely atrazine, was targeted as a drift tracer, making this monitoring approach different from most other studies which have used fluorescent dyes as tracers. This chapter presents the experimental details of the sampling campaign, during which a total of 124 samples were taken, as well as details of the collection of additional input parameter values required by the model. Data collection and treatment is also described.

4.1.1 The study area

Pesticide spray drift monitoring was conducted during spraying of weeds in a 7.6 ha sorghum field in Standerton, South Africa (S27°0', 48.96'', E29°, 33' 27.58'') on 28 January 2014 under calm meteorological conditions. At the time of spraying, the sorghum crop was about 0.9 m tall and the field was surrounded by the farm house and grazing land for farm animals. A total of approximately 1 000 ha of sorghum was grown on this farm. A John Deere 4720 'Hi-Boy' ground sprayer (Figures 4.1 and 4.2) was employed which was equipped with 56 TwinJet® hydraulic nozzles (TeeJet® Technologies) which were uniformly distributed at 0.5 m intervals along a 32 m boom. The pesticide concentrate (Terbusien Super 600 SC, Villa Crop Protection Pty Ltd.) contained atrazine (291 g L^{-1}), terbuthylazine (291 g L^{-1}), and other related active triazines (18 g L^{-1}). Spraying was done at about 400 mm above the crop canopy and it took only 10 min to spray the whole field.

Figure 4.1 The "Tall-boy" ground sprayer used for pesticide application. The sprayer had a 32 m wide boom on which 56 TwinJet nozzles were distributed.

Figure 4.2 Spray material being applied with spray drift away from the target sorghum crop evident due to wind effects.

4.2   Sample Collection

Samplers were distributed downwind of the application site as shown in Figure 4.3. The distances were determined using a Nikon LASER range finder (model 1200S). Ideally, downwind samplers should be set up parallel to the wind direction when monitoring spray drift. Therefore the wind direction was estimated to setup a sampling direction line and, when compared to the measured wind data collected during the sampling event, it deviated by only 29° from the average wind direction.

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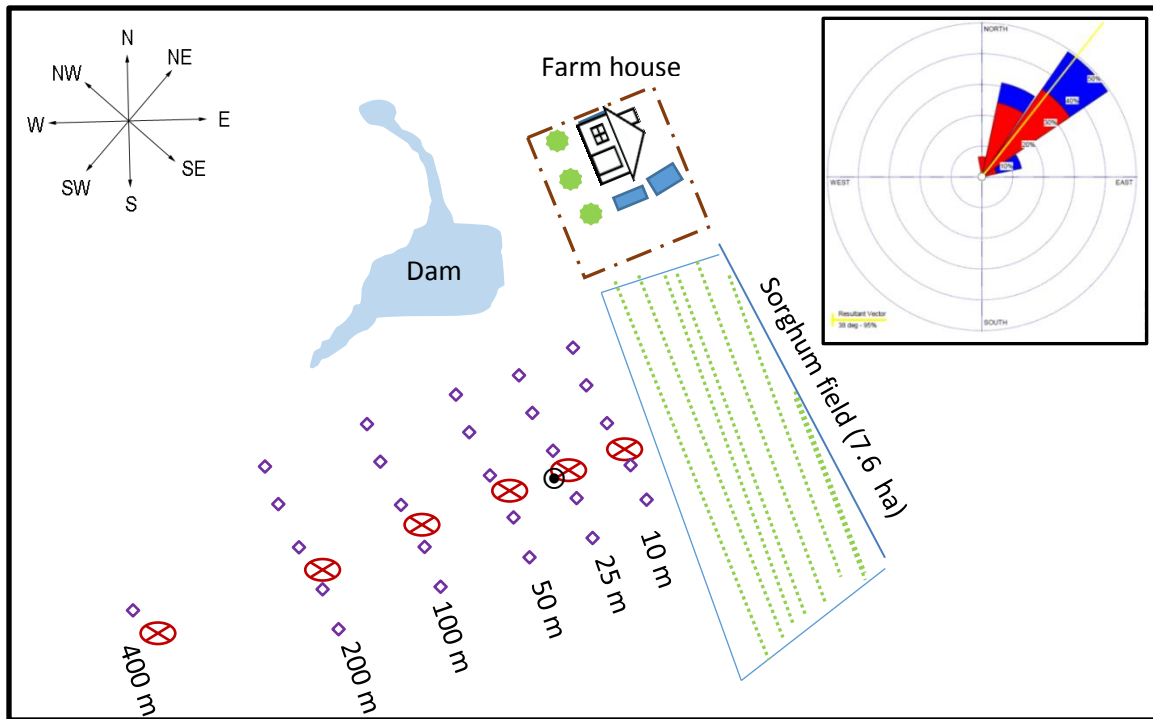
Figure 4.3 Schematic diagram showing sampling positions downwind from the pesticide application site (sorghum field). Airborne drift samplers ⊗ were located at six positions as shown. The deposition and passive flux collectors ◊ were positioned 5 m apart at each sampling location. A weather station ⊙ was set up at the site as indicated. The inserted wind rose shows average wind direction during the 1 hour sampling period (adapted from a Google Earth image of the area).

4.2.1 Deposition sampling

The samplers used for deposition sampling are shown in Figure 4.4 and they were distributed downwind from the application site as shown in Figure 4.3. Each of the samplers comprised a 27 × 15 cm piece of Whatman™ chromatography paper (Sigma-Aldrich®) which was used without prior treatment. This material has been used in previous studies for spray drift deposition monitoring (Miller *et al.*, 2011; Woods *et al.*, 2001). Each piece was placed on an aluminum foil covered support stand which was mounted 20 cm above ground and held in place with paper clamps (Figure 4.4). Deposition was collected over 60 min (including the 10 min spraying time) to allow enough time for transport of the pesticide to the sampler locations and to enhance detection. After sampling the chromatography paper was carefully removed from the stand, covered with aluminum foil, and sealed in plastic bags. Deposition samples were marked and named according to the waypoint location of the sampling position before they were taken for

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storage in a refrigerator at 3 °C prior to analysis. Non-exposed papers were also taken to the field but remained in sealed bags and were used as field blank samples for quality control purposes.

Figure 4.4 Chromatography paper (27×15 cm) mounted 20 cm above the ground and held in place with clamps on an aluminium surface for spray drift deposition sampling.

4.2.2 Active airborne sampling

Polyurethane foam (PUF) plugs (6 cm diameter, 4 cm long) were used to trap atrazine during active air sampling, as done previously by Gish *et al.* (1995). These were prepared by loading two pre-cleaned PUF plugs in-series inside an aluminum cartridge. This setup caters for possible breakthrough from the first plug, thereby improving collection efficiency (Raina & Hall, 2010). Sample blanks were also treated in a similar way for quality control purposes. At each sampling location, four of these cartridges were supported by means of a mast at four different heights above ground level (0.5, 1.0, 1.5, and 2.0 m) and each were connected through a manifold to a WAP air pump (Figure 4.5). Air was continuously drawn through the 24 samplers continuously for 60 min (which included the 10 min of pesticide application) and the flow rate through each PUF cartridge was measured with a Planton GAP air flow meter. A blank air sample was also taken before the spray event to correct for possible atrazine residues in the air from previous applications. After sampling, each cartridge was sealed in aluminium foil and stored in a refrigerator below 0 ˚C prior to analysis.

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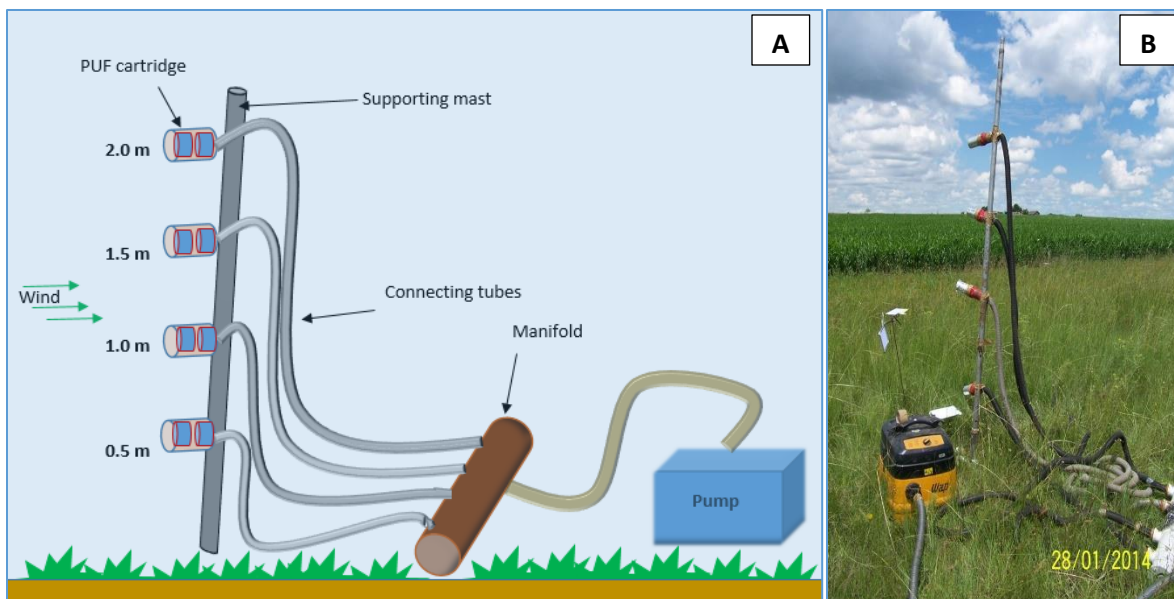
Figure 4.5 (a) Schematic diagram showing the active air samplers that were used. Each cartridge had two PUF plugs in series and the flow rate through each cartridge was over 220 L min^{-1}, while (b) shows the actual setup in the field.

4.2.3 Passive airborne flux sampling

Wool traps made of 21×21 cm aluminium frames into which 3 mm grooves at 5 mm intervals had been machined, were used where wool had been wound in between the grooves in a zigzag pattern (Figure 4.6a-b). The wool, 5 mm thick 100% acrylic polymer, was pre-cleaned by soaking it in a 50:50 (v/v) mixture of acetone and hexane, after which it was allowed to air dry under ambient conditions. The traps were held onto a metal rod 90 cm above the ground with clamps (Figure 4.6c). They were positioned vertically and horizontally to intercept airborne flux and to collect deposition, respectively. Five of these traps were placed 10 m apart at each of the six downwind locations as shown in Figure 4.3. After the sampling period, each wool trap was wrapped in aluminium foil and placed in a sealed plastic bag. They were then taken to the laboratory where they were stored in a refrigerator. Due to budgetary constraints, these samples were not analysed, but were archived for future studies.

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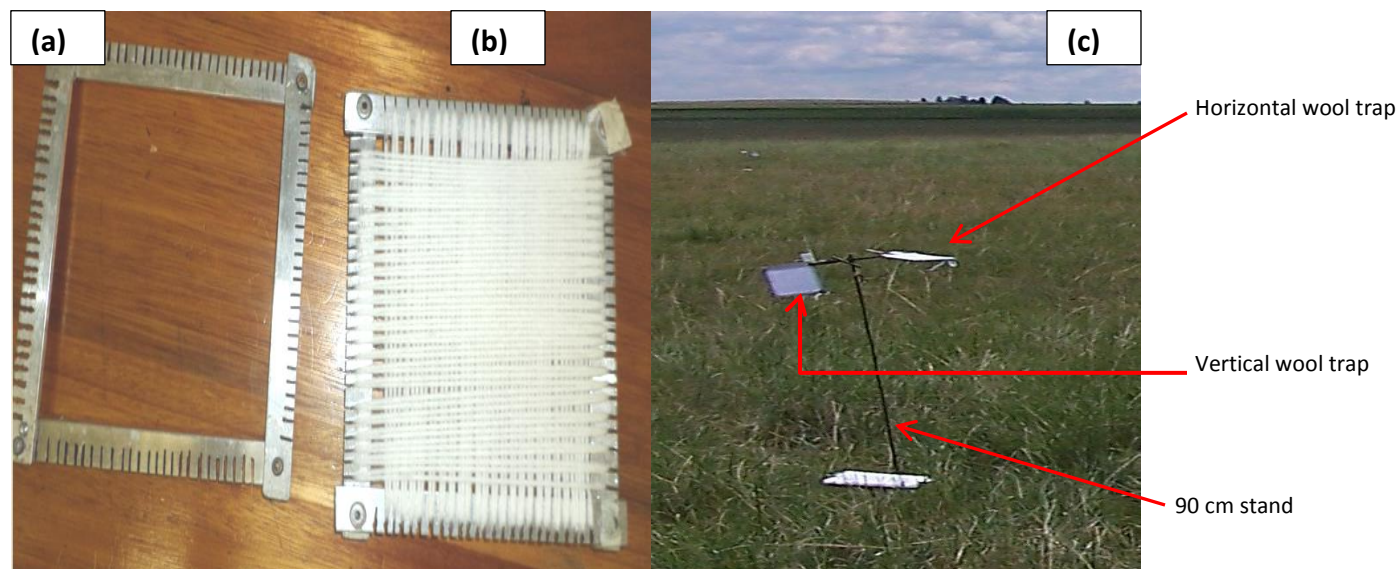
Figure 4.6 (a) Aluminum frame with 3 mm grooves at 5 mm intervals (b) Wool trap made by winding wool into the groves (c) Field set-up of the wool traps.

4.3   Extraction & Analysis of Samples

4.3.1   PUF samples

PUF samples were extracted by means of a plunger and solvent technique previously validated by the Agricultural Research Council (van der Walt, 2000). The method was, however, slightly modified for this particular analysis. Briefly, an acetone:hexane (1:3) mixture was prepared and used as an extraction solvent since other studies have used it for atrazine extraction (Majewski *et al.*, 1998). Both solvents were high purity pesticide grade (Burdick & Jackson obtained from Anatech Pty Ltd). Each PUF plug was extracted with 25 mL of the solvent by repeatedly squeezing it with a stainless steel plunger (Figure 4.7) 10 times and collecting the extract. This was repeated 5 times, adding 25 mL of the solvent each time. All extracts from the PUF plugs of the same cartridge were combined and filtered through filter paper (Grade 480, Lasec SA Pty Ltd). The extracts were pre-concentrated using a rotor evaporator, at 40 °C, then reconstituted to a final volume depending on where the samples were taken from, as dilutions were necessary for samples taken closer to the field.

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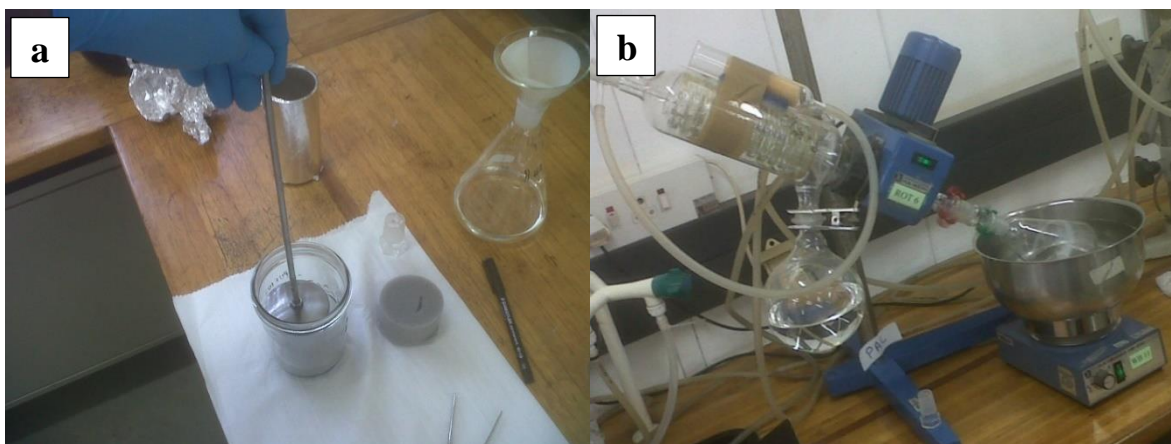
Figure 4.7 (a) Plunger extraction of PUF plugs by squeezing 10 times in acetone:hexane (1:3) solvent with a stainless steel plunger (b) Filtered extracts were pre-concentrated using rotary evaporation before GC analysis.

Analysis and quantification of atrazine was carried out using an Agilent 6870N gas chromatograph equipped with a nitrogen phosphorous detector (GC-NPD) (Agilent Technologies, Inc). 1 μL of sample was injected in splitless mode and the carrier gas was nitrogen at a flow rate of 1.0 mL min^{-1}. A DB-5MS fused silica column (30 m × 0.25 mm ID) with a 0.25 μm film thickness (J & W Scientific, obtained from Agilent Technologies) 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}. All gasses were supplied by Air Products (Pty) Ltd.

4.1.1   Quality assurance/quality control

An atrazine standard, PESTANAL[®] (98.8% purity, Sigma-Aldrich), was used for all method development and analyte identification and quantification. The limit of detection (LOD) was determined from the peak height of an atrazine standard by using the signal-to-noise method (Shrivastava & Gupta, 2011). The noise magnitude was measured manually from the chromatogram printout. A 3:1 ratio was used to calculate the LOD and a 10:1 ratio was used to determine the limit of quantitation (LOQ).

The analyte extraction recovery was also determined to establish the efficiency and reliability of the extraction method. Cartridges with clean PUF plugs were spiked using three different concentrations of atrazine standard (54.34 pg μL^{-1}; 108.68 pg μL^{-1} and 1.09 ng μL^{-1}

respectively). For each concentration, triplicate spikes were made, giving a total of nine fortified matrices, and the recovery was calculated according to Equation 1.

$$\%Recovery = \frac{Peak\ area\ of\ fortified\ matrix}{Peak\ area\ of\ atrazine\ standard} \times 100 \qquad (Equation\ 1)$$

The repeatability of the method is important where a series of analyses are conducted using the same instrument and it is a measure of the consistency of the instrumental response. To test the repeatability, one atrazine standard concentration (108.68 pg μL^{-1}) was chosen and 1 μL was injected six times into the instrument.

Analyte carryover between samples can potentially be a source of error when analyzing a series of samples on the same instrument. To ensure that there was no analyte carryover, a blank solvent (hexane) was periodically injected between sample runs. No significant atrazine peaks were found on the chromatograms of these blank samples, therefore carryover was not significant.

The linearity of the method was determined by accurately preparing a 108.87 ng μL^{-1} atrazine stock solution from which aliquots were taken to prepare a series of dilutions. These were then injected into the instrument at different intervals between field sample runs. This was to ensure that the instrument and method performed linearly throughout the analysis. A nine-point calibration curve was generated from the standard concentrations and was then used for quantification of field samples.

4.1.2 Deposition samples

A 5 cm × 2 cm strip was cut from the middle of each of the chromatography paper sampling sheets and was extracted with 5 mL hexane:acetone (3:1) mixture in an ultrasonic bath for 30 min. To assess recoveries, clean chromatography paper samples were cut into same size as the field samples, then spiked with 5 μL atrazine standard (same as in section 4.3.1) for a range of concentrations from 10 – 1090 pg μL^{-1}. The spiked samples were allowed to dry before being extracted using the same method as for the field samples.

These extracts were stored in a refrigerator with the chromatography paper inside the vials until analysis. Semi-quantitative analysis of the extracts was conducted using a Perkin Elmer AxION® 2 time-of-flight mass spectrometer integrated with the AxION® Direct Sample Analysis™ inlet (DSA-TOFMS). Internal calibration of the instrument was performed using m/z 121.05087 and 622.02896 as lock mass ions (Agilent APCI/APPI tuning mix). The rest of the operating conditions are shown in Table 4-1. A 5 μL portion of the extracted sample was injected onto the mesh grid (sample holder) for introduction into the DSA-TOFMS system. The instrument uses a nitrogen plasma to desorb and ionise the sample from the mesh grid and the stream of ions thus produced enters the time-of-flight mass spectrometer. The analysis of each sample was extremely fast and took 25 seconds per sample. A pesticide library (AxION Solo™) was used for identification of atrazine peaks.

During analysis the instrument could not detect the atrazine in the spiked paper sample extracts, possibly because they were 1000 times diluted during preparation (5 μL in 5 mL). Due to instrument availability limitations it was not possible to prepare additional spiked paper samples. (These samples were kept and later analysed by GC-NPD). Thus in order to generate a calibration curve for semi-quantitation, a range of atrazine standards (10 – 1090 pg μL^{-1}) in hexane:acetone (3:1) were injected directly onto the sample inlet mesh of the instrument. Standards below 86.94 pg μL^{-1} were not detected, therefore only points above this concentration were used to generate a calibration curve which was then used for semi-quantitation of the field samples.

In addition to the DSA-TOFMS analyses, all the field and spiked paper sample extracts were analysed by GC-NPD for comparative purposes, using the same method used for the airborne PUF samples (section 4.3.1). The GC instrumental conditions were kept the same except the column was changed to a 30 m HP-5MS with 0.25 mm i.d. and 0.25 μm film thickness (Agilent Technologies).

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Table 4-1: Operating conditions of the Perkin Elmer AxION® DSA-TOFMS instrument used to analyse pesticide spray drift deposition paper extracts.

MS Conditions		DSA parameters	
Ionization source	AxION® DSA™	DSA heater temperature	250 °C
Ionization mode	Positive	Auxiliary gas	80 psi
Spectral acquisition rate	5 spectra s^{-1}	Drying gas flow rate	3 L min^{-1}
Capillary exit voltage	100 V	Drying gas temperature	25 °C
Detector voltage	8 000 V	Corona needle voltage	2 000 V

4.4 Spray Drift Modelling

The Agricultural DISPersal (AGDISP) model (v8.27) was used to predict the pesticide spray drift. The model uses both Lagrangian and Gaussian-type equations to calculate the droplet trajectories as they are released from the nozzles (section 3.2 in Chapter 3). The model's predictions of pesticide deposition and downwind drift are dependent on a set of parameters which must be consistent with those under which the pesticide application was carried out. This set of inputs must represent the equipment conditions, the nozzles and the drop size distribution (DSD) they create, spray material properties, surface features, and ambient meteorology. Such information was therefore collected during the sampling campaign and is presented in Table 4-2.

4.4.1 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. Sampled 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, Inc.) and later downloaded to a computer with LoggerNet software (version 7.0). The data was then averaged over the 60 min sampling period corresponding to the 10 min application time and 50 min post-application sampling time, similar to previous spray drift studies (Fritz *et al.*, 2011). Wind data was entered into WRPLOT View (v 7.0.0) software from Lakes Environmental ™ to generate a wind rose plot. The 60 min average meteorological measurements are shown in Table 4-2.

4.4.2 Droplet size distribution

To determine the droplet size distribution (DSD) produced by the sprayer, the magnesium oxide method initially described by May (1950) was used. Although this method is not as reliable as a laser diffraction spectrometer, it is cheap and was readily available for use. It has also been employed in the SDTF studies aimed at validating the AGDISP model in 1994 (Hewitt *et al.*, 2010). Briefly, magnesium oxide-coated glass slides were prepared by burning magnesium ribbon strips inside a box that had one end covered by a microscope glass slide. As the ribbon burnt, the magnesium oxide aerosol which was generated coated the microscope slide to form a thin layer. All the slides prepared in this way were taken to the field during monitoring where they were clamped on rods at 1 m above ground and placed along the edge of the sorghum field to capture spray droplets during pesticide application. The droplets made crater impressions on the magnesium oxide slides and images of these impressions 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 (Figure 4.8). The Droplet Retrograde software (2004 version) was then used to convert the images into binary form (Figure 4.9) which was then manually cleaned by eliminating experimental artifacts that were not due to droplets. A droplet size distribution (DSD) was then generated for use as a "User-defined" input to the AGDISP model. The droplet distribution from three slides that were located at the edge of the application area were chosen and used as input for model simulation. This was because slides taken at the edge of the field better represent the actual droplet size produced by the nozzles before significant evaporation could occur.
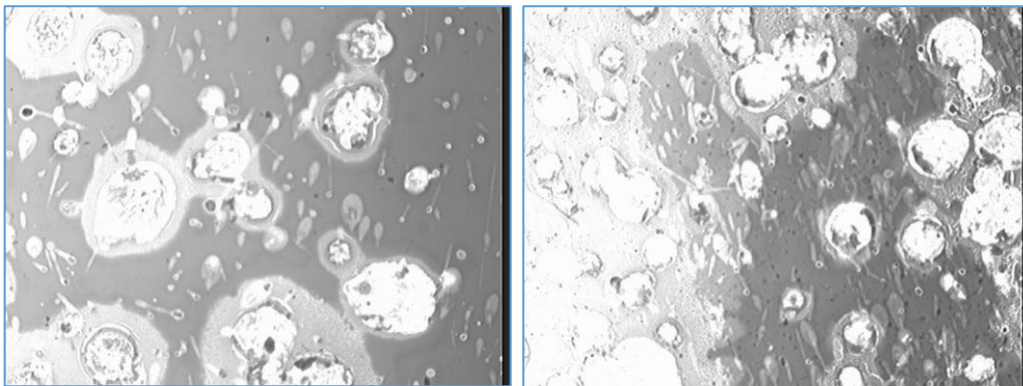
Figure 4.8 Two microscope images (20× magnification) showing droplet impressions on magnesium oxide coated slides.
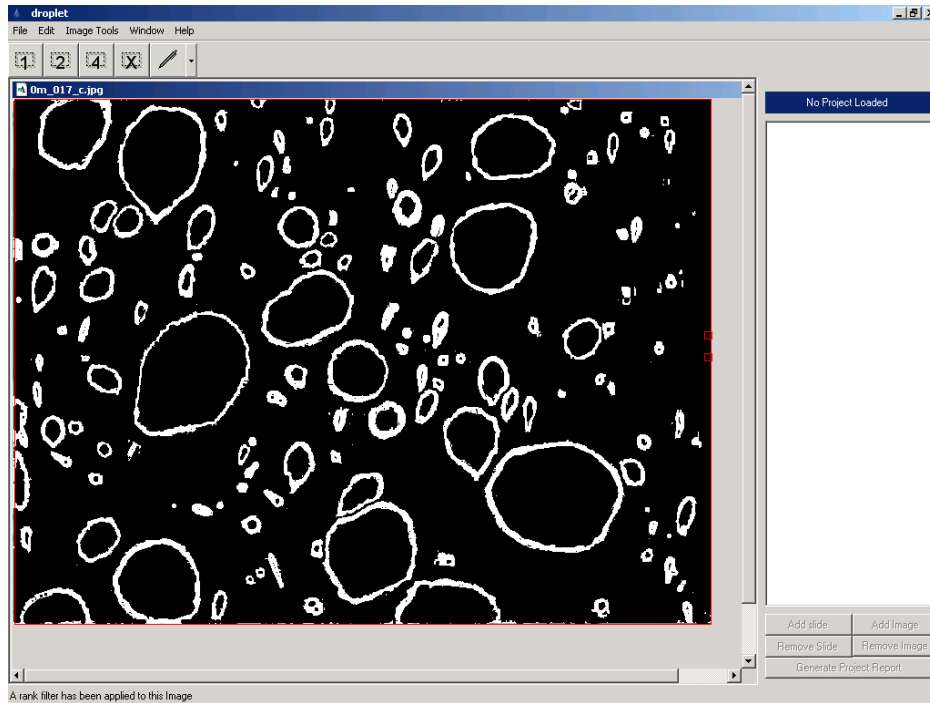
Figure 4.9 Droplet Retrograde software was used to convert the slide image into binary form allowing for the analysis of droplet size distributions.

4.4.3 Other input parameters

Default values for other parameters that were not changed in the model are listed in Appendix A1. Since the spray material was predominantly water, the evaporation rate of water (84.76 μm^2 $°C^{-1}$ s^{-1}) was used as a good estimate of the evaporation rate of the atrazine spray material (Holterman, 2003; Riley *et al.*, 1995; Teske *et al.*, 1998). This assumption is also supported by the SDTF studies which showed that agrichemicals in water-based carriers will behave similar to water in terms of evaporation (Hewitt *et al.*, 2002c). Model sensitivity studies (section 4.4.4) were also carried out to test the effect of 10% variation of this parameter on the model output.

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Table 4-2 AGDISP input parameters used for modelling 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

4.4.4   Sensitivity studies

Additionally, 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 4-3. 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.

Table 4-3 AGDISP sensitivity test matrix

Parameter	Input values		
	Min/Trial 1	*Average/Trial 2*	*Max/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
Volume median diameter (µm)	534.34	600.64	693.27
Application rate (L ha^{-1})	100.00	150.00	200.00

This chapter has provided details of the materials and procedures that were used in this study. The results thus obtained are presented and discussed in Chapter 5.

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Chapter 5   Results and Discussion

5.1   Airborne Spray Drift

5.1.1   GC-NPD analytical validation

The optimized GC-NPD method for the PUF extract analyses was found to have very good analytical parameters. The limit of detection (LOD) was found to be 8.66 pg while the limit of quantitation (LOQ) was 25.99 pg. These low detection levels were suitable for the purpose of this study because most of the field samples were found to contain much higher concentrations of atrazine. Low detection limits are desirable in spray drift monitoring at longer downwind distances where the target analyte is present at low concentrations. Recoveries from spiked PUF samples are shown in Table 5-1 where the mean recovery was 94.5% (3.0% RSD). Since the recoveries were high, the field samples were not corrected for method recovery, as is common practice for environmental analyses if recoveries are good (Ratola *et al.*, 2014; Thompson *et al.*, 1999). The method also showed good linearity (Figure 5.1) with a coefficient of determination of $R^2 = 0.9956$. The full linear range of the method was not investigated but highly concentrated samples, especially those taken closer to the field, were diluted to bring their concentrations within the linear range of the standards employed (section 5.1.2). The calibration curve was used to estimate the standard deviation in the concentration of field samples using s_{xy} statistics (Theodorou *et al.*, 2012).

Furthermore the method displayed good repeatability (3.3% RSD) as determined with the 108.68 pg μL^{-1} atrazine standard as shown in Table 5-1 (n = 6).

Table 5-1 GC-NPD instrument repeatability determined using the 108.68 pg µL^{-1} atrazine standard with recoveries from fortified PUF plugs spiked with three different concentrations.

Repeatability		Extraction Recoveries	
Injection	*Peak Area*	*Spike level*	*Recovery (%)*
1	2.95777	FM1 (54.34 pg µL^{-1})	93.07
2	3.11674	FM2 (108.68 pg µL^{-1})	97.80
3	3.05301	FM3 (1.09 ng pg µL^{-1})	92.67
4	3.04144		
5	3.21621		
6	3.20865		
Mean	3.09897		94.51
σ	0.101440		2.33
% RSD	3.27		3.0

σ = standard deviation

FM = fortified matrix
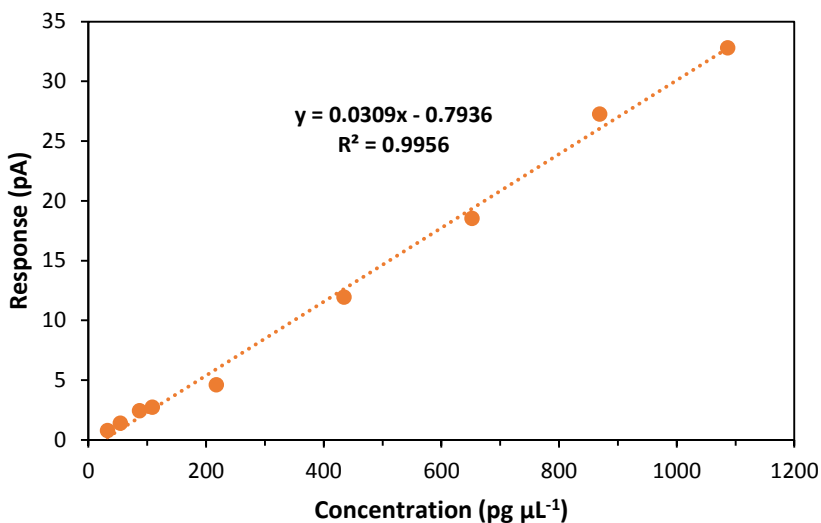
Figure 5.1 Nine-point atrazine calibration curve determined by GC-NPD analysis and used to quantify atrazine in field samples.

5.1.2   Field PUF samples

An example of a chromatogram obtained for a PUF extract is shown in Figure 5.2. The GC-NPD method showed good resolution of the atrazine peak (at 8.26 min) from the other closely eluting triazines especially terbuthylazine. Although the detector gave a relatively high baseline, the atrazine peaks were well above the detection limits for all samples, thus peak-integration, and hence quantitation, was possible. The other peaks in the chromatogram could be due to other

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organic compounds in the air samples, additives in the spray mix, or even impurities in the PUF adsorbents that were used. These peaks were, however, not further investigated because they did not interfere with the atrazine peak of interest.

Airborne atrazine concentrations in PUF samples taken from the different downwind distances and heights are shown in Table 5-2 and graphically represented in Figure 5.3. The results are expressed per volume of air sampled during the 60 min period (inclusive of 10 min of spraying). The percentage recoveries were not used in calculating these results as is common practice in environmental monitoring studies where recoveries are good, as previously mentioned (Ratola *et al.*, 2014; Thompson *et al.*, 1999). The experimental PUF results showed a decrease in airborne atrazine concentrations with downwind distance – a trend that was observed for all four sampling heights. Closer to the field (at 10 and 25 m) there was a greater variation in atrazine concentration with vertical height compared to samples collected further downwind. This could be because the effect of the moving tractor is much more significant at 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 also be noted that at near-field distances (10 and 25 m downwind) the atrazine levels were slightly lower at 0.5 m compared to 1 m above ground. This could be because the pesticide was released from the sprayer at around 1.4 m and therefore the majority of the droplets had still not settled closer to the ground. The lowest concentration (0.139 ng L^{-1}) was detected at 400 m downwind at 2 m vertical height and was above the LOD.

Single ANOVA treatment of the data showed that there was no significant difference in concentrations of samples that were taken at different heights ($p > 0.05$). However, visual comparison showed that samples taken at 2 m height had slightly lower concentrations compared to the other heights. This could be attributed to both deposition of the pesticide to the ground as well as diffusion processes.
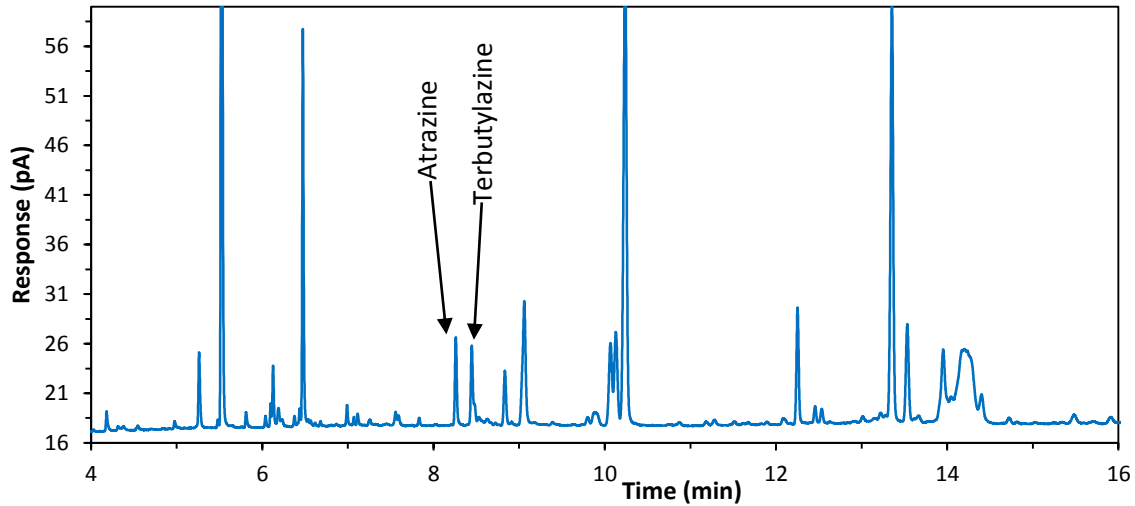
Figure 5.2 Chromatogram of the PUF extract from 400 m downwind and 2 m vertical height. It shows atrazine and terbuthylazine peaks at 8.267 and 8.457 min respectively. The other peaks did not interfere with the peak of interest and therefore were not investigated.

Table 5-2 Airborne atrazine concentration (Conc.) from PUF extract analysis by GC-NPD. The sampling time was 60 min for all samples and concentrations are reported per volume of air sampled during this period.

Downwind distance (m)	Sampling Height (m)	Sample Name	Peak Area	Measured Conc. (pg µL^{-1})	Final Extract Volume (mL)	Extract Amount (pg)	Sampling Flow Rate (L min^{-1})	Sampled Air Volume (L)	Air Conc. (ng L^{-1})
10	0.5	PUF246	10.980	378.73	250.00	94683745	375	22500	4.208
	1.0	PUF104	13.027	445.44	250.00	111360443	410	24600	4.527
	1.5	PUF99	9.711	337.36	250.00	84339975	350	21000	4.016
	2.0	PUF38	9.609	334.03	250.00	83507698	440	26400	3.163
25	0.5	PUF123	8.364	293.47	200.00	58693410	350	21000	2.795
	1.0	PUF320	16.982	574.31	200.00	114861780	425	25500	4.504
	1.5	PUF130	10.777	372.11	200.00	74422672	330	19800	3.759
	2.0	PUF259	8.533	298.99	200.00	59797044	350	21000	2.847
50	0.5	PUF21	13.541	462.17	100.00	46217260	350	21000	2.201
	1.0	PUF126	12.449	426.60	100.00	42660397	320	19200	2.222
	1.5	PUF238	12.461	426.99	100.00	42699075	330	19800	2.157
	2.0	PUF43	13.736	468.54	100.00	46853611	350	21000	2.231
100	0.5	PUF27	4.802	177.38	100.00	17738150	250	15000	1.183
	1.0	PUF122	5.867	212.11	100.00	21210590	260	15600	1.360
	1.5	PUF74	5.477	199.37	100.00	19937050	220	13200	1.510
	2.0	PUF32	3.161	123.90	100.00	12390007	250	15000	0.826
200	0.5	PUF61	2.797	112.06	100.00	11206177	350	21000	0.534
	1.0	PUF3	4.044	152.70	100.00	15269627	350	21000	0.727
	1.5	PUF229	3.115	122.41	100.00	12240566	300	18000	0.680
	2.0	PUF301	3.406	131.89	100.00	13188514	315	18900	0.698
400	0.5	PUF13	19.541	657.69	5.00	3288468	350	21000	0.157
	1.0	PUF278	22.965	769.29	5.00	3846470	350	21000	0.183
	1.5	PUF250	23.536	787.89	5.00	3939457	350	21000	0.188
	2.0	PUF107	14.697	499.85	5.00	2499270	300	18000	0.139

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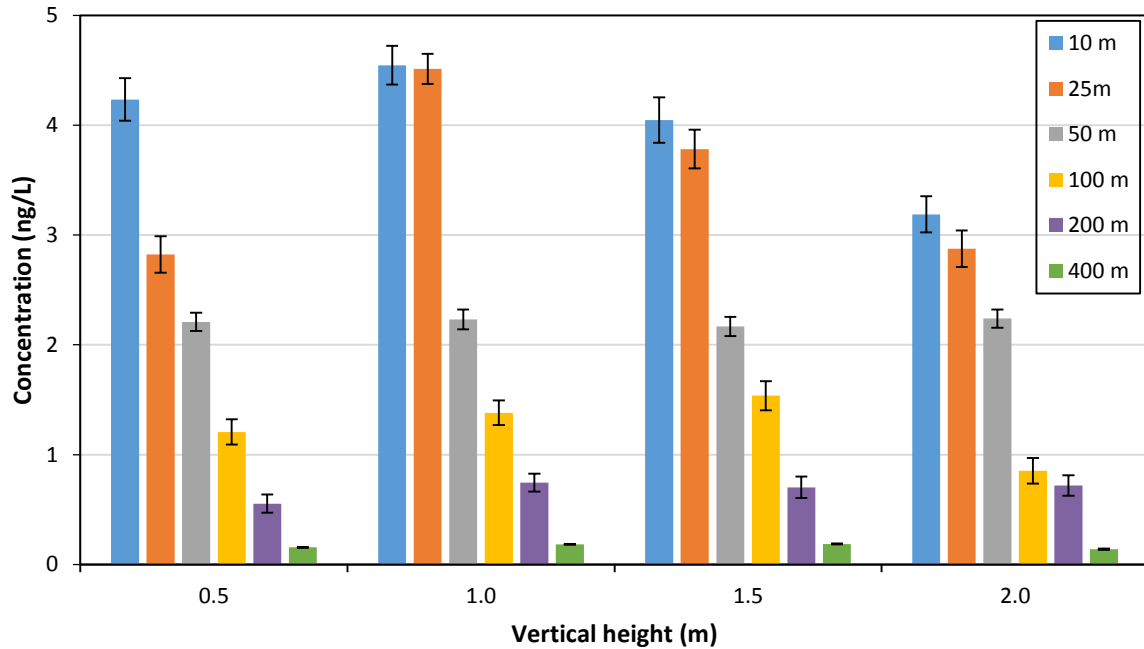
Figure 5.3 Measured atrazine concentrations in PUF samples expressed per volume of air sampled over one hour at the six downwind locations and at four vertical heights. The error bars show the standard deviation obtained using regression analysis.

5.2 Spray drift modelling

Model simulations were carried out using the input data presented in Chapter 4. The wind direction relative to the sampling points is very important when monitoring spray drift. Figure 5.4 shows the average wind direction during the 60 min sampling period. The wind speed was relatively calm and the wind direction remained north-easterly (38˚) with little variation throughout the sampling event, with only 29° variation from the actual sampling line. These stable conditions were ideal for this validation study as there was no need to move the samplers during the monitoring which would have introduced errors which are unaccounted for by the AGDISP model. The model only uses one value for wind speed and direction and cannot account for variation in these input parameters.

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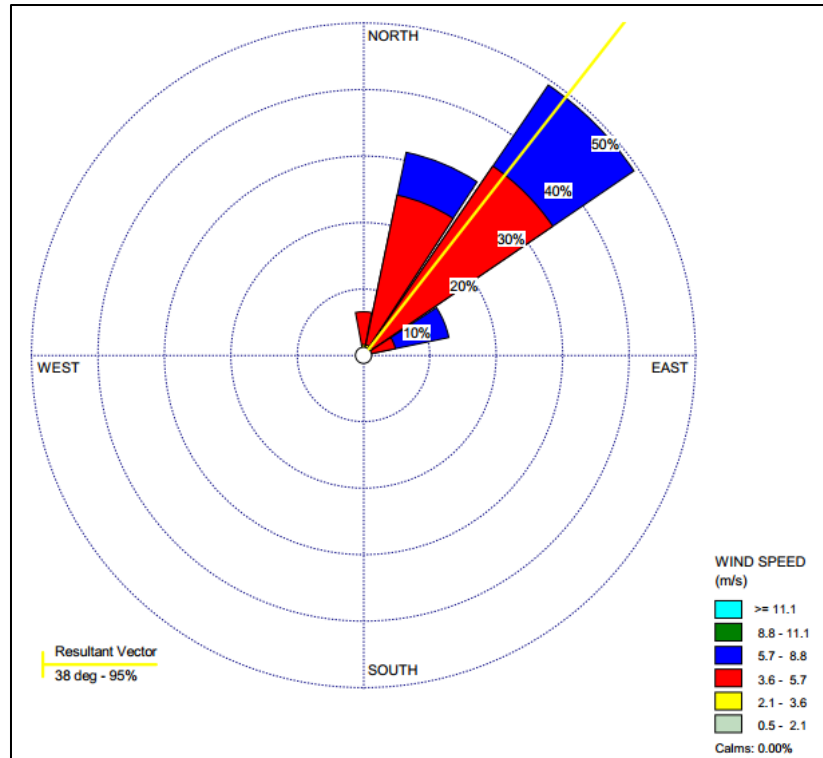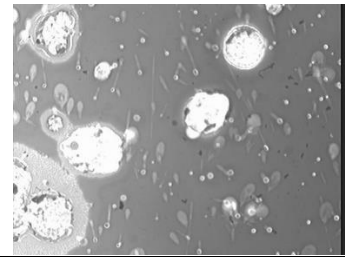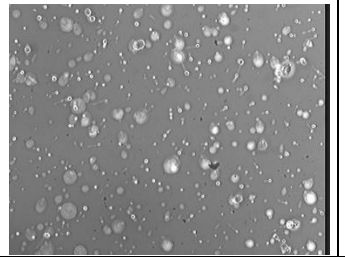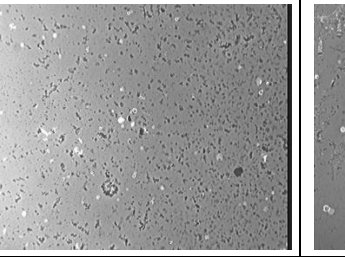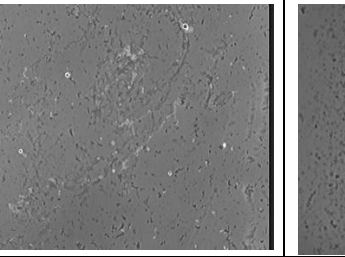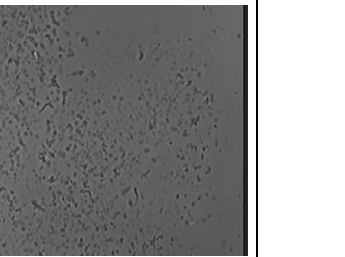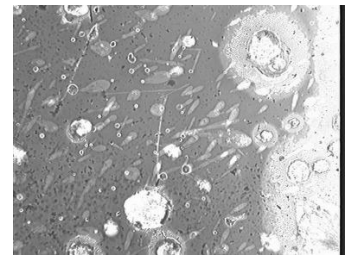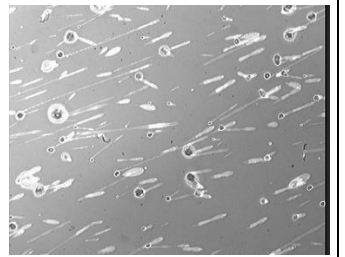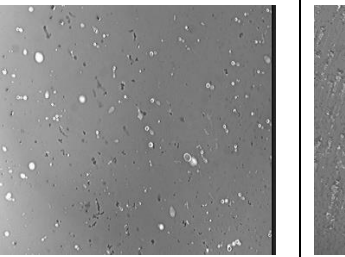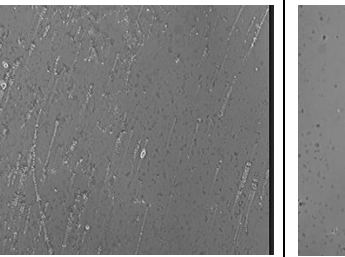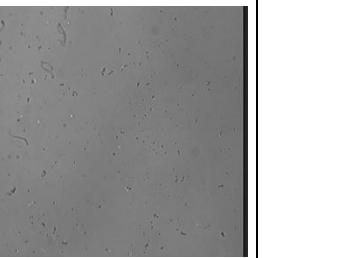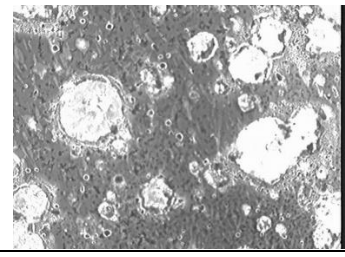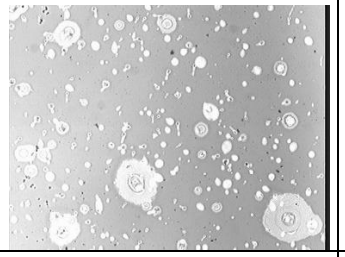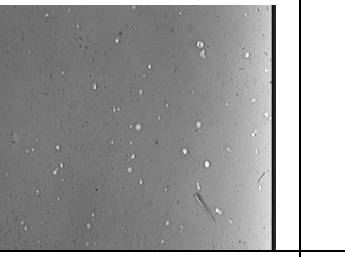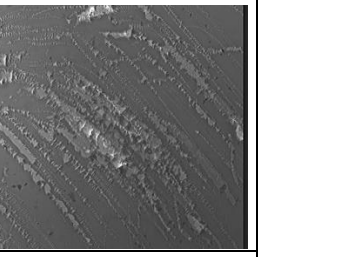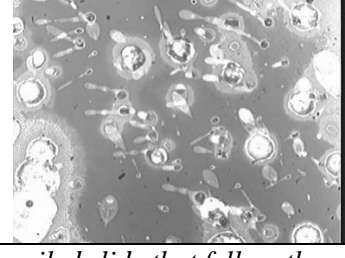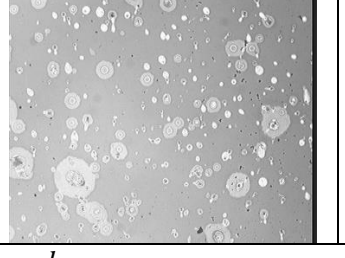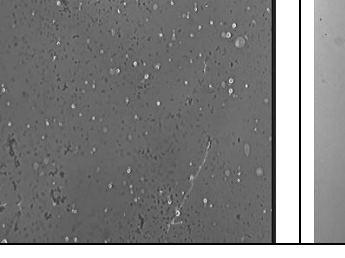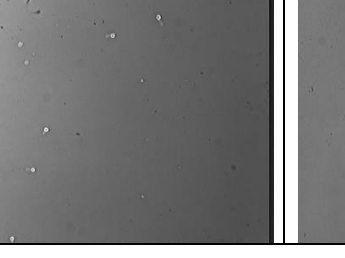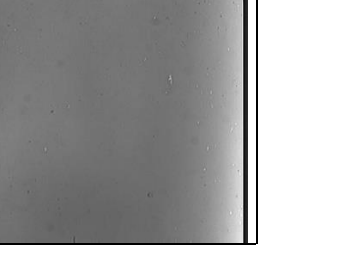
Figure 5.4 Wind rose showing that north-easterly wind conditions prevailed during the 60 min of pesticide spray drift monitoring. The average wind speed was 5.17 m s^{-1} and the average wind direction was 38˚.

Table 5.3 shows microscope images taken from magnesium oxides slides that were used to determine the droplet size distribution (DSD). Larger droplets were captured near the application area which became finer progressively as the spray cloud drifted downwind. Thus only droplets closer to the field were analysed to determine the DSD produced by the nozzles. Streaking of the droplets was evident on some slides, for example slide No. 024, and grass scratched some of them, for example slide No. 012. At 200 and 400 m no droplet impressions were found on the slides as they were positioned too far from the application site.

Table 5-4 shows three sets of droplet size distributions generated from image analysis of magnesium oxide slides, which are presented graphically in Figure 5.5. The three sets had volume median diameters (VMD) of 693.26, 600.64, and 534.34 μm which corresponded to 166.5, 208.0, and 145.3 μm average diameter, respectively. It is evident from Figure 5.5 that the VMD set for 693.26 μm had a significantly different droplet size distribution to the other two slides, with a larger fraction of larger droplets. These results show that the sprayer nozzles produced coarse droplets according to the American Society of Agricultural Engineers (ASAE)

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classification (Czaczyk *et al.*, 2012) which is preferable to increase deposition onto the target crop and reduce spray drift. The simulated airborne atrazine drift and deposition results are presented in Figures 5.6 and 5.7 respectively in the following sections.

Table 5-3 Microscope images (20 × magnification) showing droplet impressions on the magnesium oxide-coated glass slides placed downwind of the sprayed field. Slides at 200 and 400 m showed no droplet impressions and are not included in this table. Numbers next to each slide show sampling waypoints.

	0 m	10 m	25 m	50 m	100 m
Sorghum field	*017*	*025*	*027*	*028*	*037*
	018	*024*	*026*	*029*	*036*
	019	*010*	*009*	*011* #	*012*
	020	*023*	*033*	*030*	*034*

 # = spoiled slide that fell on the ground

Table 5-4 Droplet size distributions (DSD) generated from analysis of three magnesium oxide slides. For each of the three sets, the droplet diameter, incremental volume fraction (IVF) and cumulative volume fraction (CVF) were input to the AGDISP model as user defined inputs.

1	$Dv_{0.5}$ = 693.28 μm			$Dv_{0.5}$ = 600.64 μm			$Dv_{0.5}$ = 534.24 μm		
1	Diameter (μm)	IVF	CVF	Diameter (μm)	IVF	CVF	Diameter (μm)	IVF	CVF
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	0.0240	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	0.0080	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	0.3050	354.43	0.0575	0.1582
9	527.55	0	0.2640	413.82	0	0.3050	399.18	0.0548	0.2130
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	0.0950	0.4949	488.68	0.0503	0.3010
12	707.11	0.1657	0.5408	553.23	0	0.4949	533.43	0.1961	0.4971
13	766.96	0	0.5408	599.70	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
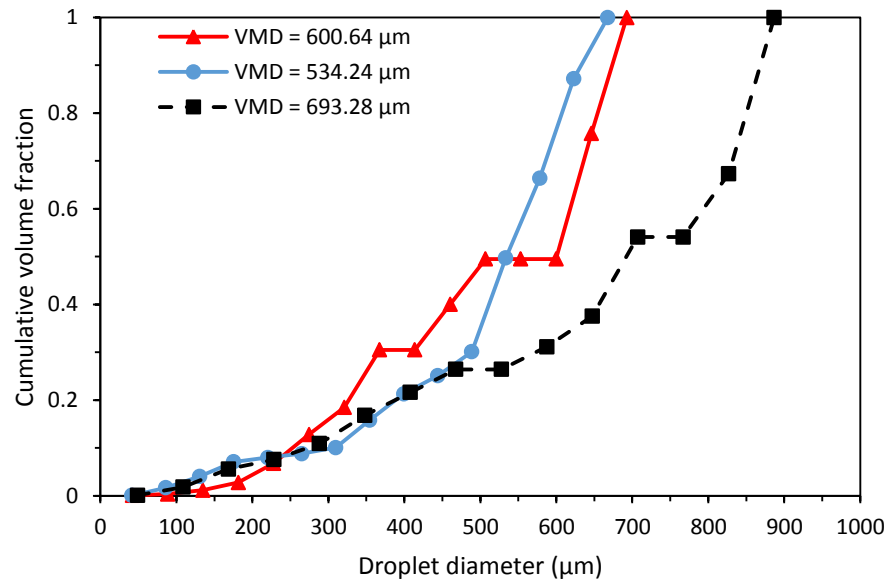
Figure 5.5 Cumulative volume fraction for the three droplet size distribution classes generated by the AGDISP model.

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5.3 Comparison Between Model Predicted and Experimental Airborne Pesticide Spray Drift

A comparison of modelled versus experimental airborne atrazine concentrations at the different vertical heights is shown in Figure 5.6. It was not possible to compare the field concentrations at 0.5 m vertical heights with predicted values because 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, a trend that 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 could be a consequence of the actual versus predicted rates of volatilization and dispersion of the spray plume or due to the droplet size distributions employed. 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 is of significant as the concentrations were very low (ng L^{-1}). Relative errors at these low concentrations can easily become significant as shown by the Horwitz trumpet (Workman Jr & Mark, 2006).

The correlation between experimental and model results was found to be very dependent on the average droplet size as shown in Figure 5.6. From the analysis of three different magnesium oxide slides, three different droplet size distributions were obtained (Table 5.4). The best correlation between experimental and modelled results was observed when the droplet distribution with an average size of 166.5μm was used (VMD = 693 μm). From Figure 5.5 it is evident that this droplet size distribution had a larger fraction of larger droplets, which were likely most closely related to the droplet size produced from the sprayer before any evaporation effects in the atmosphere had been incurred, which resulted in a good correlation between predicted and measured airborne spray drift. When simulations were done with smaller droplet size inputs (145.3 μm), the model over-predicted the concentration by up to 3 times near-field but predicted the concentration further downwind somewhat better (VMD = 534 μm). Using 207.9 μm diameter droplets (VMD = 600 μm) 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.

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No studies are known to have attempted to compare field airborne pesticide concentrations with the AGDISP model predictions for ground application validations. A study by Connell *et al.* (2012) only compared vertical flux up to 5 m downwind where they found the flux predicted by AGDISP to be much higher (6 times for flat fan nozzles, 3 – 15 times for XR8003 nozzles, and 3 – 6 times for air induction (AI) nozzles). The study did not measure the actual active ingredient to monitor drift, but rather a dye and metal cations as tracers and this could explain the differences between their study (Connell *et al.*, 2012) and this study. This study has also validated the AGDISP model up to 400 m downwind which no other published study has done for the ground application function of the model.
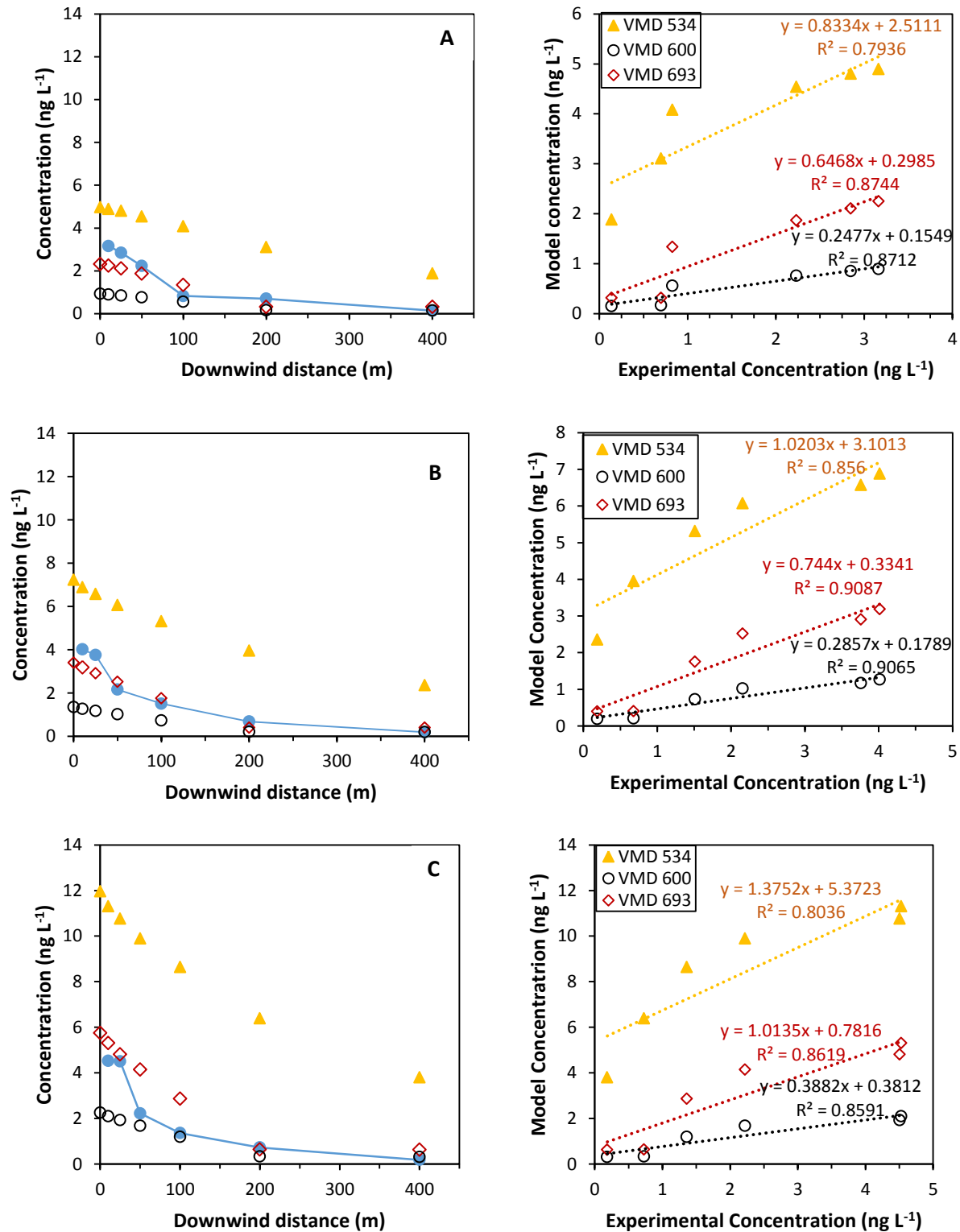
Figure 5.6 Left: Comparison of model versus experimental airborne results ● at three different vertical heights (a) 2.0 m (b) 1.5 m (c) 1.0 m. Three model runs were made using different droplet size distributions ⭕VMD 600 (208.0 μm diameter) ◇VMD 693 (166.5 μm diameter) and ▲VMD 534 (145.3 μm diameter).

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5.4 Deposition Spray Drift

5.4.1 AGDISP deposition simulation

Atrazine deposition results predicted by the AGDISP model using the set of inputs as for airborne simulation, are shown in Figure 5.7. The model revealed that the smaller droplets (145.3 µm diameter) had higher downwind deposition rates compared larger droplets. This was expected since larger droplets, because of their larger mass, are less susceptible to drift and tend to settle closer to the sprayed area while the smaller droplets are lighter and therefore are more prone to drift further and deposit downwind (Jones *et al.*, 2002).
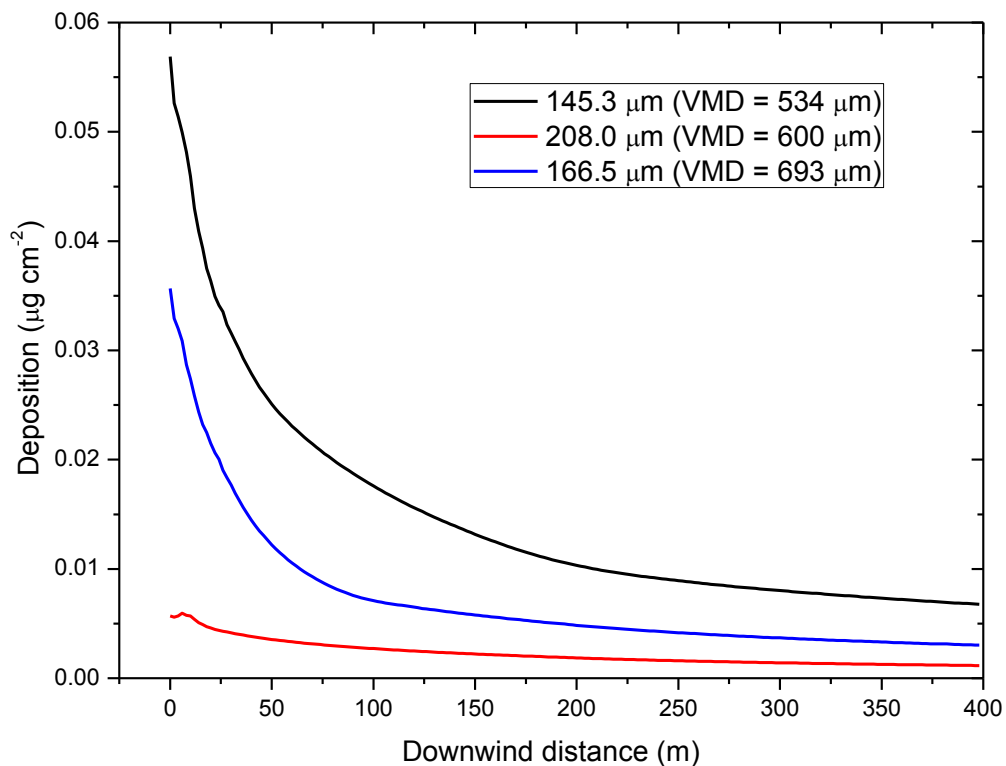
Figure 5.7 Downwind deposition rates predicted by the AGDISP model using three different droplet size distribution sets. The average droplet diameters were 145.3, 208.0, and 166.5 µm.

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5.4.2 Field Deposition Samples

5.4.2.1 Deposition determined by DSA-TOFMS

The DSA-TOFMS method was very rapid and it only took 25 seconds per sample for analysis, making it ideal as a screening technique. The method adequately identified atrazine and terbuthylazine, which were both present as active substances in the spray formulation, with very good mass accuracy (< 5 ppm) as shown in Figure 5.8. The calibration curve that was used for semi-quantitation of deposition samples is shown in Figure 5.9 and it is evident that the method showed good linearity (R^2 = 0.9934) within the measured range of concentrations. The instrument could not detect atrazine standards concentrations below 87 pg uL^{-1} therefore those points were excluded from the calibration curve.

Screening results for atrazine & terbuthylazine found in chromatography paper extracts are shown in Table 5-5. The mass accuracy was very good for samples taken closer to the field but it became poorer for samples taken further downwind because of the very low concentration levels. These results reflect the direction of the wind during sampling very well as can be seen from the wind rose. Semi-quantitation results for atrazine, which was the target analyte, are shown in Table 5-6. Although atrazine was detected in samples taken from 200 and 400 m downwind, the levels were too low for the instrument to integrate the peak area, hence they are reported to be below the detection limit in Table 5-6. This is because less deposition occurred at these distances during the sampling period as most of the coarse spray droplets were heavy enough to undergo deposition close to the field before drifting downwind to these distances. For some samples at 100 m, a mass spectrum was obtained which indicated the presence of atrazine but the library software could not integrate the signal to give a peak area at these low levels, hence they are also reported to be below instrumental detection limit.
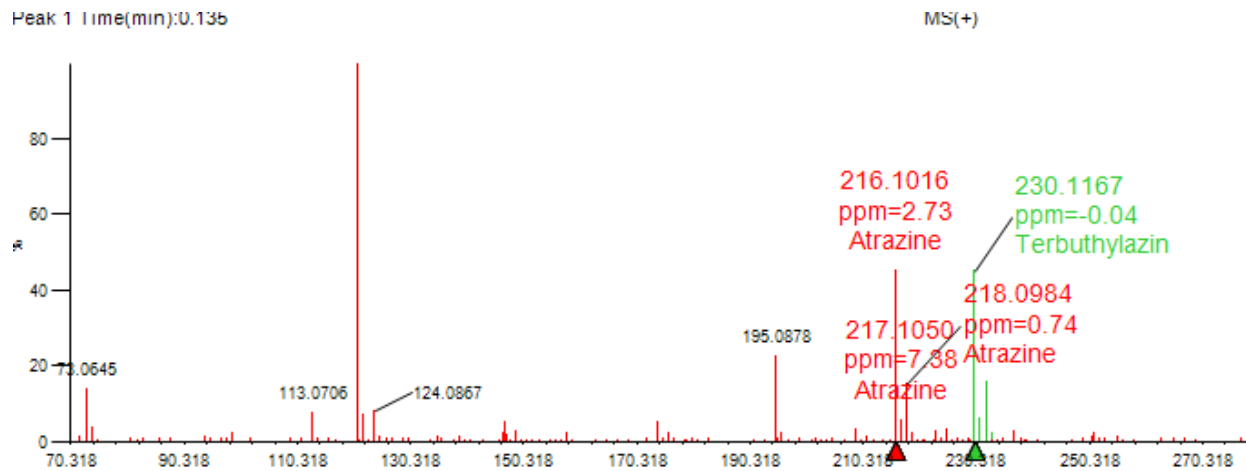
Figure 5.8 Example of a mass spectrum obtained from DSA-TOFMS analysis of a deposition sample extract. The atrazine peaks with m/z 216.1016 mass spectra were used for semi-quantitation of downwind deposition.

y = 0.4206x - 28.813
R^2 = 0.9934
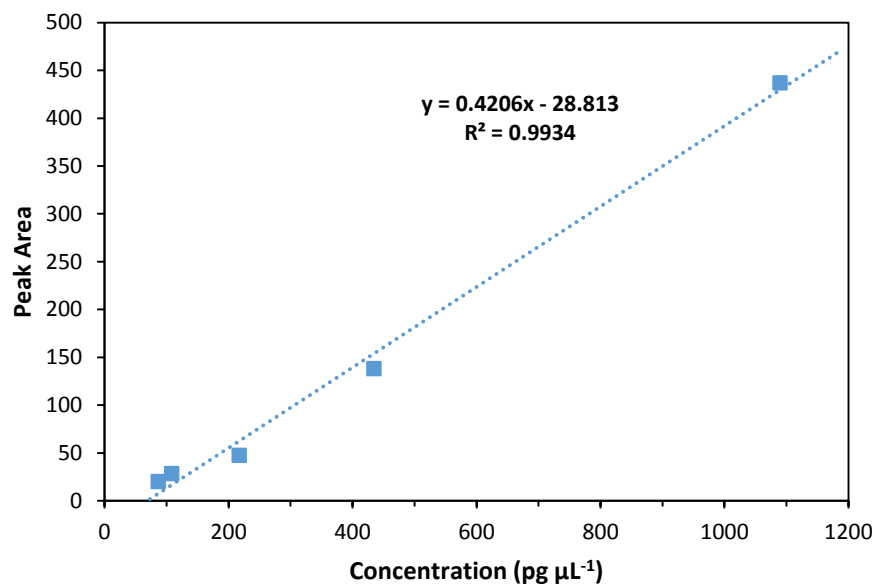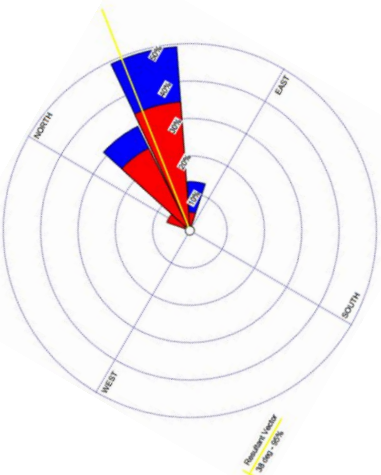
Figure 5.9 Calibration curve for atrazine semi-quantitation using DSA-TOFMS analysis.

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Table 5-5 Compounds detected from chromatography paper extracts using the DSA-TOFMS screening method. Values in parenthesis show mass accuracy in ppm units. Overlaid is a wind rose showing the wind direction relative to the sampling position.

Downwind distance (m)	Sorghum Field								
	P044	P043	P042	P021	P020	*P019	P018	P017	P015
0	Atrazine (3.15) Terbuthylazine (3.26)	Atrazine (2.68) Terbuthylazine (2.87)	Atrazine (2.68) Terbuthylazine (1.65)	Atrazine (4.58) Terbuthylazine (4.39)	Atrazine (2.59) Terbuthylazine (2.91)	Atrazine (2.82) Terbuthylazine (1.96)	Atrazine (3.98) Terbuthylazine (3.00)	Atrazine (2.82) Terbuthylazine (2.26)	Atrazine (3.56) Terbuthylazine (2.00)
				P022	P023	*P010	P024	P025	
10				Atrazine (-28.78) Terbuthylazine (-28.07)	Atrazine (-27.16) Terbuthylazine (-26.51)	Atrazine (-24.25) Terbuthylazine (25.64)	Atrazine (-25.31) Terbuthylazine (-23.77)	Atrazine (-25.590) Terbuthylazine (-24.55)	
				P031	P030	*P009	P026	P027	
25				Atrazine (-25.22) Terbuthylazine (-22.73)	Atrazine (-20.59) Terbuthylazine (-23.42)	Atrazine (-23.09) Terbuthylazine (-24.38)	Atrazine (-7.87) Terbuthylazine (-8.08)	Δ	
				P032	P033	*P011	P029	P028	
50				Atrazine (-23.28) Terbuthylazine (-24.29)	nd	Atrazine (-21.89) Terbuthylazine (-22.12)	Atrazine (-18.32) Terbuthylazine (-18.43)	Atrazine (-19.57) Terbuthylazine (-18.86)	
				P035	P034	*P012	P036	P037	
100				Atrazine (-18.79)	Atrazine (-16.66) Terbuthylazine (-14.91)	Atrazine (-16.94) Terbuthylazine (-14.34)	Atrazine (-14.81) Terbuthylazine (-15.34)	Atrazine (-13.84) Terbuthylazine (-14.47)	
				P041	P040	*P013	P039	P038	
200				nd	nd	nd	Atrazine (41.18) Terbuthylazine (46.06)	nd	
				P046	P045	*P049	P047	P048	
400				#	#	nd	#	#	

*=Samples taken along the sampling line
nd = not detected
# = points where no samples were taken
Δ = missing sample during analysis

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Table 5-6 Atrazine deposition determined from analysis of 10 cm^2 chromatography paper sample extracts using AxION DSA-TOFMS. The peak area of atrazine (m/z =216) was used for semi-quantitation.

Downwind Distance (m)	Sample Name	Peak Area	Concentration (pg μL^{-1})	Amount Extracted (pg)	Deposition (μg cm^{-2})
0 m	P044	55.32	200.03	1000	0.10
	P043	412.62	1049.53	5248	0.52
	P021	222.65	597.87	2970	0.30
	P020	91.92	287.05	1435	0.14
	P019*	247.82	657.71	3289	0.33
	P017	1059.6	2587.76	12939	1.3
	P018	142.69	407.75	2039	0.20
	P015	476.9	1202.36	6012	0.60
	P016	1059.6	2587.76	12939	1.3
10 m	P022	106.07	320.69	1603	0.16
	P023	109.29	328.35	1642	0.16
	P010*	231.42	618.72	3094	0.31
	P024	303.92	791.09	3955	0.40
	P025	92.07	287.41	1437	0.14
25 m	P031	nd	nd	nd	nd
	P009*	32.3	145.30	3632489	0.36
	P026	32.27	145.23	3630706	0.36
	P027	30.58	141.21	3530254	0.35
50 m	P032	42.27	169.00	4225095	0.42
	P033	44.47	174.23	4355861	0.44
	P011*	nd	nd	nd	nd
	P029	nd	nd	nd	nd
	P028	nd	nd	nd	nd
100 m	P037	nd	nd	nd	nd
	P036	nd	nd	nd	nd
	P012*	nd	nd	nd	nd
	P034	nd	nd	nd	nd
	P035	nd	nd	nd	nd
Control	Blank	nd	nd	nd	Nd

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5.4.2.2 Deposition Determined by GC-NPD

When the GC-NPD method was used for analysis of paper sample extracts very high recoveries (over 100%) were found (Table 5-7). Extracts spiked below 435 pg μL^{-1} were too dilute upon extraction with 5 mL of solvent, hence were not detected by the instrument. The enhanced recoveries suggest possible matrix effects that may have been enhanced due to sample storage for a long time before analysis, as the paper was stored in the vials with extracts and evaporation of solvents could have occurred which would result in raised recovery values. When pure atrazine standards prepared in the same solvent were used for calibration, the method showed good linearity with (R^2 = 0.9991) within the 32.60 – 400 pg μL^{-1} concentration range, as shown in Figure 5.10, and therefore was applied to quantify the field deposition samples (Table 5-8).

Table 5-7 Recoveries from chromatography paper extracts spiked with four different concentrations of atrazine. Each fortified matrix (FM) was extracted with 5 mL of 3:1 hexane:acetone solvent mixture.

Spike level	Recovery (%)
FM1 (217 pg μL^{-1})	nd
FM2 (435 pg μL^{-1})	203
FM3 (1086 pg μL^{-1})	17
FM4 (10868 pg μL^{-1})	145

nd=not detected by instrument
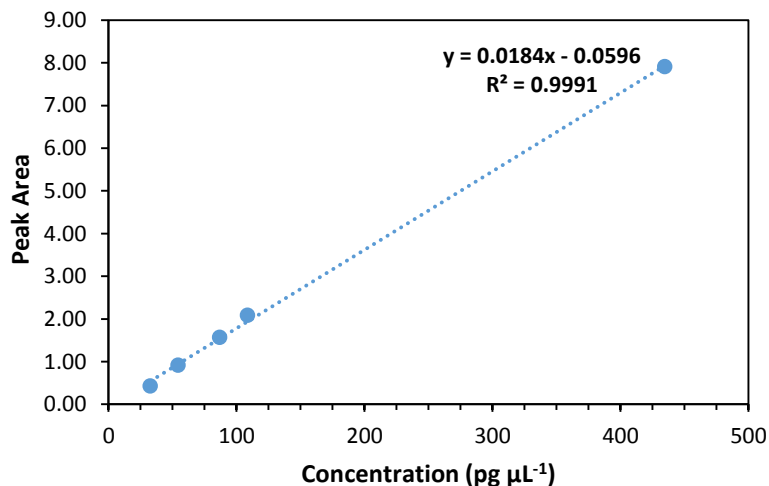
Figure 5.10 GC-NPD calibration curve for atrazine standards.

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Figure 5.11 shows overlaid chromatograms from deposition paper sample extracts taken along the sampling line from 10 m up to 100 m. The peak heights diminished from 10 to 100 m corresponding to the decrease in downwind deposition with increasing distance. It is important to note that the retention times are different from those obtained from airborne PUF samples. This is because a different GC column was used for analysis of the paper sample extracts.
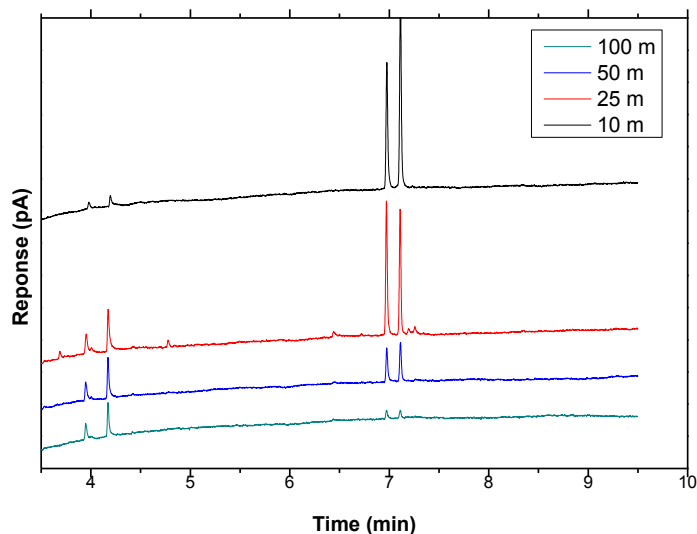
Figure 5.11 Overlaid chromatograms showing atrazine (6.9 min) and terbuthylazine (7.2 min) peaks from deposition paper extracts taken along the sampling line at 10 m to 100 m downwind distances.

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Table 5-8 Deposition concentrations determined from GC-NPD analysis of extracts from 10 cm^2 portions of chromatography paper. 1 µL injection was made for all samples.

Downwind distance (m)	Sample Name	Peak Area	Concentration (pg µL^{-1})	Dilution factor	Final Volume (mL)	Extracted amount (pg)	Deposition (µg cm^{-2})
0 m	P044	4.969	274.31	1000	5.00	1371563869	137
	P043	2.420	181.29	1000	5.00	1551737750	155
	P021	0.972	128.46	1000	5.00	1353423950	135
	P020	2.421	181.36	1000	5.00	1552020300	155
	P019*	0.840	123.63	1000	5.00	1335301800	134
	P017	2.947	200.54	1000	5.00	1624017350	162
	P018	2.312	177.33	1000	5.00	1536902350	154
	P015	2.53	185.58	1000	5.00	1567861750	157
	P016	3.346	215.09	1000	5.00	1678643000	168
10 m	P022	52.638	2014.05	1	5.00	8431572	0.843
	P023	13.022	568.24	1	5.00	3004274	0.300
	P010*	5.084	278.52	1	5.00	1916744	0.192
	P024	95.617	3582.63	1	5.00	14319692	1.43
	P025	50.638	1941.06	1	5.00	8157588	0.818
25 m	P031	1.647	153.09	1	5.00	1445875	0.145
	P009*	4.978	274.64	1	5.00	1902185	0.190
	P026	2.084	169.03	1	5.00	1505743	0.152
	P027	2.475	183.32	1	5.00	1559358	0.156
50 m	P032	6.781	340.47	1	5.00	2149271	0.215
	P033	6.136	316.91	1	5.00	2060850	0.206
	P011*	1.371	143.00	1	5.00	1408007	0.141
	P029	1.226	137.70	1	5.00	1388114	0.139
	P028	0.9.31	126.94	1	5.00	1347713	0.135
100 m	P037	0.678	117.73	1	5.00	1313158	0.131
	P036	0.733	119.73	1	5.00	1320675	0.132
	P012*	0.395	107.39	1	5.00	1274315	0.1275
	P034	0.568	113.71	1	5.00	1298084	0.130
	P035	0.365	106.29	1	5.00	1270212	0.127
200 m	P038	0.103	96.72	1	1.50	19719	0.002
	P039	0.237	101.61	1	1.50	286290000	2862
	P013*	0.279	103.15	1	1.50	32946	0.003
	P040	0.958	96.47	1	1.50	19201	0.002
	P041	0.140	98.07	1	1.50	22494	0.002
400 m	P049*	0.101	96.67	1	1.50	19616	0.002
Control	Blank	nd	nd	1	1.50	nd	nd

* = Samples along the downwind sampling line
nd = not detected by instrument

5.4.3 Comparison between model and field deposition results

Figure 5.12 shows the experimentally determined downwind deposition rates which were measured using GC-NPD and DSA-TOFMS techniques of the same sample extract solutions. Note that the LOD was plotted for DSA-TOFMS measurements between 50 and 400 m as a worst case scenario because the analyte was below the instrument detection limit, which resulted in the graph being flat in this region. Even though these techniques showed a similar trend in terms of a decrease in deposition rates with downwind distance, much higher deposition rates were obtained from analysis using the DSA-TOFMS method compared to those measured with the GC-NPD method. There was an even greater difference between the two techniques for samples taken closer to the field (at 10 m downwind). This could be because the samples were first analyzed on the DSA-TOFMS instrument before they were taken for analysis by GC-NPD which was done after some weeks. During this period it is possible that a portion of the analyte (atrazine) was lost due to adsorption onto the walls of the glassware during storage or onto the paper stored in the vials, hence resulting in the lower concentration determined by GC-NPD. Another reason could be purely due to the different sensitivities of the two instrumental techniques. A repeat analysis to further investigate the cause of these different concentrations could not be carried out because of instrument time constraints.

A comparison of the experimentally measured atrazine deposition rates with those predicted by the AGDISP model is also shown in Figure 5.12 for the central sampling line, as that is what the model predicts. The results showed that the model under-predicted the deposition by up to one order of magnitude compared to the GC-NPD results and by even more compared to the DSA-TOFMS results. This is in contrast to a study by Woodward *et al.* (2008) which also attempted to validate the ground application feature of AGDISP. They found that the model over-predicted the downwind deposition by a factor of 3.5 – 100. A very similar study by Zabkiewicz *et al.* (2009) also reported an over-prediction of downwind deposition by the AGDISP model. The difference between the results could be due to the different field monitoring approaches. The other studies used metal ions as tracers while this study used the actual active ingredient in the spray solution to monitor the pesticide drift and deposition rates, as well as differences in the collection efficiency of the deposition samplers employed makes it difficult to adequately compare different studies.
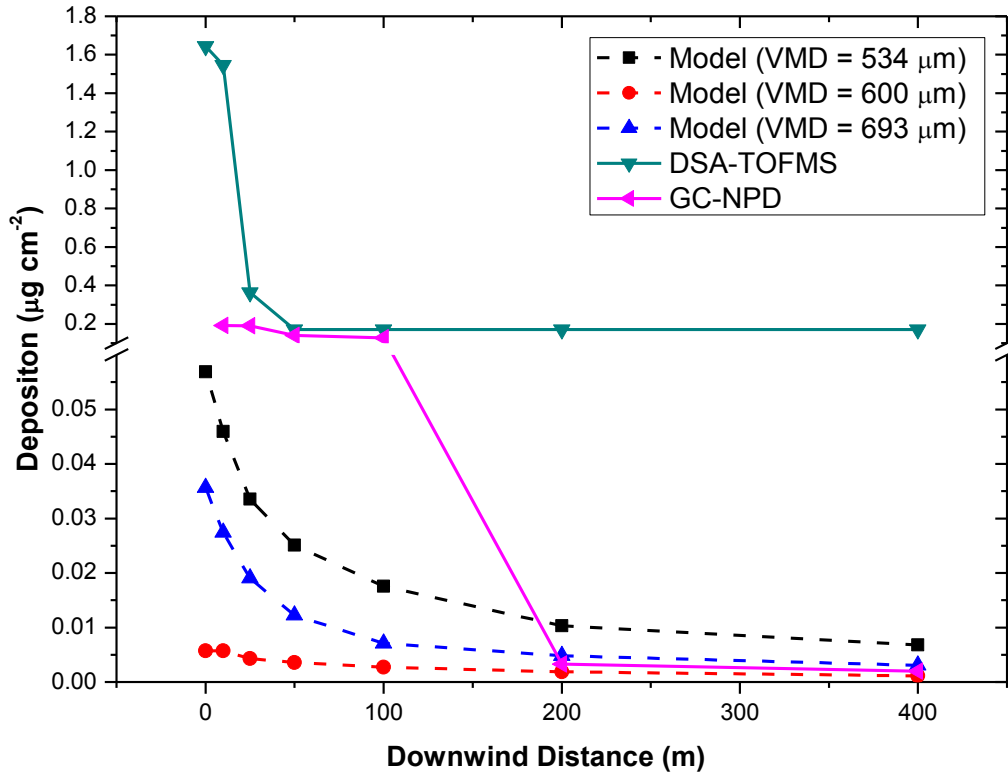
Figure 5.12 Comparison of model predicted deposition (dotted lines) with experimental deposition (solid lines) along the sampling line. The experimental deposition was measured with two techniques, GC-NPD and AxION DSA-TOFMS.

The big difference between the model predicted and field deposition results show that the model may not predict deposition accurately. Therefore caution should be employed when using this feature especially when the results are used for risk assessments, as under-predictions of the model may not identify potential environmental risks.

5.5   Model Sensitivity

All the airborne sensitivity studies were done at 1.5 m height as this is relevant for human exposure in risk assessment studies. Among the parameters that were investigated, the model was found to be most sensitive by far to the droplet size distribution for both deposition (Figure 5.13) and airborne concentrations (Figure 5.14). The variability within each parameter is shown in Figure 5.15 for airborne simulations and Figure 5.16 for deposition simulations. In both cases there was variability with distance from the application site (mainly from 100 – 200 m for airborne and 50 – 100 m for deposition). Variability within the temperature values was the least,

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showing that any fluctuations that occurred during monitoring did not significantly affect the modelling outcome.

For lighter, smaller droplets the model predicted a higher airborne concentration, suggesting that they are more likely to remain airborne, whilst larger droplets precipitate to the ground more readily. The results also showed that varying the evaporation rate by $\sim\pm10\%$ from the default value 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 indeed there was 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 most 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; Nuyttens *et al.*, 2013) and that wind speed was reported to be the most significant meteorological parameter (Bird *et al.*, 1996; Phillips & Miller, 1999). Hoffmann (2006b) also performed some sensitivity studies with the AGDISP model and found that a 1.5 m s^{-1} increase in wind speed corresponded to a 100% increase in spray flux at 50 m. Another AGDISP model sensitivity study by Huang *et al.* (2010) concluded that wind speed is more significant than the droplet size. This could be because their simulation was for aerial application while 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 the range in this study was from 145 to 208 μm. Also, they simulated the effects of wind speed using minimum and maximum wind speeds of 0.45 to 6.71 m s^{-1} respectively, while in this study minimum and maximum values from the measured data were used, which were 3.35 to 7.27 m s^{-1}, respectively. This shows that the most significant variable may be different for different pesticide application scenarios.
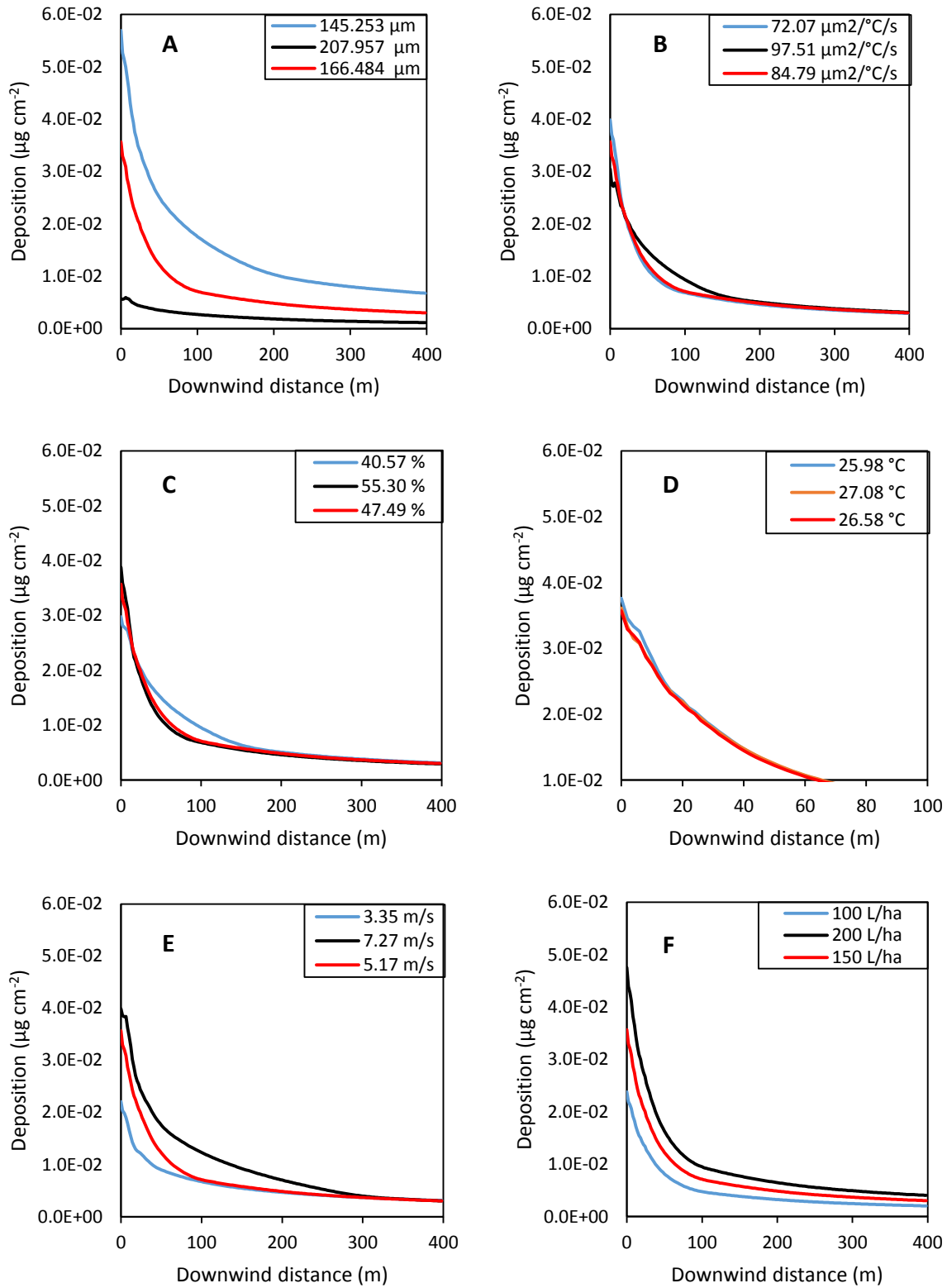
Figure 5.13 Sensitivity of the pesticide deposition rates predicted by the AGDISP model to six different input parameters (a) Droplet size (b) Evaporation rate (c) Relative humidity (d) Temperature (e) Wind speed (f) Application rate.
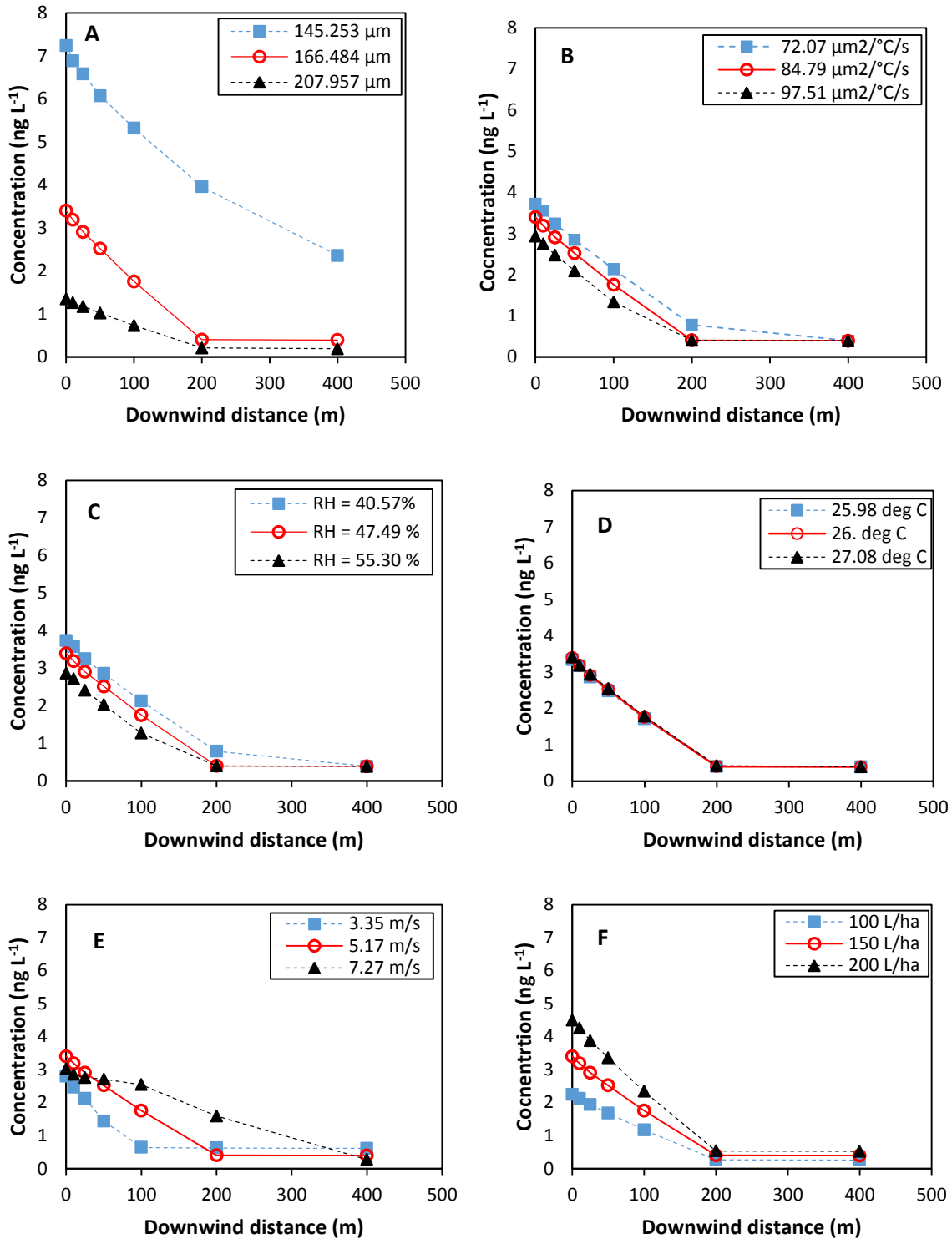
Figure 5.14 Sensitivity of the airborne concentrations of atrazine predicted at 1.5 m height by the AGDISP model to the variation in six different input parameters (a) Droplet size (b) Evaporation rate (c) Relative humidity (d) Temperature (e) Wind speed (f) Application rate.

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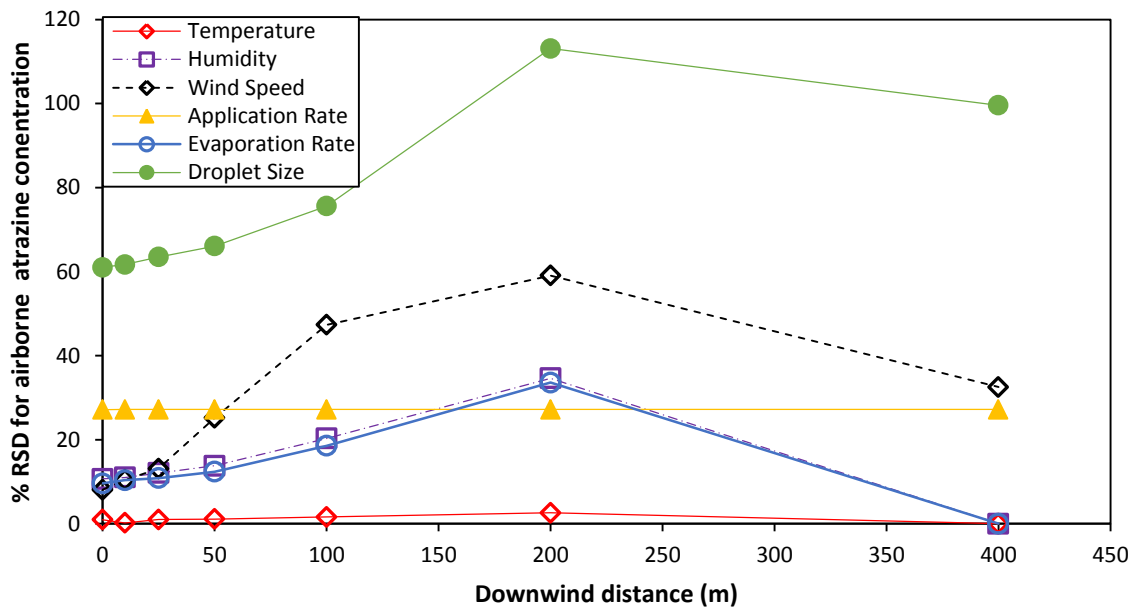
Figure 5.15 Variability in predicted airborne atrazine concentrations at 1.5 m height due to changes in model input parameters. Results show droplet size is the most important factor followed by wind speed at most downwind distances.
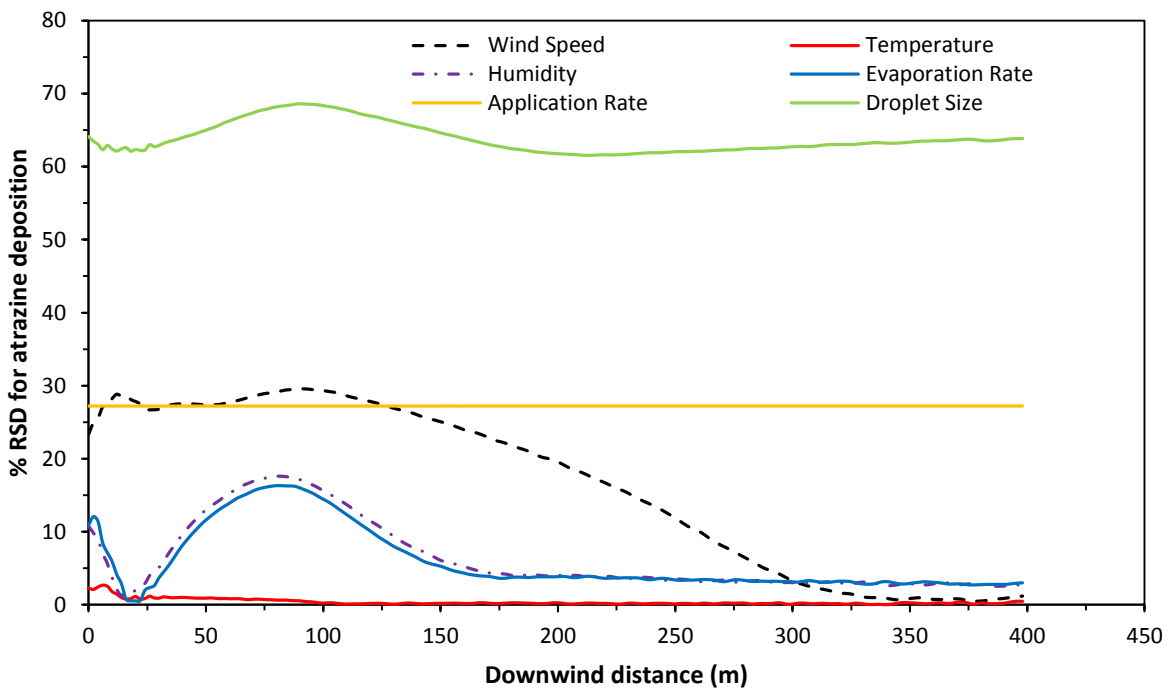
Figure 5.16 Variability in AGDISP predicted atrazine deposition concentrations due to changes in input parameters.

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5.6   Some Limitations of the AGDISP Model

Previous studies that have conducted validation of the AGDISP model have reported some limitations on the ground application part of the model. Woodward *et al.* (2008) found that, compared to experimental data, the AGDISP 2003 ground application model over-predicted downwind deposition by a factor of 3.5 − 100. After doing some sensitivity studies and varying the humidity (which affects evaporation) they still found discrepancies between modelled and experimental values. They then recommended that that there is strong need to improve the evaporation algorithm employed in AGDISP. Similarly, Zabkiewicz *et al.* (2009) also found AGDISP to overestimate spay drift depositions.

Connell *et al.* (2012) found a number of discrepancies between the AGDISP (version 8.25) ground model and experimental data. They found the spray drift deposition ratio of model to experimental data ranged between a factor of 1.5 and 12.4 from the different studies that they did. They also found that the measured flux was much higher than that calculated by AGDISP and they suggested that there is a need to improve the model so that it considers the wake effects from boom sprayers.

Although extensive modification has been done to the model for aerial application, validation studies for aerial applications have also reported some shortcomings of the model. Hoffmann (2006b) found that the AGDISP model predicted 1 − 6 times higher levels of spray materials compared to that measured by field samplers. Hoffmann *et al.* (2007) found that although the vertical deposition values at canopy heights between 0.3 and 0.8 m were comparable between field-collected and AGDISP (version 8.08) data, the model over-predicted by a factor of 10 the levels of spray drift at 1 m for the trials conducted for 0 or 1 m crop canopy heights. They also found the model not satisfactory for crop canopies that are >80% closed.

Schleier and Peterson (2010) showed that AGDISP and AgDRIFT were inadequate for estimating environmental concentrations from applications using ultra-low-volume sprayers. They concluded that the use of these models could result in an underestimation of exposures, but this could be because the researchers in this study used inputs from assumptions outlined in a different study to run the models.

The current study noted that the model does not account for variations in meteorological conditions during the monitoring period. This is particularly important for wind direction variations which can affect the amount of tracer material that reaches the sampling points. It is therefore recommended that the software developers incorporate algorithms that will account for these variations. Fortunately wind direction was consistent during this sampling campaign, therefore should not have had major impact on the results.

Chapter 6 Conclusions and Recommendations

In this 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 1 day (De Rossi, 2010), as well as to its compatibility with the sampling and analytical methods that were developed and employed.

For airborne spray drift monitoring, the PUF adsorbents proved to be suitable samplers for atrazine in the atmosphere and high extraction recoveries were obtained with the plunger extraction method that was used. This method however, required large amounts of solvent per cartridge hence there is a need to optimize it in this regard in future. The Nitrogen Phosphorus Detector on the GC was also excellent for this application, being both selective and sensitive, which allowed for the determination of atrazine down to 0.139 ng L^{-1} at 400 m downwind. These low detection limits are desirable for downwind monitoring because the pesticide ingredient gets highly diluted with increasing distance.

Satisfactory agreement was found between the modelled and experimental results when using the larger droplet size distribution, suggesting that coarse droplets were produced by the sprayer. We suggest, therefore, that the model can provide a good estimate of airborne spray drift concentrations which can be used for risk assessments or regulatory measures around sensitive areas. This, however, is provided one has reliable input parameters that are representative of the actual application conditions. Previous validation studies have shown variation in airborne spray drift of approximately two orders of magnitude between field and AGDISP modelled results (Teske *et al.*, 2004; Woodward *et al.*, 2008). In comparison, this study has shown promising correlations between experimental results and those predicted by the model. This improvement could be in part because the actual active pesticide ingredient was monitored instead of a tracer compound.

Atrazine downwind deposition was successfully captured using horizontal chromatography paper surfaces. These were easy to extract using an ultrasonic bath and the extracts were analysed by DSA-TOFMS as well as the traditional GC-NPD method. Compared to the deposition predicted by the AGDISP model, the experimental deposition obtained using both analytical techniques

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was considerably higher than what the model predicted. The reasons for this are not fully understood but could be because the initial droplet size distribution (DSD) that input to the model consisted of relatively coarse droplets, hence the model predicted that these would immediately settle onto the sprayed area and less would drift downwind. However reasonable this assumption is, it does not match the field results. Thus it is recommended that the model be used with caution for deposition assessments.

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.*, 2002b). Depending on the DSD input, the model may either overestimate or underestimate the atrazine concentration. It is therefore recommended that more accurate determination of the actual DSD be considered in future studies using modern equipment such as laser diffraction spectrophotometry. In light of this, it is important for farmers to maintain their nozzle tips in good condition to prevent blockages which cause fine aerosol generation during spraying which are not desirable because of their susceptibility to drift.

Analysis of the wool samples that were used to collect passive spray drift flux during the spraying event could yield valuable information to compliment the results that were found in this study. This can also provide additional useful information for bystander exposure in risk assessment studies.

It is also recommended that future validation studies of the AGDISP model be carried out using different molecular classes of pesticides to confirm the model use as a general predictor. Different pesticide molecular classes have different physical properties which can affect the evaporation rate of the spray mixture. Therefore using these classes one can probe the use of $84.76 \ \mu m^2 \ °C^{-1} \ s^{-1}$ by the model as a general evaporation rate.

Field monitoring can also be extended further downwind beyond 800 m to validate the model up to its maximum distance. De Rossi (2010) stated that if $\cdot OH$ radical attack is the main degradation pathway, then atrazine can potentially travel up to $250 - 500$ km in the atmosphere within a day under wind speeds of between $3 - 5$ m s^{-1}. An improved analytical method may

however be necessary because the active ingredient would be present at very low concentrations at these distances.

During this study, the model was found to under predict pesticide deposition. It is recommended that further deposition studies be carried out and the collection efficiency of the deposition samplers be investigated. This is important because electrostatic effects of the sampling paper could repel some of the small droplets as they land from the atmosphere onto the surface of the sampler (although this would not explain the high experimental levels found in comparison to model predictions). Additional optimization and validation of the DSA-TOFMS and GC-NPD methods for paper extracts is also required.

Although the aerial pesticide application component of the model has been extensively validated, it is yet to be validated under local South African conditions. It is therefore recommended that validation of this component be carried out for local conditions using aircraft typically employed, as this would be beneficial for local risk assessments and regulatory use of the model.

In this study, the AGDISP pesticide air dispersion model was validated for the first time for ground application use in South Africa. In contrast to other international validation studies conducted on this model, the actual pesticide active ingredient was used for model validation and validated the model at longer downwind distances.

References

Alexandrou, N., Smith, M., Park, R., Lumb, K., & Brice, K. (2001). The Extraction of Polycyclic Aromatic Hydrocarbons from Atmospheric Particulate Matter Samples by Accelerated Solvent Extraction (ASE). *International Journal of Environmental Analytical Chemistry, 81*(4), 257-280. doi: 10.1080/03067310108044248

APVMA. (2010, 17 November 2010). Standard Spray Drift Risk Assessment Scenarios.   Retrieved 26 November 2014, 2014, from http://archive.apvma.gov.au/archive/spray_drift/scenarios.php

Armstrong, J. L., Fenske, R. A., Yost, M. G., Tchong-French, M., & Yu, J. (2013). Comparison of polyurethane foam and XAD-2 sampling matrices to measure airborne organophosphorus pesticides and their oxygen analogs in an agricultural community. *Chemosphere, 92*(4), 451-457. doi: http://dx.doi.org/10.1016/j.chemosphere.2013.01.109

Arvidsson, T., Bergström, L., & Kreuger, J. (2011). Spray drift as influenced by meteorological and technical factors. *Pest Management Science, 67*(5), 586-598. doi: 10.1002/ps.2114

Baetens, K., Nuyttens, D., Verboven, P., De Schampheleire, M., Nicolaï, B., & Ramon, H. (2007). Predicting drift from field spraying by means of a 3D computational fluid dynamics model. *Computers and Electronics in Agriculture, 56*(2), 161-173. doi: http://dx.doi.org/10.1016/j.compag.2007.01.009

Barriada-Pereira, M., Concha-Grana, E., Gonzalez-Castro, M. J., Muniategui-Lorenzo, S., Lopez-Mahia, P., Prada-Rodriguez, D., & Fernandez-Fernandez, E. (2003). Microwave-assisted extraction versus Soxhlet extraction in the analysis of 21 organochlorine pesticides in plants. *Journal of Chromatography A, 1008*(1), 115-122.

Bedos, C., Cellier, P., Calvet, R., Barriuso, E., & Gabrielle, B. (2002). Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: overview. *Agronomie*, 21-33. doi: 10.1051/agro

Bilanin, A. J., Teske, M., Barry, J., & Ekblad, R. (1989). AGDISP-The aircraft spray dispersion model, code development and experimental validation. *Transactions of the ASAE, 32*(1), 327-334.

Bird, S. L., Esterly, D. M., & Perry, S. G. (1996). Off-Target Deposition of Pesticides from Agricultural Aerial Spray Applications. *Journal of Environment Quality, 25*(5), 1095-1104. doi: 10.2134/jeq1996.00472425002500050024x

BLM (Producer). (2005). AgDrift modeling for the human health risk assessment. Retrieved from http://www.blm.gov/pgdata/etc/medialib/blm/wo/Planning_and_Renewable_Resources/veis.Par.99022.File.dat/AgDrift%20Model.pdf

Blume, E., Bischoff, M., Moorman, T. B., & Turco, R. F. (2004). Degradation and Binding of Atrazine in Surface and Subsurface Soils. *Journal of Agricultural and Food Chemistry, 52*(24), 7382-7388. doi: 10.1021/jf049830c

Borras, E., Sanchez, P., Munoz, A., & Tortajada-Genaro, L. A. (2011). Development of a gas chromatography-mass spectrometry method for the determination of pesticides in gaseous and particulate phases in the atmosphere. *Analytica Chimica Acta, 699*(1), 57-65. doi: 10.1016/j.aca.2011.05.009

Briand, O., Bertrand, F., Seux, R., & Millet, M. (2002). Comparison of different sampling techniques for the evaluation of pesticide spray drift in apple orchards. *Science of the Total Environment, 288*(3), 199-213. doi: http://dx.doi.org/10.1016/S0048-9697(01)00961-5

Brown, M. A., Petreas, M. X., Okamoto, H. S., Mischke, T. M., & Stephens, R. D. (1993). Monitoring of malathion and its impurities and environmental transformation products on surfaces and in air following an aerial application. *Environmental Science & Technology, 27*(2), 388-397. doi: 10.1021/es00039a020

Brusselman, E., Van Driessen, K., Steurbaut, W., Gabriels, D., Cornelis, W., Nuyttens, D., Sonck, B., Baetens, K., Nicolai, B., Verboven, P., & Ramon, H. (2004). Wind tunnel evaluation of several

tracer and collection techniques for the measurement of spray drift. *Communications in Agricultural and Applied Biological Sciences, 69*(4), 829-836.

Bui, Q., Womac, A., Howard, K., Mulrooney, J., & Amin, M. (1998). Evaluation of samplers for spray drift. *Transactions of the ASAE, 41*(1), 37-41.

Burgett, C. A., Smith, D. H., & Bente, H. B. (1977). The nitrogen-phosphorus detector and its applications in gas chromatography. *Journal of Chromatography A, 134*(1), 57-64. doi: http://dx.doi.org/10.1016/S0021-9673(00)82569-8

Bussolaro, D., Filipak Neto, F., Glinski, A., Roche, H., Guiloski, I. C., Mela, M., Silva de Assis, H. C., & Oliveira Ribeiro, C. A. (2012). Bioaccumulation and related effects of PCBs and organochlorinated pesticides in freshwater fish Hypostomus commersoni. *Journal of Environmental Monitoring, 14*(8), 2154-2163. doi: 10.1039/C2EM10863A

Butler Ellis, M. C., & Miller, P. C. H. (2010). The Silsoe Spray Drift Model: A model of spray drift for the assessment of non-target exposures to pesticides. *Biosystems Engineering, 107*(3), 169-177. doi: 10.1016/j.biosystemseng.2010.09.003

Butler Ellis, M. C., Underwood, B., Peirce, M. J., Walker, C. T., & Miller, P. C. H. (2010). Modelling the dispersion of volatilised pesticides in air after application for the assessment of resident and bystander exposure. *Biosystems Engineering, 107*(2), 149-154. doi: 10.1016/j.biosystemseng.2010.08.002

Cai, S. S., & Stark, J. D. (1997). Evaluation of five fluorescent dyes and triethyl phosphate as atmospheric tracers of agricultural sprays. *Journal of Environmental Science & Health Part B, 32*(6), 969-983. doi: 10.1080/03601239709373123

Carlsen, S. C., Spliid, N. H., & Svensmark, B. (2006a). Drift of 10 herbicides after tractor spray application. 1. Secondary drift (evaporation). *Chemosphere, 64*(5), 787-794. doi: 10.1016/j.chemosphere.2005.10.061

Carlsen, S. C., Spliid, N. H., & Svensmark, B. (2006b). Drift of 10 herbicides after tractor spray application. 2. Primary drift (droplet drift). *Chemosphere, 64*(5), 778-786. doi: 10.1016/j.chemosphere.2005.10.060

Celen, I. (2010). The effect of spray mix adjuvants on spray drift. *Bulgarian Journal of Agricultural Science, 16*(1), 105-110.

Cessna, A. J., Waite, D. T., Bailey, J., Kerr, L. A., & Quiring, D. V. (2011). Desorption of Herbicides from Atmospheric Particulates During High-Volume Air Sampling. *Atmosphere, 2*(4), 671-687. doi: 10.3390/atmos2040671

Chaemfa, C., Barber, J. L., Gocht, T., Harner, T., Holoubek, I., Klanova, J., & Jones, K. C. (2008). Field calibration of polyurethane foam (PUF) disk passive air samplers for PCBs and OC pesticides. *Environmental Pollution, 156*(3), 1290-1297. doi: 10.1016/j.envpol.2008.03.016

Connell, R., Hewitt, A., Wolf, T., & Miller, P. (2009). WTDISP–Adapting a Lagrangian ground sprayer model using wind tunnel data. Paper presented at the 18th World IMACS Congress and MODSIM09 International Congress on Modelling and Simulation, Cairns, Australia. Conference Contribution - Paper in Published Proceedings retrieved from http://researcharchive.lincoln.ac.nz/handle/10182/4299

Connell, R., Schou, W., Nuyttens, D., Wolf, T., & Praat, J. (2012). Comparison of the mechanistic AGDISP ground boom spray model with experimental data. *New Zealand Plant Protection, 65*, 93-99.

Cooper, J. F., Smith, D. N., & Dobson, H. M. (1996). An evaluation of two field samplers for monitoring spray drift. *Crop Protection, 15*(3), 249-257. doi: http://dx.doi.org/10.1016/0261-2194(95)00113-1

Coscollà, C., Castillo, M., Pastor, A., & Yusà, V. (2011). Determination of 40 currently used pesticides in airborne particulate matter (PM 10) by microwave-assisted extraction and gas chromatography coupled to triple quadrupole mass spectrometry. *Analytica Chimica Acta, 693*(1-2), 72-81. doi: 10.1016/j.aca.2011.03.017

Coscollà, C., Yusà, V., Beser, M. I., & Pastor, A. (2009). Multi-residue analysis of 30 currently used pesticides in fine airborne particulate matter (PM 2.5) by microwave-assisted extraction and liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A, 1216*(51), 8817-8827. doi: 10.1016/j.chroma.2009.10.040

Coscollà, C., Yusà, V., Marti, P., & Pastor, A. (2008). Analysis of currently used pesticides in fine airborne particulate matter (PM 2.5) by pressurized liquid extraction and liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A, 1200*(2), 100-107. doi: 10.1016/j.chroma.2008.05.075

Craig, I., Woods, N., & Dorr, G. (1998). A simple guide to predicting aircraft spray drift. *Crop Protection, 17*(6), 475-482. doi: http://dx.doi.org/10.1016/S0261-2194(98)00006-4

Cross, J., Walklate, P., Murray, R., & Richardson, G. (2001). Spray deposits and losses in different sized apple trees from an axial fan orchard sprayer: 1. Effects of spray liquid flow rate. *Crop Protection, 20*(1), 13-30.

Czaczyk, Z., Kruger, G., & Hewitt, A. (2012). Droplet size classification of air induction flat fan nozzles. *Journal of Plant Protection Research, 52*(4), 415-420.

Dabrowski, J. M., Aneck-Hahn, N., Chamier, J., De Jager, C., Forbes, P., Genthe, B., Meyer, J. A., Pieters, R., Shadung, J., Thwala, M., & Van Zijl, M. C. (2013). Sampling and Analysis of Water and Sediments for Endocrine Disrupting Activity and Concentrations of Pesticide Active Ingredients. Water Research Commission. Pretoria, South Africa.

Dabrowski, J. M., Bollen, A., Bennett, E. R., & Schulz, R. (2005). Pesticide interception by emergent aquatic macrophytes: Potential to mitigate spray-drift input in agricultural streams. *Agriculture, Ecosystems & Environment, 111*(1-4), 340-348. doi: 10.1016/j.agee.2005.06.004

Dabrowski, J. M., & Schadung, J. (2011). *Chemical Prioritisation*. (WRC Project No: K5/1956 – Deliverable 5). Water Research Commission. Pretoria, South Africa.

Dabrowski, J. M., & Schulz, R. (2003). Predicted and measured levels of azinphosmethyl in the Lourens River, South Africa: Comparison of runoff and spray drift. *Environmental Toxicology and Chemistry, 22*(3), 494-500.

Dabrowski, J. M., Shadung, J. M., & Wepener, V. (2014). Prioritizing agricultural pesticides used in South Africa based on their environmental mobility and potential human health effects. *Environ Int, 62*, 31-40. doi: 10.1016/j.envint.2013.10.001

DAFF. (2010). *Pesticide Management Policy for South Africa*. (General Notice No. 1120 of 2010). South African Government Retrieved from http://www.nda.agric.za/docs/Policy/PesticideManag.pdf

Dalvie, M. A., Africa, A., & London, L. (2009). Change in the quantity and acute toxicity of pesticides sold in South African crop sectors, 1994 –1999. *Environment International, 35*(4), 683-687. doi: 10.1016/j.envint.2008.12.004

Daugherty, S., & Crowe, H. (2013). Automated Direct Sample Analysis (DSA/TOF) for the Rapid Screening and Confirmation of Illicit Street Drugs. In I. PerkinElmer (Ed.). Seer Green, Beaconsfiled, United Kingdom: PerkinElmer, Inc.

de Castro, M. L., & Ayuso, L. G. (2000). Soxhlet extraction. *Environmental Applications*, 2701-2705.

De Rossi, C. (2010). *Pesticides in the atmosphere - Occurrence, distribution and behaviour of selected pesticides in the vinicultural area of Trier, Germany.* (PhD), Universitätsbibliothek Trier, Trier. Retrieved from http://ubt.opus.hbz-nrw.de/volltexte/2010/573

De Schampheleire, M., Baetens, K., Nuyttens, D., & Spanoghe, P. (2008). Spray drift measurements to evaluate the Belgian drift mitigation measures in field crops. *Crop Protection, 27*(3-5), 577-589. doi: 10.1016/j.cropro.2007.08.017

De Schampheleire, M., Nuyttens, D., Baetens, K., Cornelis, W., Gabriels, D., & Spanoghe, P. (2009). Effects on pesticide spray drift of the physicochemical properties of the spray liquid. *Precision Agriculture, 10*(5), 409-420. doi: 10.1007/s11119-008-9089-6

De Schampheleire, M., Spanoghe, P., Brusselman, E., & Sonck, S. (2007). Risk assessment of pesticide spray drift damage in Belgium. *Crop Protection, 26*(4), 602-611. doi: http://dx.doi.org/10.1016/j.cropro.2006.05.013

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Donkersley, P., & Nuyttens, D. (2011). A meta analysis of spray drift sampling. *Crop Protection, 30*(7), 931-936. doi: 10.1016/j.cropro.2011.03.020

Dores, E. F. G. C., Navickiene, S., Cunha, M. L. F., Carbo, L., Ribeiro, M. L., & De-Lamonica-Freire, E. M. (2006). Multiresidue determination of herbicides in environmental waters from Primavera do Leste Region (Middle West of Brazil) by SPE-GC-NPD. *Journal of the Brazilian Chemical Society, 17*, 866-873.

Du Preez, L. H., Jansen van Rensburg, P. J., Jooste, A. M., Carr, J. A., Giesy, J. P., Gross, T. S., Kendall, R. J., Smith, E. E., Van Der Kraak, G., & Solomon, K. R. (2005). Seasonal exposures to triazine and other pesticides in surface waters in the western Highveld corn-production region in South Africa. *Environmental Pollution, 135*(1), 131-141. doi: 10.1016/j.envpol.2004.09.019

Enz, J. W., Hofman, V., & Thostenson, A. (2014). Air Temperature Inversions Causes, Characteristics and Potential Effects on Pesticide Spray Drift. (EA1705). NDSU Extension Service. Retrieved from http://www.ag.ndsu.edu/publications/landing-pages/crops/air-temperature-inversions-ae-1705

Escoffier, C., & Scire, J. S. (2013, 6-9 May 2013). Further afield transport of spray drift using a coupling approach. Paper presented at the 15th conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes, Madrid, Spain.

Fan, W., Yanase, T., Morinaga, H., Gondo, S., Okabe, T., Nomura, M., Komatsu, T., Morohashi, K., Hayes, T., & Takayanagi, R. (2007). Atrazine-induced aromatase expression is SF-1 dependent: Implications for endocrine disruption in wildlife and reproductive cancers in humans. *Environmental Health Perspectives, 115*(5), 720.

Ferrari, F., Trevisan, M., & Capri, E. (2003). Predicting and measuring environmental concentration of pesticides in air after soil application. *Journal of Environment Quality, 32*(5), 1623-1633.

Foqué, D., Pieters, J. G., & Nuyttens, D. (2014). Effect of spray angle and spray volume on deposition of a medium droplet spray with air support in ivy pot plants. *Pest Management Science, 70*(3), 427-439. doi: 10.1002/ps.3584

Foreman, W. T., Majewski, M. S., Goolsby, D. A., Wiebe, F. W., & Coupe, R. H. (2000). Pesticides in the atmosphere of the Mississippi River Valley, part II — air. *Science of the Total Environment, 248*(2–3), 213-226. doi: http://dx.doi.org/10.1016/S0048-9697(99)00544-6

Frank, R., Ripley, B. D., Lampman, W., & Morrow, D. (1994). Comparative spray drift studies of aerial and ground applications 1983-1985. *Environmental Monitoring and Assessment, 29*, 167-181.

Fritz, B., Hoffman, W. C., Bagley, W., & Hewitt, A. J. (2011). Field scale evaluation of spray drift reduction technologies from ground and aerial application systems. *Journal of ASTM International, 8*(5), 1-11. doi: 10.1520/JAI103457

Fritz, B., Hoffmann, W., & Bagley, B. (2010). Effects of spray mixtures on droplet size under aerial application conditions and implications on drift. *Applied Engineering in Agriculture, 26*, 21-29. doi: 10.13031/2013.29467

Gavrilescu, M., Demnerova, K., Aamand, J., Agathos, S., & Fava, F. (2014). Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. *New Biotechnology*. doi: 10.1016/j.nbt.2014.01.001

Gil, E., Llorens, J., Llop, J., Fàbregas, X., & Gallart, M. (2013). Use of a Terrestrial LIDAR Sensor for Drift Detection in Vineyard Spraying. *Sensors (Basel, Switzerland), 13*(1), 516-534. doi: 10.3390/s130100516

Gil, Y., & Sinfort, C. (2005). Emission of pesticides to the air during sprayer application: A bibliographic review. *Atmospheric Environment, 39*(28), 5183-5193. doi: 10.1016/j.atmosenv.2005.05.019

Gilliom, R. J. (2007). Pesticides in US streams and groundwater. *Environmental Science & Technology, 41*(10), 3408-3414.

Gish, T. J., Sadeghi, A., & Wienhold, B. J. (1995). Volatilization of alachlor and atrazine as influenced by surface litter. *Chemosphere, 31*(4), 2971-2982. doi: http://dx.doi.org/10.1016/0045-6535(95)00157-4

Giusi, G., Facciolo, R., Canonaco, M., Alleva, E., Belloni, V., Dessi, F., & Santucci, D. (2006). The endocrine disruptor atrazine accounts for a dimorphic somatostatinergic neuronal expression pattern in mice. *Toxicological Sciences, 89*(1), 257-264.

Gregorio, E., Rosell-Polo, J. R., Sanz, R., Rocadenbosch, F., Solanelles, F., Garcerá, C., Chueca, P., Arnó, J., del Moral, I., Masip, J., Camp, F., Viana, R., Escolà, A., Gràcia, F., Planas, S., & Moltó, E. (2014). LIDAR as an alternative to passive collectors to measure pesticide spray drift. *Atmospheric Environment, 82*(0), 83-93. doi: http://dx.doi.org/10.1016/j.atmosenv.2013.09.028

Gregorio, E., Solanelles, F., Rocadenbosch, F., Rosell, J. R., & Sanz, R. (2011). Airborne spray drift measurement using passive collectors and lidar systems. Paper presented at the Remote Sensing for Agriculture, Ecosystems, and Hydrology XIII, Antonino Maltese Prague, Czech Republic.

Gregorio López, E. (2012). *Lidar remote sensing of pesticide spray drift.* (PhD), Universitat de Lleida. Retrieved from http://repositori.udl.cat/handle/10803/96788

Guilhaus, M. (1995). Special feature: Tutorial. Principles and instrumentation in time-of-flight mass spectrometry. Physical and instrumental concepts. *Journal of Mass Spectrometry, 30*(11), 1519-1532. doi: 10.1002/jms.1190301102

Hanna, M., & Schaefer, K. (2009). Spray drift potential increases during warm weather applications. *Intergrated Crop Management News.* Retrieved 05 March, 2015, from http://www.extension.iastate.edu/CropNews/2009/0611schaefer.htm

Harner, T., Shoeib, M., Diamond, M., Stern, G., & Rosenberg, B. (2004). Using Passive Air Samplers To Assess Urban−Rural Trends for Persistent Organic Pollutants. 1. Polychlorinated Biphenyls and Organochlorine Pesticides. *Environmental Science & Technology, 38*(17), 4474-4483. doi: 10.1021/es040302r

Hass, U., Boberg, J., Christiansen, S., Jacobsen, P. R., Vinggaard, A. M., Taxvig, C., Poulsen, M. E., Herrmann, S. S., Jensen, B. H., Petersen, A., Clemmensen, L. H., & Axelstad, M. (2012). Adverse effects on sexual development in rat offspring after low dose exposure to a mixture of endocrine disrupting pesticides. *Reproductive Toxicology, 34*(2), 261-274. doi: http://dx.doi.org/10.1016/j.reprotox.2012.05.090

Hassen, N. S., Sidik, N. A. C., & Sheriff, J. M. (2013). Effect of nozzle type, angle and pressure on spray volumetric distribution of broadcasting and banding application. *Journal of Mechanical Engineering Research, 5*(4), 76-81. doi: 10.5897/JMER2013.0272

Hassen, N. S., Sidik, N. A. C., & Sheriff, J. M. (2014). Effects of nozzle angle on spray losses reduction. *Applied Mechanics and Materials, 564*, 216-221. doi: 10.4028/www.scientific.net/AMM.564.216

Hayes, T. B., Khoury, V., Narayan, A., Nazir, M., Park, A., Brown, T., Adame, L., Chan, E., Buchholz, D., Stueve, T., & Gallipeau, S. (2010). Atrazine induces complete feminization and chemical castration in male African clawed frogs (Xenopus laevis). *Proceedings of the National Academy of Sciences USA, 107*(10), 4612-4617. doi: 10.1073/pnas.0909519107

Hayward, S. J., Gouin, T., & Wania, F. (2010). Comparison of Four Active and Passive Sampling Techniques for Pesticides in Air. *Environmental Science & Technology, 44*(9), 3410-3416. doi: 10.1021/es902512h

He, J., Balasubramanian, R., Karthikeyan, S., & Joshi, U. M. (2009). Determination of semi-volatile organochlorine compounds in the atmosphere of Singapore using accelerated solvent extraction. *Chemosphere, 75*(5), 640-648. doi: 10.1016/j.chemosphere.2009.01.025

Hewitt, A., Balsari, P., Carpenter, P., Cooper, S., Glass, C., Magri, B., Mountford-Smith, C., Robinson, T., Stock, D., & Taylor, W. (2010). Tracer and collector systems for field deposition research. *Aspects of Applied Biology, 99*, 283-289.

Hewitt, A., Teske, M., & Thistle, H. (2002a). The development of the AgDRIFT® model for aerial application from helicopters and fixed-wing aircraft. *Australasian Journal of Ecotoxicology, 8*, 3-6.

Hewitt, A. J., Johnson, D. R., Fish, J. D., Hermansky, C. G., & Valcore, D. L. (2002b). Development of the spray drift task force database for aerial applications. *Environmental Toxicology and Chemistry, 21*(3), 648-658.

94

Hewitt, A. J., Solomon, K. R., & Marshall, E. J. (2009). Spray droplet size, drift potential, and risks to nontarget organisms from aerially applied glyphosate for coca control in Colombia. *Journal of Toxicology and Environmental Health, Part A, 72*(15-16), 921-929. doi: 10.1080/15287390902929667

Hewitt, A. J., Teske, M. E., & Thistle, H. W. (2002c). The development of the AgDRIFT model for aerial application from helicopters and fixed-wing aircraft. *Australian Journal of Ecotoxicology, 8*, 3-6.

Hobson, P., Miller, P., Walklate, P., Tuck, C., & Western, N. (1993). Spray drift from hydraulic spray nozzles: the use of a computer simulation model to examine factors influencing drift. *Journal of Agricultural Engineering Research, 54*(4), 293-305.

Hodzic, A., Madronich, S., Aumont, B., Lee-Taylor, J., Karl, T., Camredon, M., & Mouchel-Vallon, C. (2013). Limited influence of dry deposition of semivolatile organic vapors on secondary organic aerosol formation in the urban plume. *Geophysical Research Letters, 40*(12), 3302-3307. doi: 10.1002/grl.50611

Hoffmann, W., Fritz, B., & Martin, D. (2007). AGDISP sensitivity to crop canopy characterization. *Transactions of the ASABE, 50*(4), 1117-1122.

Hoffmann, W. C. (2006a). Field-collected and AGDISP-predicted spray flux from an aerial application. *Journal of ASMT International, 3*(1), 1-12. doi: 10.1520/JAI12908

Hoffmann, W. C. (2006b). Field-collected and AGDISP-predicted spray flux from an aerial application. *Journal of ASTM International, 3*(1), 1-12.

Hoffmann, W. C., Fritz, B. K., Thornburg, J. W., Bagley, W., Birchfield, N. B., & Ellenberger, J. (2010). Spray Drift Reduction Evaluations of Spray Nozzles Using a Standardized Testing Protocol. *Journal of ASTM International, 7*(8), 1-8.

Holland, P., Maber, J., May, W., & Malcolm, C. (1997). Drift from orchard spraying. Paper presented at the Proceedings of the New Zealand plant protection conference.

Holterman, H. (2003). *Kinetics and evaporation of water drops in air*. (IMAG Report No. 9054062347). Institute for Environmental and Agricultural Engineering. Wageningen, The Netherlands. Retrieved from http://holsoft.nl/idefics/pdf/kinevap.pdf

Holterman, H., Van De Zande, J., Porskamp, H., & Huijsmans, J. (1997). Modelling spray drift from boom sprayers. *Computers and Electronics in Agriculture, 19*(1), 1-22.

Hrouzková, S., & Matisová, E. (2012). Endocrine disrupting pesticides. In R. P. Soundararajan (Ed.), *Pesticides—Advances in Chemical and Botanical pesticides* (pp. 99-126). Croatia: InTech.

Huang, Y., & Thomson, S. J. (2012). Characterization of spray deposition and drift from a low drift nozzle for aerial application at different application altitudes. *International Journal of Agricultural and Biological Engineering, 4*(4), 28-33.

Huang, Y., Zhan, W., Fritz, B., Thomson, S., & Fang, A. (2010). Analysis of impact of various factors on downwind deposition using a simulation method. *Journal of ASTM International, 7*(6), 1-11. doi: 10.1520/JAI102771

Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., & Jones, K. C. (2003). Passive Air Sampling of PCBs, PBDEs, and Organochlorine Pesticides Across Europe. *Environmental Science & Technology, 38*(1), 34-41. doi: 10.1021/es034705n

Jin, G.-Z., Kim, S.-M., Lee, S.-Y., Park, J.-S., Kim, D.-H., Lee, M.-J., Sim, K.-T., Kang, H.-G., Kim, I.-G., Shin, S.-K., Seok, K.-S., & Hwang, S.-R. (2013). Levels and potential sources of atmospheric organochlorine pesticides at Korea background sites. *Atmospheric Environment, 68*(0), 333-342. doi: http://dx.doi.org/10.1016/j.atmosenv.2012.10.036

Jones, E., Hanks, J., & Wills, G. (2002). Effect of Different Nozzle Types on Drift and Efficacy of Roundup Ultra. Mississippi Agricultural and Forestry Experiment Station Technical Bulletin. Technical Bulletin. (Technical Bulletin 1119). Mississippi Agricultural and Forestry Experiment Station. Mississippi, USA. Retrieved from http://msucares.com/pubs/bulletins/b1119.pdf

Jongen, M. J., Engel, R., & Leenheers, L. H. (1991). Determination of the pesticide chlorothalonil by HPLC and UV detection for occupational exposure assessment in greenhouse carnation culture. *Journal of Analytical Toxicology, 15*(1), 30-34.

Kasiotis, K. M., Glass, C. R., Tsakirakis, A. N., & Machera, K. (2014). Spray drift reduction under Southern European conditions: a pilot study in the Ecopest Project in Greece. *Science of the Total Environment, 479-480*, 132-137. doi: 10.1016/j.scitotenv.2014.01.088

Khot, L., Salyani, M., Farooq, M., Walker, T., Sweeb, R., Larbi, P., Smith, V., Pomolis, R., & Stoops, C. (2011). Assessment of aerosol deposition and movement in open field conditions. *Agricultural Engineering International: CIGR Journal, 13*(3), 1-11.

Kojima, H., Katsura, E., Takeuchi, S., Niiyama, K., & Kobayashi, K. (2004). Screening for estrogen and androgen receptor activities in 200 pesticides by in vitro reporter gene assays using Chinese hamster ovary cells. *Environmental Health Perspectives, 112*(5), 524-531.

Kosikowska, M., & Biziuk, M. (2010). Review of the determination of pesticide residues in ambient air. *TRAC Trends in Analytical Chemistry, 29*(9), 1064-1072. doi: 10.1016/j.trac.2010.06.008

Kuang, Z., McConnell, L. L., Torrents, A., Meritt, D., & Tobash, S. (2003). Atmospheric deposition of pesticides to an agricultural watershed of the Chesapeake Bay. *Journal of environmental quality, 32*(5), 1611-1622.

Lammel, G., Ghim, Y.-S., Grados, A., Gao, H., Hühnerfuss, H., & Lohmann, R. (2007). Levels of persistent organic pollutants in air in China and over the Yellow Sea. *Atmospheric Environment, 41*(3), 452-464.

Lebeau, F., Verstraete, A., Schiffers, B., & Destain, M. F. (2009). Evaluation of realtime spray drift using RTDrift Gaussian advection-diffusion model. *Communications in Agricultural and Applied Biological Sciences, 74*(1), 11-24.

Liess, M., & Ohe, P. C. V. D. (2005). Analyzing effects of pesticides on invertebrate communities in streams. *Environmental Toxicology and Chemistry, 24*(4), 954-965.

MacBean, C. (2012). *The Pesticide Manual* (16th ed.). Omega Park, Alton, Hampshire, GU34 2QD, UK: British Crop Production Council.

MacLeod, K. E., & Lewis, R. G. (1982). Portable sampler for pesticides and semivolatile industrial organic chemicals in air. *Analytical Chemistry, 54*(2), 310-315. doi: 10.1021/ac00239a038

Majewski, M. S. (1999). Micrometeorologic Methods for Measuring the Post-Application Volatilization of Pesticides. *Water, Air, and Soil Pollution, 115*(1-4), 83-113. doi: 10.1023/A:1005297121445

Majewski, M. S., Foreman, W. T., Goolsby, D. A., & Nakagaki, N. (1998). Airborne Pesticide Residues along the Mississippi River. *Environmental Science & Technology, 32*(23), 3689-3698. doi: 10.1021/es9802403

May, K. (1950). The Measurement of Airborne Droplets by the Magnesium Oxide Method. *Journal of Scientific Instruments, 27*, 128-130.

Maybank, J., Yoshida, K., & Grover, R. (1978). Spray Drift from Agricultural Pesticide Applications. *Journal of the Air Pollution Control Association, 28*(10), 1009-1014. doi: 10.1080/00022470.1978.10470699

Miles, J. W., Fetzer, L. E., & Pearce, G. W. (1970). Collection and determination of trace quantities of pesticides in air. *Environmental Science & Technology, 4*(5), 420-425.

Miller, D., Stoughton, T., Steinke, W., Huddleston, E., & Ross, J. (2000). Atmospheric stability effects on pesticide drift from an irrigated orchard. *Transactions of the ASAE, 43*(5), 1057-1066.

Miller, D. R., Huddleston, E. W., Ross, J., & Steinke, W. (2003a). Airblast spray partitioning in a mature pecan orchard. *Transactions of the ASAE, 46*(6), 1495-1501.

Miller, D. R., Salyani, M., & Hiscox, A. (2003b). Remote measurement of spray drift from orchard sprayers using LIDAR. *Proceedings of the American Society of Agricultural and Biological Engineers*.

Miller, D. R., & Stoughton, T. E. (2000). Response of spray drift from aerial applications at a forest edge to atmospheric stability. *Agricultural and Forest Meteorology, 100*(1), 49-58. doi: http://dx.doi.org/10.1016/S0168-1923(99)00084-2

Miller, P., & Ellis, B. (2000). Effects of formulation on spray nozzle performance for applications from ground-based boom sprayers. *Crop Protection, 19*(8), 609-615.

96

Miller, P., Ellis, M. B., Lane, A., O'Sullivan, C., Tuck, C., Orson, J., Bush, M., Cook, S., Boys, E., & Cussans, J. (2011). Methods for minimising drift and off-target exposure from boom sprayer applications. *Aspects of Applied Biology, 106*, 281-288.

Miller, P. C. H., & Hadfield, D. J. (1989). A simulation model of the spray drift from hydraulic nozzles. *Journal of Agricultural Engineering Research, 42*(2), 135-147. doi: http://dx.doi.org/10.1016/0021-8634(89)90046-2

Muir, D., & Sverko, E. (2006). Analytical methods for PCBs and organochlorine pesticides in environmental monitoring and surveillance: a critical appraisal. *Analytical and Bioanalytical Chemistry, 386*(4), 769-789. doi: 10.1007/s00216-006-0765-y

Muir, D. C. G., Teixeira, C., & Wania, F. (2004). Empirical and modeling evidence of regional atmospheric transport of current-use pesticides. *Environmental Toxicology and Chemistry, 23*(10), 2421-2432. doi: 10.1897/03-457

Murray, J. A., & Vaughan, L. M. (1970). Measuring pesticide drift at distances to four miles. *Journal of Applied Meteorology, 9*(1), 79-85.

Naidoo, V., & Buckley, C. A. (2003). *Survey of pesticide wastes in South Africa and review of treatment options*. Research Report. (1128/01/03). Water Reserch Commission. Pretoria, South Africa. Retrieved from http://www.wrc.org.za/knowledge%20hub%20documents/research%20reports/1128-1-03.pdf

NEMAQA. (2014). *National Environmental Management: Air Quality Amendment Act 20 of 2014*. (37666). Cape Town: South African Government Retrieved from http://www.gov.za/sites/www.gov.za/files/37666_gon390.pdf.

Norgaard, K. B., & Cedergreen, N. (2010). Pesticide cocktails can interact synergistically on aquatic crustaceans. *Environmental Science and Pollution Research International, 17*(4), 957-967. doi: 10.1007/s11356-009-0284-4

Nuyttens, D., Baetens, K., De Schampheleire, M., & Sonck, B. (2007). Effect of nozzle type, size and pressure on spray droplet characteristics. *Biosystems Engineering, 97*(3), 333-345.

Nuyttens, D., De Baerdemaeker, J., Dekeyser, & Verboven, P. (2013). Spray drift from field crop sprayers. Paper presented at the 12th Curso Internacional de Agricultura de Precisión, Estación Experimental INTA Manfredi, Córdoba.

Nuyttens, D., De Schampheleire, M., Baetens, K., Dekeyser, D., & Sonck, B. (2008). Direct and indirect drift assessment means. Part 3: field drift experiments. *Communications in Agricultural and Applied Biological Sciences, 73*(4), 763-767.

Nuyttens, D., De Schampheleire, M., Steurbaut, W., Baetens, K., Verboven, P., Nicolaï, B., Ramon, H., & Sonck, B. (2006a). Experimental study of factors influencing the risk of drift from field sprayers Part 2: Spray application technique. *Aspects of Applied Biology, 77*(2), 331-339.

Nuyttens, D., De Schampheleire, M., Steurbaut, W., Baetens, K., Verboven, P., Nicolaï, B., Ramon, H., & Sonck, B. (2006b). Experimental study of factors influencing the risk of drift from field sprayers, Part 1: Meteorological conditions. *Aspects of Applied Biology, 77*, 321-330.

Oehme, M. (1991). Further Evidence for Long-Range Air Transport of Polychlorinated Aromates and Pesticides: North America and Eurasia to the Arctic. *Ambio, 20*(7), 293-297.

Osibanjo, O., Bouwman, H., Bashir, N., Okond'Ahoka, J., Choong Kwet Yve, R., & Onyoyo, H. (2002). *Regionally based assessment of persistent toxic substances. Sub-Saharan Africa regional report*. UNEP Chemicals, Geneva. Retrieved from http://iwlearn.net/iw-projects/14/reports/sub-saharan-africa-report

Patterton, H. (2013). *Scoping study and research strategy development on currently known and emerging contaminants influencing drinking water quality*. (WRC Report No. 2093/1/13). Water Research Commission. Retrieved from http://goo.gl/qy9R9X

Pepper, T., Arnold, D., Murray, C., & Reeves, G. (2001). The influence of wind speed and spray nozzle geometry on the drift of chlorpyrifos to surface water. Paper presented at the The BCPC Conference: Weeds, 2001, Volume 1 and Volume 2. Proceedings of an international conference held at the Brighton Hilton Metropole Hotel, Brighton, UK, 12-15 November 2001.

PerkinElmer. (2012). Mass spec results in seconds with Direct Sample Analysis: AxION DSA System. Waltham, MA, USA. Retrieved from http://www.perkinelmer.com/CMSResources/Images/44-132906BRO_AxION_DSA.pdf

Phillips, J. C., & Miller, P. C. H. (1999). Field and Wind Tunnel Measurements of the Airborne Spray Volume Downwind of Single Flat-Fan Nozzles. *Journal of Agricultural Engineering Research, 72*(2), 161-170. doi: http://dx.doi.org/10.1006/jaer.1998.0359

Pick, F. E., van Dyk, L. P., & Botha, E. (1992). Atrazine in ground and surface water in maize production areas of the Transvaal, South Africa. *Chemosphere, 25*(3), 335-341. doi: http://dx.doi.org/10.1016/0045-6535(92)90550-B

Psathaki, M., Manoussaridou, E., & Stephanou, E. G. (1994). Determination of organophosphorus and triazine pesticides in ground- and drinking water by solid-phase extraction and gas chromatography with nitrogen-phosphorus or mass spectrometric detection. *Journal of Chromatography A, 667*(1-2), 241-248.

Qiao, X., Ma, L., & Hummel, H. E. (1996). Persistence of Atrazine and Occurrence of Its Primary Metabolites in Three Soils. *Journal of Agricultural and Food Chemistry, 44*(9), 2846-2848. doi: 10.1021/jf960178y

Quinn, L., de Vos, J., Fernandes-Whaley, M., Roos, C., Bouwman, H., Kylin, H., Pieters, R., & van den Berg, J. (2011). Pesticide Use in South Africa: One of the Largest Importers of Pesticides in Africa. In S. Margarita (Ed.), *Pesticides in the Modern World: Pesticides Use and Management*.

Rafferty, J. E., & Bowers, J. F. (1993). Comparison of FSCBG spray model predictions with field measurements. *Environmental Toxicology and Chemistry, 12*(3), 465-480. doi: 10.1002/etc.5620120308

Raina, R., & Hall, P. (2010). Field Evaluation of Solid Sorbents for Ambient Air Sampling of Pesticides. *Air, Soil and Water Research, 3*, 57-66. doi: 10.4137/ASWR.S5924

Ratola, N., Homem, V., Silva, J. A., Araujo, R., Amigo, J. M., Santos, L., & Alves, A. (2014). Biomonitoring of pesticides by pine needles - Chemical scoring, risk of exposure, levels and trends. *Science of the Total Environment, 476-477*, 114-124. doi: 10.1016/j.scitotenv.2014.01.003

Ravier, I., Haouisee, E., Clement, M., Seux, R., & Briand, O. (2005). Field experiments for the evaluation of pesticide spray-drift on arable crops. *Pest Management Science, 61*(8), 728-736. doi: 10.1002/ps.1049

Riley, C., Sears, I., Picot, J., & Chapman, T. (1995). Spray drift task force droplet evaporation studies. *Pesticide Formulations and Application Systems, 14*, 225-236.

Salyani, M., & Cromwell, R. (1992). Spray drift from ground and aerial applications. *Transactions of the ASAE, 35*(4), 1113-1120.

Salyani, M., Sweeb, R., & Farooq, M. (2006). Comparison of string and ribbon samplers in orchard spray applications. *Transactions of the ASABE, 49*(6), 1705-1710.

Sanderson, J. T., Seinen, W., Giesy, J. P., & van den Berg, M. (2000). 2-Chloro-s-Triazine Herbicides Induce Aromatase (CYP19) Activity in H295R Human Adrenocortical Carcinoma Cells: A Novel Mechanism for Estrogenicity? *Toxicological Sciences, 54*(1), 121-127. doi: 10.1093/toxsci/54.1.121

Sanusi, A., Millet, M., Mirabel, P., & Wortham, H. (1999). Gas–particle partitioning of pesticides in atmospheric samples. *Atmospheric Environment, 33*(29), 4941-4951. doi: http://dx.doi.org/10.1016/S1352-2310(99)00275-7

Sauret, N., Wortham, H., Putaud, J.-P., & Mirabel, P. (2008). Study of the effects of environmental parameters on the gas/particle partitioning of current-use pesticides in urban air. *Atmospheric Environment, 42*(3), 544-553. doi: http://dx.doi.org/10.1016/j.atmosenv.2007.09.012

Scheyer, A., Morville, S., Mirabel, P., & Millet, M. (2007). Variability of atmospheric pesticide concentrations between urban and rural areas during intensive pesticide application. *Atmospheric Environment, 41*(17), 3604-3618. doi: http://dx.doi.org/10.1016/j.atmosenv.2006.12.042

Schleier, J. J., 3rd, & Peterson, R. K. (2010). Deposition and air concentrations of permethrin and naled used for adult mosquito management. *Archives of Environment Contamination and Toxicology, 58*(1), 105-111. doi: http://dx.doi.org/10.1007/s00244-009-9353-4

Schulz, R. (2001). Comparison of spray drift- and runoff-related input of azinphos-methyl and endosulfan from fruit orchards into the Lourens River, South Africa. *Chemosphere, 45*(4–5), 543-551. doi: http://dx.doi.org/10.1016/S0045-6535(00)00601-9

Schummer, C., Mothiron, E., Appenzeller, B. R., Wennig, R., & Millet, M. (2010). Gas/particle partitioning of currently used pesticides in the atmosphere of Strasbourg (France). *Air Quality, Atmosphere & Health, 3*(3), 171-181. doi: http://dx.doi.org/10.1007/s11869-010-0065-8

SDTF. (1997). A summary of aerial application studies. Spray Drift Task Force. Retrieved from http://www.agdrift.com/PDF_FILES/Aerial.pdf

Shoeib, M., & Harner, T. (2002). Characterization and Comparison of Three Passive Air Samplers for Persistent Organic Pollutants. *Environmental Science & Technology, 36*(19), 4142-4151. doi: 10.1021/es020635t

Shrivastava, A., & Gupta, V. B. (2011). Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chronicles of Young Scientists, 2*(1), 21.

Sipin, M. F., Guazzotti, S. A., & Prather, K. A. (2003). Recent Advances and Some Remaining Challenges in Analytical Chemistry of the Atmosphere. *Analytical Chemistry, 75*(12), 2929-2940. doi: http://dx.doi.org/10.1021/ac030143e

Stellman, S. D., & Stellman, J. M. (2004). Exposure opportunity models for Agent Orange, dioxin, and other military herbicides used in Vietnam, 1961-1971. *Journal of Exposure Analysis and Environment Epidemiology, 14*(4), 354-362. doi: http://dx.doi.org/10.1038/sj.jea.7500331

Stoughton, T. E., Miller, D. R., Yang, X., & Ducharme, K. M. (1997). A comparison of spray drift predictions to lidar data. *Agricultural and Forest Meteorology, 88*(1), 15-26.

Teske, M., Hermansky, C., & Riley, C. (1998). Evaporation rates of agricultural spray material at low relative wind speeds. *Atomization and Sprays, 8*(4), 471-478.

Teske, M., Thistle, H., & Ice, G. (2003). Technical advances in modeling aerially applied sprays. *Transactions of the ASAE, 46*(4), 985-993.

Teske, M. E. (1996). An introduction to aerial spray modeling with FSCBG. Forest Service Cramer-Barry-Grim. *Journal of the American Mosquito Control Association, 12*(2 Pt 2), 353-358.

Teske, M. E., Bentson, K. P., Sandquist, R. E., Barry, J. W., & Ekblad, R. B. (1991). Comparison of FSCBG model predictions with heather seed orchard deposition data. *Journal of Applied Meteorology, 30*(9), 1366-1375.

Teske, M. E., Birchfield, N., & Bird, S. (2004, 1-4 August 2004). Development and validation of a mechanistic ground sprayer model. Paper presented at the 2004 American Society of Agricultural Engineers/Canadian Society of Agricultural Engineering International Meeting, Ottawa, Canada.

Teske, M. E., Bird, S. L., Esterly, D. M., Curbishley, T. B., Ray, S. L., & Perry, S. G. (2002). AgDrift®: A model for estimating near-field spray drift from aerial applications. *Environmental Toxicology and Chemistry, 21*(3), 659-671. doi: http://dx.doi.org/10.1002/etc.5620210327

Teske, M. E., & Curbishley, T. B. (2012). AGDISP Version 8.27 User Manual. (C.D.I. Report No. 09-27D). Continuum Dynamics Inc. Ewing, New Jersey. Retrieved from http://www.continuum-dynamics.com/pr-agdisp.html

Teske, M. E., Miller, P. C. H., Thistle, H. W., & Birchfield, N. B. (2009). Initial development and validation of a mechanistic spray drift model for ground boom sprayers. *Transactions of the ASABE, 52*(4), 1089-1097.

Teske, M. E., Valcore, D., & Hewitt, A. (2000). A review of ground sprayer data and a preliminary analytical model. Paper presented at the 2000 ASAE Annual International Meeting, Milwaukee, Wisconsin, USA, 9-12 July 2000.

Teske, M. E., Valcore, D., & Hewitt, A. (2001). An analytical ground sprayer model. Paper presented at the ASAE Paper, St. Joseph, Michigan.

Theodorou, D., Zannikou, Y., & Zannikos, F. (2012). Estimation of the standard uncertainty of a calibration curve: application to sulfur mass concentration determination in fuels. *Accreditation and Quality Assurance, 17*(3), 275-281. doi: 10.1007/s00769-011-0852-4

Thistle, H. W., Ice, G., & Karsky, R. (2007). Spray capture by a riparian barrier. Paper presented at the American Society of Agricultural and Biological Engineers, Minneapolis, USA.

Thompson, M., Ellison, S. L., Fajgelj, A., Willetts, P., & Wood, R. (1999). Harmonized guidelines for the use of recovery information in analytical measurement. *Pure and Applied Chemistry, 71*(2), 337-348.

Thurman, E. M., & Cromwell, A. E. (2000). Atmospheric Transport, Deposition, and Fate of Triazine Herbicides and Their Metabolites in Pristine Areas at Isle Royale National Park. *Environmental Science & Technology, 34*(15), 3079-3085. doi: 10.1021/es000995l

Tsai, M., Elgethun, K., Ramaprasad, J., Yost, M., Felsot, A., Hebert, V., & Fenske, R. (2005). The Washington aerial spray drift study: Modeling pesticide spray drift deposition from an aerial application. *Atmospheric Environment, 39*(33), 6194-6203. doi: http://dx.doi.org/10.1016/j.atmosenv.2005.07.011

Tupper, K., Kegley, S., Jacobs, N., Marquez, E., Jim, S., Bjorkqvist, S., Wang, A., & Kaastrup, K. (2012). *Pesticide Drift monitoring in Minnesota*. Pesticide Action Network. San Francisco. Retrieved from
http://www.pesticideresearch.com/site/docs/DriftCatcher/TechReport_MN_May2012_FINAL.pdf

Turner, B. C., & Glotfelty, D. E. (1977). Field air sampling of pesticide vapors with polyurethane foam. *Analytical Chemistry, 49*(1), 7-10. doi: http://dx.doi.org/10.1021/ac50009a009

Unsworth, J., Wauchope, R., Klein, A., Dorn, E., Zeeh, B., Yeh, S., Akerbloom, M., Racke, K., & Rubin, B. (1999). Significance of the long range transport of pesticides in the atmosphere. *Journal of Pure and Applied Chemistry, 71*(7), 1359-1383.

USEPA. (2014a, 8/5/2014). About Pesticides: Types of Pesticides. Retrieved 04 December 2014, 2014, from http://www.epa.gov/pesticides/about/types.htm

USEPA. (2014b, 8/6/2014). Pesticides: Science and Policy - Models. Retrieved 26 November 2014, 2014, from http://www.epa.gov/pesticides/science/models_pg.htm

van den Berg, F., Kubiak, R., Benjey, W. G., Majewski, M. S., Yates, S. R., Reeves, G. L., Smelt, J. H., & van der Linden, A. M. A. (1999). Emission of Pesticides into the Air. *Water, Air, and Soil Pollution, 115*(1-4), 195-218. doi: http://dx.doi.org/10.1023/A:1005234329622

van der Hoff, G. R., & van Zoonen, P. (1999). Trace analysis of pesticides by gas chromatography. *Journal of Chromatography A, 843*(1–2), 301-322. doi: http://dx.doi.org/10.1016/S0021-9673(99)00511-7

van der Walt, E. (2000, 24-26 March 1999). Research at PPRI on environmental effects of quelea control operations. Paper presented at the Workshop on Research Priorities for Migrant Pests of Agriculture in Southern Africa, Plant Protection Research Institute, Pretoria, South Africa.

van Dijk, H. G., & Guicherit, R. (1999). Atmospheric Dispersion of Current-Use Pesticides: A Review of the Evidence from Monitoring Studies. *Water, Air, and Soil Pollution, 115*(1-4), 21-70. doi: http://dx.doi.org/10.1023/A:1005293020536

Vischetti, C., Cardinali, A., Monaci, E., Nicelli, M., Ferrari, F., Trevisan, M., & Capri, E. (2008). Measures to reduce pesticide spray drift in a small aquatic ecosystem in vineyard estate. *Science of the Total Environment, 389*(2-3), 497-502. doi: http://dx.doi.org/10.1016/j.scitotenv.2007.09.019

Vryzas, Z., & Papadopoulou-Mourkidou, E. (2002). Determination of Triazine and Chloroacetanilide Herbicides in Soils by Microwave-Assisted Extraction (MAE) Coupled to Gas Chromatographic Analysis with Either GC−NPD or GC−MS. *Journal of Agricultural and Food Chemistry, 50*(18), 5026-5033. doi: http://dx.doi.org/10.1021/jf020176f

Waite, D. T., Droneck, N. R., Tuduri, L., Sproull, J. F., Chau, D. F., & Quiring, D. V. (2005). Comparison of Active versus Passive Atmospheric Samplers for Some Current-Use Pesticides.

Bulletin of Environmental Contamination and Toxicology, 74(6), 1011-1018. doi: http://dx.doi.org/10.1007/s00128-005-0681-4

Wang, M., & Rautmann, D. (2008). A simple probabilistic estimation of spray drift—factors determining spray drift and development of a model. *Environmental Toxicology and Chemistry, 27*(12), 2617-2626. doi: http://dx.doi.org/10.1897/08-109.1

Williams, R. L., Bernard, C. E., & Krieger, R. I. (2001). Child-like mannequin for observation and measurement of spray drift particle deposition for pesticide exposure assessment. *Bulletin of Environmental Contamination and Toxicology, 67*(2), 179-186.

Wolters, A., Linnemann, V., van de Zande, J. C., & Vereecken, H. (2008). Field experiment on spray drift: deposition and airborne drift during application to a winter wheat crop. *Science of the Total Environment, 405*(1-3), 269-277. doi: http://dx.doi.org/10.1016/j.scitotenv.2008.06.060

Woods, N., Craig, I. P., Dorr, G., & Young, B. (2001). Spray drift of pesticides arising from aerial application in cotton. *Journal of Environment Quality, 30*(3), 697-701. doi: http://dx.doi.org/10.2134/jeq2001.303697x

Woodward, S., Connell, R., Zabkiewicz, J., Steele, K., & Praat, J. (2008). Evaluation of the AGDISP ground boom spray drift model. *New Zealand Plant Protection, 61*, 168-168.

Workman Jr, J., & Mark, H. (2006). Limitations in Analytical Accuracy, Part I: Horwitz's Trumpet. *Spectroscopy, 21*(9), 18-24.

WRC. (2013). Knowledge Review 2012/13. Water Research Commission. Retrieved from http://www.wrc.org.za/Pages/DisplayItem.aspx?ItemID=10473&FromURL=%2fPages%2fKH_KnowledgeReviews.aspx%3fdt%3d8%26ms%3d59%3b%26d%3dKnowledge+Review+2012%2f13%26start%3d1

Yao, Y., Galarneau, E., Blanchard, P., Alexandrou, N., Brice, K. A., & Li, Y. F. (2007). Atmospheric atrazine at Canadian IADN sites. *Environmental Science and Technology, 41*(22), 7639-7644.

Yarpuz-Bozdogan, N., & Bozdogan, A. M. (2009). Comparison of field and model percentage drift using different types of hydraulic nozzles in pesticide applications. *International Journal of Environmental Science & Technology, 6*(2), 191-196. doi: http://dx.doi.org/10.1007/BF03327621

Yusà, V., Coscolla, C., Mellouki, W., Pastor, A., & de la Guardia, M. (2009). Sampling and analysis of pesticides in ambient air. *Journal of Chromatography A, 1216*(15), 2972-2983. doi: http://dx.doi.org/10.1016/j.chroma.2009.02.019

Zabkiewicz, J., Steele, K., & Connell, R. (2009). Multiple metal cations as spray deposit tracers and evaluation of the AGDISP ground boom spray drift model. *Journal of ASTM International (JAI), 6*(5).

Zabkiewicz, J., Steele, K., & Praat, J. (2008). Determination of spray drift using multiple metal cations as tracers. *New Zealand Plant Protection, 61*, 159-163.

Zhang, G., Pan, Z., Bai, A., Li, J., & Li, X. (2014). Distribution and bioaccumulation of organochlorine pesticides (OCPs) in food web of Nansi Lake, China. *Environmental Monitoring and Assessment, 186*(4), 2039-2051. doi: http://dx.doi.org/10.1007/s10661-013-3516-5

Zhao, H., Xie, C., Liu, F., He, X., Zhang, J., & Song, J. (2014a). Effects of sprayers and nozzles on spray drift and terminal residues of imidacloprid on wheat. *Crop Protection, 60*, 78-82. doi: http://dx.doi.org/10.1016/j.cropro.2014.02.009

Zhao, Z., Wang, Y., Zhang, L., Cai, Y., & Chen, Y. (2014b). Bioaccumulation and tissue distribution of organochlorine pesticides (OCPs) in freshwater fishes: a case study performed in Poyang Lake, China's largest lake. *Environmental Science and Pollution Research, 21*(14), 8740-8749. doi: 10.1007/s11356-014-2805-z

Zhu, H., Derksen, R., Krause, C., Fox, R., Brazee, R., & Ozkan, H. (2005). Effect of solution pH conditions on fluorescence of spray deposition tracers. *Applied Engineering in Agriculture, 21*(3), 325-329.

Zhu, H., Reichard, D., Fox, R., Brazee, R., & Ozkan, H. (1994). Simulation of drift of discrete sizes of water droplets from field sprayers. *Transactions of the ASAE, 37*(5), 1401-1407. doi: doi: 10.13031/2013.28220

Appendices

A1   AGDISP Model Inputs

Figures A1 − A4 show screenshots of the graphic user interface of the AGDISP software where input values are keyed in for the different input parameters.
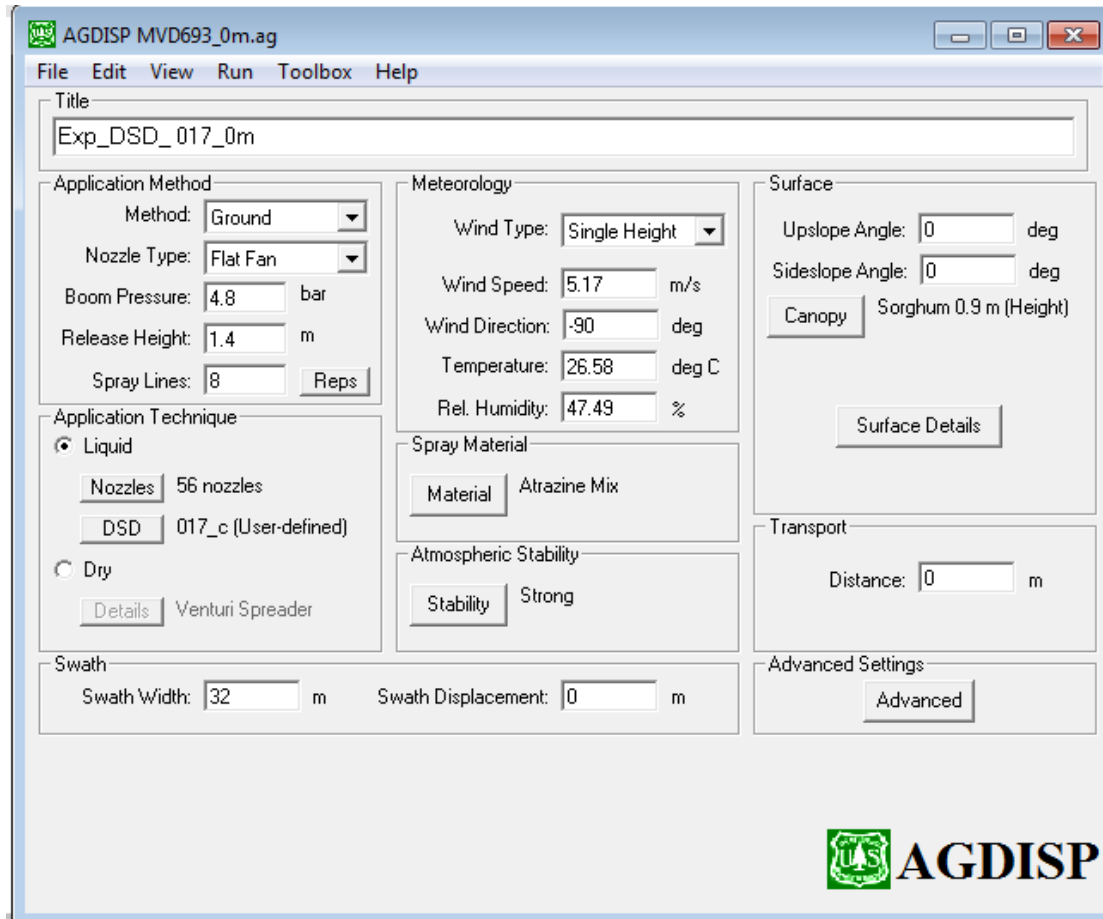
Figure A1 The graphic user interface (GUI) of the AGDISP model software showing some of the input parameters needed to run the model.

Figure A2 AGDISP screen for entering droplet size distribtion (DSD).

Figure A3 AGDISP screen where information on tank mix composition is specified.

Figure A4 Input screen of AGDIDP software where evaporation rate and other parameters mainly used for aerial application scenarios are entered.

Table A1 Summary of the AGDISP input parameters using a droplet size distribution of 166 μm average diameter as an example.

```
┌─────────────────────────────────────────────────────────────────────────┐
│ AGDISP MVD693_0m.ag 8.27 10-29-2014 12:41:10              Page 1          │
└─────────────────────────────────────────────────────────────────────────┘


AGDISP Input Data Summary

Title: Exp_DSD_ 017_0m
Notes:

Calculations Done: Yes
Run ID: AGDISP MVD693_0m.ag 8.27 10-29-2014 12:41:10

--APPLICATION METHOD--              ----------------------------
Method                                                   Ground
--Ground Sprayer--                  ----------------------------
Nozzle Type                                            Flat Fan
Boom Pressure (bar)                                         4.8
--Spray Lines--                     ----------------------------
Release Height (m)                                         1.4
Spray Lines                                                  8
Optimize Spray Reps                                         No
Spray Line Reps                     #                     Reps
                                    1                        1
                                    2                        1
                                    3                        1
                                    4                        1
                                    5                        1
                                    6                        1
                                    7                        1
                                    8                        1


--APPLICATION TECHNIQUE--           ----------------------------
Application Technique                                    Liquid
--Nozzles--                         ----------------------------
Boom Length (%)                                          85.94
Nozzle Locations          #      Hor(m)    Ver(m)    Fwd(m)
                          1      -13.75       0         0
                          2      -13.25       0         0
                          3      -12.75       0         0
                          4      -12.25       0         0
                          5      -11.75       0         0
                          6      -11.25       0         0
                          7      -10.75       0         0
                          8      -10.25       0         0
                          9       -9.75       0         0
                         10       -9.25       0         0
                         11       -8.75       0         0
                         12       -8.25       0         0
                         13       -7.75       0         0
                         14       -7.25       0         0
                         15       -6.75       0         0
                         16       -6.25       0         0
                         17       -5.75       0         0
                         18       -5.25       0         0
                         19       -4.75       0         0
                         20       -4.25       0         0
                         21       -3.75       0         0
                         22       -3.25       0         0
                         23       -2.75       0         0
                         24       -2.25       0         0
                         25       -1.75       0         0
                         26       -1.25       0         0
                         27       -0.75       0         0
                         28       -0.25       0         0
                         29        0.25       0         0
                         30        0.75       0         0
                         31        1.25       0         0
                         32        1.75       0         0
                         33        2.25       0         0
                         34        2.75       0         0
```

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35	3.25	0	0
36	3.75	0	0
37	4.25	0	0
38	4.75	0	0
39	5.25	0	0
40	5.75	0	0
41	6.25	0	0
42	6.75	0	0
43	7.25	0	0
44	7.75	0	0
45	8.25	0	0
46	8.75	0	0
47	9.25	0	0
48	9.75	0	0
49	10.25	0	0
50	10.75	0	0
51	11.25	0	0
52	11.75	0	0
53	12.25	0	0
54	12.75	0	0
55	13.25	0	0
56	13.75	0	0

```
--Drop Size Distribution--        ----------------------------
Name                                                   017 c
Type                                              User-defined
Drop Categories                 #      Diam (um)          Frac
                                1          48.74        0.0010
                                2         108.59        0.0168
                                3         168.44        0.0381
                                4         228.29        0.0195
                                5         288.14        0.0336
                                6         348.00        0.0593
                                7         407.85        0.0477
                                8         467.70        0.0480
                                9         527.55        0.0000
                               10         587.40        0.0475
                               11         647.25        0.0636
                               12         707.11        0.1657
                               13         766.96        0.0000
                               14         826.81        0.1325
                               15         886.66        0.3268

--SWATH--                         ----------------------------
Swath Width                                             32 m
Swath Displacement                                       0 m

--METEOROLOGY--                   ----------------------------
Wind Speed (m/s)                                        5.17
Wind Direction (deg)                                     -90
Temperature (deg C)                                    26.58
Relative Humidity (%)                                  47.49

--SPRAY MATERIAL--                ----------------------------
Name                                             Atrazine Mix
Spray Material Evaporates                                 Yes
Spray Volume Rate (L/ha)                                 150
Active Fraction                                        0.003
Nonvolatile Fraction                                   0.003
Active Fraction of Tank Mix                            0.003
Fraction of Active Solution that is Nonvolatile            1
Additive Fraction of Tank Mix                              0
Fraction of Additive Solution that is Nonvolatile          1

--ATMOSPHERIC STABILITY--         ----------------------------
Atmospheric Stability                                 Strong
```

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```
--SURFACE--                                    ----------------------------
Upslope Angle (deg)                                                       0
Sideslope Angle (deg)                                                     0
--Canopy--                                     ----------------------------
Type                                                                Height
Name                                                               Sorghum
Height (m)                                                             0.9

--TRANSPORT--                                  ----------------------------
Flux Plane Distance (m)                                                   0

--ADVANCED SETTINGS--                          ----------------------------
Wind Speed Height (m)                                                     2
Max Compute Time (sec)                                                  600
Max Downwind Dist (m)                                                   400
Vortex Decay Rate (OGE) (m/s)                                         0.15
Vortex Decay Rate (IGE) (m/s)                                         0.56
Aircraft Drag Coeff                                                    0.1
Propeller Efficiency                                                   0.8
Ambient Pressure (mb)                                                 1013
Ground Reference (m)                                                     0
Save Trajectory Files                                                   No
Half Boom                                                               No
Default Swath Offset                                            1/2 Swath
Specific Gravity (Carrier)                                               1
Specific Gravity (Active/Additive)                                       1
Evaporation Rate (µm²/deg C/sec)                                    84.76
```

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A2   Outputs from this Project

1. Journal Publications

<u>Sifiso A. Nsibande</u>, James M. Dabrowski, Etienne van der Walt, Anette Venter and Patricia B.C. Forbes (2015). Validation of the AGDISP model for predicting airborne atrazine spray drift: A South African ground application case study. *Chemosphere*, 138, 454-461. doi: http://dx.doi.org/10.1016/j.chemosphere.2015.06.092

2. Reports

Forbes, P.B.C, Castleman, B. and <u>Nsibande, S.A.</u> (2015), Air dispersion modelling and monitoring of pesticides. In J.M. Dabrowski (Ed), *Investigation of the Contamination of Water Resources by Agricultural Chemicals and the Impact on Environmental Health. Volume 1: Risk Assessment of Agricultural Chemicals to Human and Animal Health*. WRC Project No. 1956/1/15, Water Research Commission, Pretoria, South Africa.

3. Oral/Conference Presentations

i. <u>Sifiso A. Nsibande</u>, James M. Dabrowski, Etienne van der Walt and Patricia B.C. Forbes, "Atrazine spray drift monitoring for model validation" *Invited presentation at SACI Postgraduate Student Symposium*, University of North-West, Potchefstroom, 11 November 2014.

ii. <u>Sifiso A. Nsibande</u>, James M. Dabrowski, Etienne van der Walt and Patricia B.C. Forbes, "Atrazine spray drift monitoring for model validation" *SACI Postgraduate Student Symposium*, Limpopo Region, 23 October 2014.

iii. Sifiso A. Nsibande, James M. Dabrowski, Etienne van der Walt, Annette Venter and <u>Patricia B.C. Forbes</u>[*] "Air dispersion modelling: a South African pesticide validation case study", *National Association for Clean Air Conference*, 8 – 10 October 2014, Umhlanga, Durban. *([*]Patricia Forbes won the Best Scientific Paper prize at the conference for this presentation)*.

iv. <u>Sifiso A. Nsibande</u>[*], James M. Dabrowski, Etienne van der Walt and Patricia B.C. Forbes, "Atrazine spray drift monitoring for model evaluation" *Analitika Conference*, 7-11 September 2014, Parys. *(*Sifiso Nsibande won the ChromSA Best Student Oral presentation prize for this presentation)*.

4. Poster Presentations

i.   <u>Sifiso A. Nsibande</u>, Lisa Swanepoel and Patricia B.C. Forbes, "How fast is fast? Using DSA-TOFMS for pesticide drift sample screening", *National Association for Clean Air Conference*, 8-10 October 2014, Umhlanga, Durban.

ii. <u>Sifiso A. Nsibande</u>, Lisa Swanepoel and Patricia B.C. Forbes, "How fast is fast? Using DSA-TOF MS for pesticide drift sample screening", *Analitika Conference*, 7-11 September 2014, Parys, South Africa. *(*Sifiso Nsibande won the SAAMS Best Student Poster award for this presentation).*

iii. <u>Sifiso A. Nsibande</u>, James M. Dabrowski, Etienne van der Walt, Anette Venter, and Patricia B.C. Forbes, "Comparative pesticide air monitoring in validation of air dispersion models", *16^{th} IUAPPA World Clean Congress*, September 2013, Cape Town, South Africa.

5. Awards

This work has resulted in the receipt of three awards which are indicated in sub-sections 3 and 4 above.