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Comparison of pesticide deposition sampling methods for spray drift of atrazine

by

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Declaration of Authorship

I, Basil Kudakwashe Munjanja, declare that this dissertation, which I submit for the degree Master of Science at the University of Pretoria, is my own work, and has not been previously submitted by me for a degree at this or any other institution.

Signed__________________________________ Date______________________________

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Abstract

Off-target deposition is a potential route of pesticide entry into the environment. To determine off-target deposition of pesticides, various deposition samplers are used. A study was carried out to compare a number of deposition samplers (chromatography paper, glass microscope slides, glass petri dishes, polyacrylic rods) used in spray drift determination of atrazine (and terbuthylazine when present in the formulation). The first sampling campaign was conducted to compare three horizontally oriented deposition samplers (glass microscope slides, chromatography paper, and glass petri dishes) and two vertically oriented deposition samplers. The second sampling campaign consisted of horizontal and vertical chromatography paper only, as this sampler provided the best results in the first sampling campaign. In each of the spraying events of atrazine three sampling lines were used. In the first application, the sampling distances were 0, 10, 25, 50, 100, 200, and 400 m. In the second application, the sampling distances were 0, 10, 30, 50, and 100 m. In addition, corresponding upwind control deposition samplers were also included in each pesticide sampling campaign. Analysis of pesticide deposition samples for both sampling campaigns was done by GC-MSD. The limit of detection (LOD) for atrazine was 0.006 $\mu g.ml^{-1}$ (1st sampling campaign) and 0.01 $\mu g.ml^{-1}$ (2nd sampling campaign), and 0.02 $\mu g.ml^{-1}$, for terbuthylazine (2nd sampling campaign) respectively. Excellent recoveries of >70% were obtained by sonication extraction of chromatography paper, glass petri dishes, glass microscope slides, and polyacrylic rods. The precision in terms of %RSD was less than 20%. In the first sampling campaign, the chromatography paper was the best deposition sampler, and atrazine levels deposited on the samplers were up to 0.012 $\mu g.cm^{-2}$. In the second sampling campaign, both atrazine and terbuthylazine were detected, and deposition levels were up to 11 $\mu g.cm^{-2}$, and 12 $\mu g.cm^{-2}$ respectively. Comparison of field deposition data and AgDISP modelled data showed that the model under-predicted the amount of atrazine in the first sampling campaign. In the second sampling campaign, the model under-predicted only at 0 m, but as the distance increased, there was agreement between the AgDISP and the field deposition results. Thus, the findings of this study make it apparent that field deposition studies are still important to arrive at buffer distances that accurately reflect environmental concentrations of off-target deposition during pesticide application. For the first time, this project has shown the comparison of various samplers with different materials of construction in the off-target deposition of a pesticide active ingredient (atrazine), under local South African conditions.

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Table of Abbreviations

AGDISP	Agricultural Dispersal
AGDRIFT	Agricultural Drift Model
ANOVA	Analysis of Variance
APVMA	Australian Pesticides and Veterinary Medicines Authority
ASAE	American Society of Agricultural Engineers
ASABE	American Society of Agricultural and Biological Engineers
ATZ	Atrazine
BCPC	British Crop Protection Council
BSF	Brilliant Sulfo Flavin
CP	Chromatography Paper
DCM	Dichloromethane
DF	Degrees of Freedom
DRT	Drift Reducing Technology
DSA-TOFMS	Direct Sample Analyser coupled to Time of Flight Mass Spectrometer
DSD	Droplet Size Distribution
EC	Emulsifiable Concentrate
ECM	Environmental Chemistry Methods
ELISA	Enzyme Linked Immunosorbent Assay
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FLD-BLK	Field Blank
GC-ECD	Gas Chromatography Electron Capture Detector
GC-ECD-NPD	Gas Chromatography Electron Capture Detection Nitrogen Phosphorus Detector
GC-MS	Gas Chromatography-Mass Spectrometer
GC-MSD	Gas chromatography-Mass Selective Detector
GC-MS/MS	Gas Chromatography Tandem Mass Spectrometer
GC-NPD	Gas Chromatography-Nitrogen Phosphorus Detector
GC-TOFMS	Gas chromatography-Time-of-Flight Mass Spectrometer
GC-PFPD	Gas Chromatography-Pulsed Flame Photometric Detector
GDP	Gross Domestic Product
GIMP	Graphic Image Manipulation Program
GLC	Gas Liquid Chromatography
GPS	Global Positioning System
HPLC-QTrap MS	High Performance Liquid Chromatography-Quadrupole Linear Ion Trap Mass Spectrometer
HPLC-TripleTOF	High Performance Liquid Chromatography coupled to a Triple Quadrupole and Time of Flight Mass Spectrometer
I.S.	Internal Standard
ICP	Inductively Coupled Plasma Spectroscopy
LC-DAD	Liquid Chromatography-Diode Array Detector
LC-MS/MS	Liquid Chromatography-Tandem Mass Spectrometer
LLE	Liquid-Liquid Extraction
LOD	Limit of Detection
LOQ	Limit of Quantification
MCA	Monochloroacetic Acid
MeCN	Acetonitrile
MeOH	Methanol
MS	Microscope Slide
m/z	Mass-to-charge ratio
PD	Petri Dish
PMRA	Pesticide Management Regulatory Agency

PR	Polyacrylic Rod
QC	Quality Control
RHPLC	Reverse Phase High Performance Liquid Chromatography
RSD	Relative Standard Deviation
SC	Suspension Concentrate
SIM	Selected Ion Monitoring
SL	Soluble Liquid
SPE	Solid Phase Extraction
STATSSA	Statistics South Africa
TERB	Terbuthylazine
US EPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet Visible Spectroscopy
VMD	Volume Median Diameter
WRC	Water Research Commission
XC	Extra Coarse droplet size spectrum

Chapter 1 Background to the Study

1.1 Pesticide use in South Africa

Pesticides play a fundamental role in agriculture in terms of increasing crop and livestock yields, and improving food security among other reasons (Cooper and Dobson, 2007). For instance it was estimated that without their use, heavy losses from pest damage ranging from 32-78% for various fruits, vegetables, and cereals were reported in China (Cai, 2008). For this reason, their use significantly increased from 1990 to 2016 as shown by **Figure 1-1**, only to decline slightly thereafter as most countries are increasingly becoming aware of the adverse effects of pesticides on the environment (Zhang, 2018). Despite the observed trend, the annual global consumption still remains at an estimated two million tonnes, and the largest consumers of pesticides are China, United States, France, Brazil, and Japan (Zhang et al., 2011, De et al., 2014).

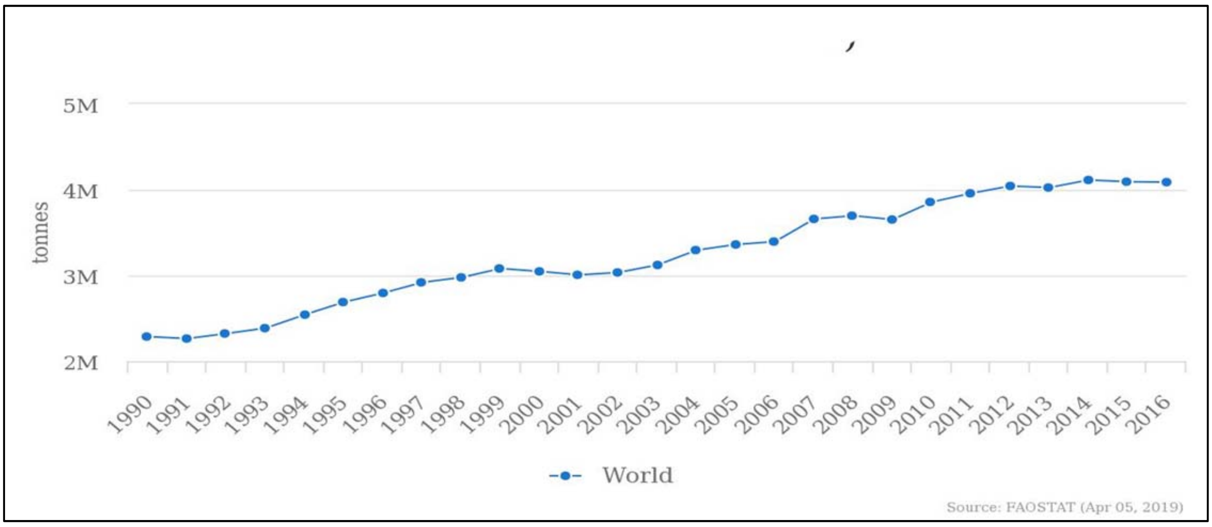

Figure 1-1: Global pesticide use since 1990 adapted from (FAOSTAT 2019)

Interestingly, the pesticide consumption trend in South Africa has followed the global upward trend increasing from 16.5 k tonnes in 1990 (**Figure 1-2)**, and remaining constant at 27 k tonnes from 2000 to 2016 (FAOSTAT, 2019). South Africa's economy depends on agriculture to a large extent as proven by a study carried out by Statistics South Africa, in which it was found that the agriculture industry increased the gross domestic product (GDP) by 2.5% (STATSSA, 2017). Thus to-date, over 3000 pesticide products are registered for use, and the majority of these are applied to different crops, and a smaller proportion is used for vector and domestic pest control (Dabrowski, 2015, Dalvie et al., 2009). Although the effectiveness of pesticides in South Africa cannot be denied, some adverse effects have occurred as a result of their use locally. For instance, some studies have reported their occurrence in water bodies (Dabrowski and Schulz, 2003, Dalvie et al., 2003), where spray drift is increasingly recognised as one of the major routes of pesticide entry into the environment during application.

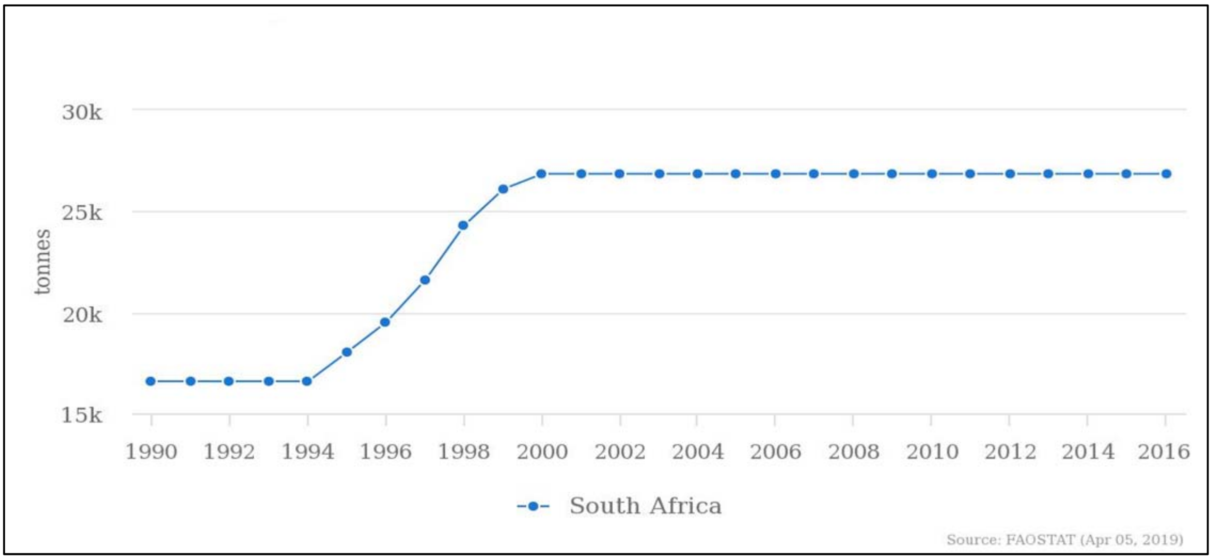

Figure 1-2: Pesticide consumption in South Africa 1990-2016 adapted from (FAOSTAT 2019)

1.2 Pesticide spray drift

Spray drift or primary drift is the movement of pesticide vapour or droplets from their target area by the action of air currents during the application (ISO, 2005). This definition does not include pesticides that volatilise from the surface of the plant, a phenomenon known as secondary drift (Carlsen et al., 2006a). Instead, it refers to airborne flux and ground deposited spray (off-target deposition). Spray drift may be beneficial to a plant because it increases the bioavailability of the pesticide within the canopy itself (Felsot et al., 2010). On the other hand, off-target spray drift may have adverse effects on non-target vegetation, land and aquatic organisms, and bystanders (Lee et al., 2011, Cunha et al., 2012, Schrübbers et al., 2014, Hewitt et al., 2009). Bystanders refer to people who are not involved in pesticide application but who are at risk of exposure to pesticide drift (Glass, 2006).

1.3 Pesticide deposition monitoring

Off-target deposition of pesticides has received considerable attention over the past decades, because it is one of the potential routes of their entry into the environment. Its contribution to aquatic pollution is less than that of runoff, another route of pesticide entry into aquatic bodies, because, the latter integrates potential pesticide input over both time and space and is less dependent on pesticide application factors and meteorological conditions than off-target deposition (Dabrowski and Schulz, 2003, Schulz et al., 2001, Schulz, 2001, Meli et al., 2003). Spray drift has gained vast attention from regulatory authorities in many countries including Australia, USA, Canada, and the Netherlands. For instance, in Australia the Spray Drift Task Force was set up to provide a comprehensive database on off-target spray drift and deposition of pesticides during application in order to improve data for regulatory decision making (Hewitt et al., 2002). In the USA, the Environmental Protection Agency (EPA) developed a set of guidelines on spray drift field deposition to meet the testing requirements of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (USEPA, 1998). A generic protocol for testing pesticide application spray drift reduction technologies for row and field crops, was developed to provide the pesticide application technology industry with a standard method to test their technologies for potential reductions in spray drift (USEPA, 2015). Similarly, in the Netherlands, legislation has also been put in place to assess spray drift, and promote the use of drift reducing technology (Van de Zande et al., 2012). The drift reducing guidelines in both the USA and the Netherlands recommend the use of drift reducing technology (DRT), spraying at specific wind speeds, and temperature, and humidity conditions. Finally, in Canada and Australia policies have been formulated by the Pesticide Management Regulatory Agency (PMRA), and Australian Pesticides and Veterinary Medicine Authority (AVPMA), respectively (Felsot et al., 2010). Monitoring of pesticide deposition is thus ongoing, as it enables regulatory authorities to make informed decisions, as well as implement the necessary changes in order to mitigate the effects of spray drift.

Pesticide deposition monitoring studies are usually carried out under field conditions or in a wind tunnel, with the latter producing more reproducible results than the former (Nuyttens et al., 2009) although field experiments are useful for validating spray drift models (Baetens et al., 2007, Nsibande et al., 2015). Hence the two techniques are complimentary. Deposition monitoring can be costly and labour intensive, hence it can be complemented by the use of computer modelling and mathematical simulations in order to enhance understanding of off-target deposition (Gil and Sinfort, 2005).

1.4 Modelling pesticide deposition

These models can be classified as plume or droplet trajectory, depending on how the movement of droplets is calculated (Teske et al., 2011). An example of a droplet trajectory deposition modelling technique is AGricultural DISpersal (AGDISP), which can be used to calculate deposition both in the sprayed field and downwind in the surrounding areas (Connell et al., 2009). The advantage of this model is that it relies on the Lagrangian model which tracks the movement of droplets of a certain size, factoring in the effects of application equipment, and hence finds application in regulation of spray drift (Teske et al., 2002). Several studies have been carried out to compare deposition monitoring studies using different tracers to the AGDISP models. In one such study where spray deposition monitoring used metal cation tracers and plastic tape samplers, the model over-predicted deposition by a factor of 3.5, and the reasons for this were not well understood (Woodward et al., 2008). In a related study carried out by our research group, pesticide deposition of atrazine using filter paper was compared to AGDISP simulation output, and it was reported that the model under-predicted by up to ten orders of magnitude (Nsibande, 2015). The authors hypothesized that this variation might have been due to sampler conditions not having been adequately optimized. Therefore, one of the recommendations of the study was to carry out further studies to determine the collection efficiency of various pesticide deposition samplers used for spray drift determination.

1.5 Problem statement

Although pesticide deposition models such as AgDISP may serve as useful predictors of pesticide deposition, the model results may vary from measured pesticide deposition. This is in part because different samplers have different mechanisms of capturing pesticides, and hence different collection efficiencies, and also due to deficiencies in the model algorithms. Thus, we seek to devise a strategy of comparing different pesticide deposition samplers for the target pesticide which is atrazine (and terbuthylazine when present in the atrazine formulation employed). The results will be used to assess the applicability of the AgDISP model for prediction of pesticide deposition for atrazine (and terbuthylazine which is commonly part of commercial atrazine formulations), as well as to identify the optimum sampler for pesticide deposition. Hence, amounts of the pesticide that enter the aquatic environment through spray drift may be predicted with known uncertainty.

1.6 Aims and objectives of the study

1.6.1 Aim

The aim of the study was to compare different pesticide spray drift deposition sampling methods for atrazine (and terbuthylazine when present in the atrazine formulation employed).

1.6.2 Objectives

The objectives of the study were:

- To compare chromatography paper, glass microscope slides, glass petri dishes, plastic drinking straws and polyacrylic rods as passive samplers for atrazine deposition.
- To compare the monitored deposition results to those predicted based on the AgDISP pesticide modelling programme.

1.7 Justification of the study

This study seeks to assess the sampling efficiencies of a range of pesticide deposition samplers for atrazine, which is a priority pesticide in South Africa. By priority pesticide we refer to priority in terms of potential risk to human health, based on quantity used, toxicity and hazard potential (Dabrowski et al., 2014). The information from this study will provide a clearer picture of how much of the pesticide is deposited onto off-target sites from agricultural activities. Thus, the findings of this study may assist in the drafting of atrazine regulations to safeguard the aquatic environment, animals and human beings in South Africa. Although extensive research has been carried out on pesticide deposition monitoring of atrazine, no single study exists which compares a range of deposition samplers with different materials of construction. Hence, this study adds to the global body of scientific knowledge, especially on the sampling efficiency of pesticide deposition samplers made of different materials, where numerous knowledge gaps have been identified. Finally, most studies to compare field deposition data with AgDISP modelled data have used one type of sampler whilst the current study seeks to understand which type of deposition sampler best approximates that of the AgDISP model under similar application and meteorological conditions for atrazine (and terbuthylazine when present in the atrazine formulation employed). The findings will assist other researchers who focus on the AgDISP model to optimise its accuracy.

1.8 Structure of the dissertation

The overall structure of this dissertation takes the form of five thematic chapters, including this introductory chapter. Chapter 2 begins by reviewing the physicochemical properties of atrazine, environmental fate, and its adverse effects on non-target organisms. It also focuses on factors affecting spray drift, and the whole process of pesticide deposition monitoring from sampling to analysis. The third chapter is concerned with the methodology used in this study. The fourth chapter presents and discusses the findings of this study focussing on the three key themes of (1) optimisation of sample extraction method, (2) first sampling campaign, and (3) the second sampling campaign. Finally, Chapter 5 is the conclusion that gives a brief summary and critique of the findings. It also includes a discussion of the implication of the findings to future research in this area. In the Appendix, the published review article and draft journal paper are presented.

Chapter 2 Literature Review

2.1 Atrazine and terbuthylazine pesticides

Atrazine (6-chloro-4-N-ethyl-2-N-propan-2-yl-1, 3, 5-triazine-2, 4-diamine) **(Figure 2-1)** is a triazine herbicide that is widely used to prevent pre- and post-emergence broadleaf weeds in various crops such as maize and sorghum because of its high efficacy, low cost and application flexibility (Gianessi, 2008). It kills weeds by inhibiting the photosynthetic electron transport (Fuerst and Norman, 1991). Its physicochemical properties (**Table 2-1)** determine its behaviour in the environment. It has been found to be persistent in the environment, with a reported half-life ranging from 10 to 5 824 days (Salazar-Ledesma et al., 2018). It exhibits low adsorption in soil and moderate solubility in water (Singh et al., 2018). In most of the studies carried out, atrazine concentrations have been reported in ground and surface water (Hildebrandt et al., 2008, Köck-Schulmeyer et al., 2012, Sanchez-Camazano et al., 2005). In most of these studies, contamination of water bodies was by leaching or runoff. Another important route of the contamination of water bodies by atrazine is spray drift (Nsibande et al., 2015).

Terbuthylazine (**Figure 2.2**), which is also found in atrazine formulations, is a chloro-s-triazine herbicide used to control weeds in various crops (Wang et al., 2010). Like atrazine, it is a photosynthetic inhibitor (Cedergreen et al., 2005). Owing to its low water solubility, terbuthylazine adsorbs strongly to soil or organic matter, allowing for its transport into water bodies rather than in the free solute form (Baillie et al., 2015).

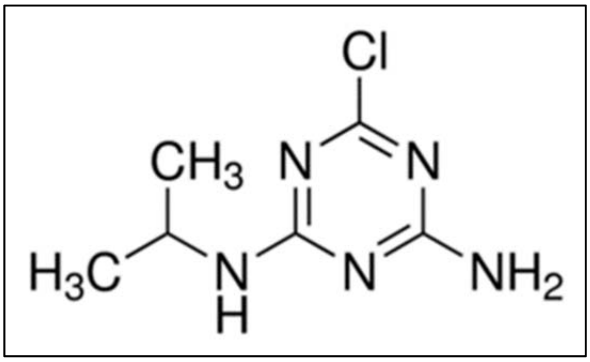

Figure 2-1: Structure of atrazine.

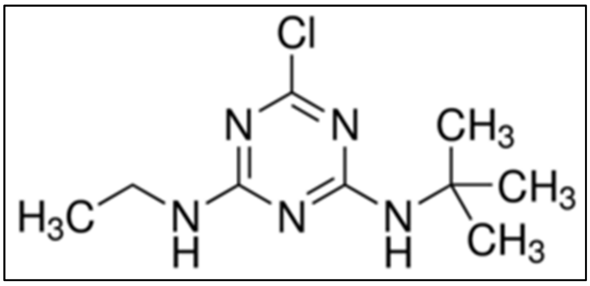

Figure 2-2: Structure of terbuthylazine.

Table 2-1: Physical properties of atrazine and terbuthylazine adapted from (Tomlin, 2009).

Property		**Atrazine**	**Terbuthylazine**
Molecular Mass ($g.mol^{-1}$)		217.7	229.7
Form		Colourless powder	Colourless powder
Boiling Point (^{0}C) (at 10l kPa)		205.0	373.1
Vapour Pressure Pa (at 25 ^{0}C)		3.85×10^{-5}	9.0×10^{-5}
Melting Point (^{0}C)		175.8	175.5
K_{ow} LogP (25 ^{0}C)		2.5	3.4
Density (at 22 ^{0}C)		1.23	1.22
Solubility ($g.L^{-1}$)	In water (at 22 ^{0}C, pH 7)	0.033	0.0085
	In acetone (at 25 ^{0}C)	31	41
	In *n*-hexane (at 25 ^{0}C)	0.11	0.36

The adverse effects of atrazine on microorganisms, animals, and even humans in the various environmental matrices where it has been detected have been critically reviewed (Singh et al., 2018). These range from oxidative stress in plants to endocrine disrupting effects in animals and humans (Hassan and Nemat Alla, 2005, Hayes et al., 2003). Recently, researchers in

South Africa carried out a study to prioritise pesticides according to their toxicity and environmental fate, and atrazine had a weighted hazard potential of 3.63, and ranked first (Dabrowski et al., 2014). Hence there is a need to carry out more studies to understand its environmental fate.

Terbuthylazine (**Figure 2-2**) is capable of bioaccumulating based on its high octanol/water partition coefficient (Garrett et al., 2015). Several adverse effects of terbuthylazine on non-target organisms have been reported such as damage to intestinal epithelial cells and renal epithelial cells of the European bass *Dicentrarchus labrax* (L), as well as oxidative stress and histopathological changes in the heptopancreas of the red swamp crayfish (Dezfuli et al., 2006, Stara et al., 2016).

For a pesticide like atrazine or terbuthylazine to enter the environment, where it may undergo different processes such as leaching, runoff, and spray drift, spraying has to first take place. Hence, in order to understand spray deposition of atrazine, we have to discuss the spraying process namely the spray equipment which can be used, and the type of nozzles employed on a range of crops.

2.2 The spraying process

Spraying of pesticides should be done timeously and consistently in order to obtain optimum yields in agriculture. For pesticides to be applied, a sprayer is required, and these are classified as knapsack, tractor mounted, foot, and aerial sprayers (Malik et al., 2012). All sprayers have a spray tank that holds the spray liquid, and a pump that moves the spray liquid to the outlets commonly known as the nozzles (Matthews, 1979). Other components that may be present in sprayers include an agitator, pressure gauge, and pressure regulator.

Different types of crops are sprayed with different sprayers because they have different ways of propelling droplets, thus improving efficacy of the pesticide application (Blanco et al., 2019). For instance, in vineyard or orchard crops the most commonly used are the non-targeted sprayers such as the air blast sprayer, or targeted sprayers like the twin row multi-head fan sprayer, and pneumatic-electrostatic sprayers (Hewitt et al., 2015). In field crops such as maize or wheat, the boom sprayer is commonly used (Zhao et al., 2014).

The function of a nozzle on all sprayers is to emit the spray liquid (Matthews, 1979). There are several types of nozzles available, and these produce different droplet size spectra (Murphy et al., 2000). Nozzles are classified as either hydraulic pressure nozzles, flat fan nozzles or air inclusion nozzles (Miller and Butler Ellis, 2000). Flat fan nozzles produce a uniform spray pattern across a spray boom because they are tapered from the centre to the edges, and they are designed to overlap with adjacent nozzles (Malik et al., 2012). Conventional flat fan nozzles produce a large amount of spray drift, however, nowadays newer designs greatly reduce drift potential (Gil et al., 2014). Other hydraulic nozzles used in the spraying process that have a similar break-up mechanism to the flat fan nozzle include the hollow cone, pre-orifice, and deflector nozzles (Matthews, 1979, Miller and Butler Ellis, 2000). In air inclusion nozzles spray liquid flows through a constricted channel resulting in the creation of negative pressure in the nozzle, a phenomenon known as the “Venturi effect” (Doruchowski et al., 2017). Thus, the spray generated will contain large, coarse droplets filled with air bubbles, which are less likely to undergo off-target drift.

2.3 Mechanism of drift formation

After dispersion from the tank of the sprayer through the nozzle, the bulky liquid pesticide formulation is converted into small droplets by a process called atomization (Lefebvre, 1993). Atomization takes place by either emission of the liquid through a small orifice at high pressure, or by impacting it at high velocity on a horizontal surface or a rapidly spinning surface (Bouse et al., 1994). This generates instability in the liquid stream, and the consequent fragmentation into small droplets of various sizes ranging from a few micrometres to thousands of micrometres (Bache and Johnstone, 1992). It is worth noting that the type of atomization, and droplet size spectrum depend on the atomizer design, and the physical properties of the liquid (Akesson et al., 1994).

The movement of the droplets is controlled by inertia, gravity, and drag (Bache and Johnstone, 1992). Thus, as the droplets fall through the atmosphere towards the ground, they may experience shear stress leading to a change in shape, or they may further disintegrate because of aerodynamic forces (Lefebvre, 1993). A drop released from rest in a stationary flow, will fall at a constant terminal velocity if the aerodynamic drag (D), and the gravitational forces are in balance (Bache and Johnstone, 1992). The force balance can be written as (Bache and Johnstone, 1992):

Equation 2-1

$$\frac{1}{2} c_d \rho_a \mathrm{A} v_s{}^2 = \frac{1}{6} \pi \mathrm{d}^3 (\rho - \rho_a) \mathrm{g}$$

Where c_d is the drag coefficient, ρ and ρ_a are the densities of the particle and the air respectively, A= ($\pi d^2/4$), is the cross sectional area of the particles, v_s is the sedimentation velocity, and g is the gravitational acceleration. However, the drag coefficient depends on the Reynolds number (Re) which is defined by Bache and Johnstone (1992):

Equation 2-2

$$\mathrm{Re} = \frac{v_s \mathrm{d}}{\mathrm{V}}$$

Where V, is the kinematic velocity of air, and v_s is the sedimentation velocity. When Re is less than 0.5, the motion is dominated by viscosity rather than particle inertia, and the drag coefficient is defined by Bache and Johnstone (1992).

Equation 2-3

$$c_d = \frac{24}{Re}$$

Although terminal velocity is affected by size, density of droplet, shape of droplet, and density and viscosity of air, it is the droplet size that affects it most (Matthews, 2000). Small droplets have smaller terminal velocities, and hence more time to fall, this is summarised by the Stokes' equation:

Equation 2-4

$$F_d = 6\pi r \eta v_s$$

Where F_d is the drag force (ms^{-1}), r is the radius of the droplet (m), and η is the viscosity of the air (Nsm^{-2}), and v_s is the sedimentation velocity.

Although droplet size is a major factor that affects the atomization of the pesticide, it also affects the rate at which spray drift takes place. In addition to droplet size, climatic conditions, and application factors are also significant factors that influence the spray drift of pesticides. For this reason, the next section will discuss the effect of droplet size, application factors, and meteorological conditions, respectively, on spray drift.

2.4 Factors affecting spray drift

2.4.1 Droplet size

Droplet size is one of the greatest factors that affects spray drift of pesticides (Bird et al., 1996). The size of droplets is measured in microns. Most commercially available nozzles produce a range of droplet sizes, and not a single size (Nuyttens, 2007). Droplet sizes are commonly described using the volume median diameter (VMD), which is the droplet size at which one-half the spray volume consists of droplets larger than the given value, and one-half consists of droplets smaller than the given value (Kruger and Klein, 2013). Using the VMD, a droplet classification system with categories from extra fine to ultra-coarse based on VMD in microns has been developed by the British Crop Protection Council (BCPC), and American Society of Agricultural and Biological Engineers (ASABE). Larger droplets have been found to be less susceptible to drift than small droplets (<100 µm), which have larger kinetic energy (Yarpuz-Bozdogan and Bozdogan, 2009, De Ruiter et al., 2003). For this reason, most farmers now use coarser sprays to minimize environmental pollution, although these may have the disadvantage of providing inadequate coverage to control pests (Matthews, 2000). Droplet size depends on a number of factors such as nozzle type, nozzle size, and spray pressure. All these factors are collectively referred to as application factors.

2.4.2 Application factors

Several studies report that the application factors that influence spray drift include orifice size, spraying pressure, sprayer type, nozzle type, spraying height, angle at which pesticides are spread, and driving (flying) speed (Murphy et al., 2000, Nuyttens et al., 2007, Zhao et al., 2014). The nozzle type is a significant factor that affects both the airborne and sedimentation drift as exemplified by a study in which airborne and sedimentation drift of imidacloprid was compared using a conventional flat fan nozzle (LU120-02) to low drift nozzles (IDK120-02 and AD120-02), and were found to be lower in the low drift nozzles (Zhao et al., 2014). This was attributed to the fact that the small orifice plate reduced operating pressure, and hence produced larger droplets with less velocity leading to more sedimentation closer to the application site, but less further away. The findings of this study were confirmed by a recent study that was carried out to compare the effects of drift reducing and conventional nozzles under both wind tunnel and field conditions (Torrent et al., 2017). In this study, the drift-reducing nozzles reduced airborne and sedimenting drift in both field and wind tunnel experiments, although they reduced airborne drift better than sedimenting drift.

The various nozzles described can be utilized by a tractor mounted boom sprayer for large pieces of land up to 500 ha. For such sprayers, the boom height and boom configuration are important factors affecting spray drift (Holterman et al., 1997). A study to determine the effect of boom configuration compared a standard boom, a deep boom (for maximum air stream disturbance), and a profile boom (for reduced vertical dispersion) (Murphy et al., 2000). It was observed that the effect of boom configuration was less significant than that of the spray quality. However, compared to a standard boom, the deep section boom increased drift by 10%, while the profile section reduced drift by 7% (Murphy et al., 2000). The boom height is another factor that influences spray drift (Holterman et al., 1997). Lowering the boom height reduces spray drift (Balsari et al., 2017). However, for this to hold, the spray pattern must be consistent (Teske and Thistle, 1999). The effect of boom height was studied for conventional and air-assisted spraying, and it was reported that both ground deposition and airborne spray drift were significantly reduced with the latter (De-Jong et al., 2000).

The driving speed is another factor that affects spray drift by affecting air circulation with its induced air turbulence (Nuyttens, 2007). Spray drift increases with increasing sprayer speed (Van de Zande et al., 2005). An increase in driving speed causes the spray to be diverted back into upward currents and vortices behind the sprayer which trap small droplets, which thus favour drift (Nuyttens, 2007). A study to determine the relationship between driving speed and spray drift reported that an increase of 1 m.s^{-1} increased spray drift deposition by 1.0% within a trajectory of 1 m.s^{-1} and 2 m.s^{-1} (Arvidsson, 1997). Similar results were also reported when air blast sprayers were used for pesticide application in vineyards (Celen et al., 2008). However, it has been observed that drift in orchards decreases with increasing sprayer speed, and this is attributed to interaction between travel speed of sprayer and tree growth stage (Lesnik et al., 2015). Finally, although all these application factors directly affect spray drift, the extent of spray drift and the size of the droplets emitted from the nozzles also depend on the physical properties of the spray liquid (Hewitt et al., 2009).

2.4.3 Physical properties of spray liquid

The physical properties of the spray liquid include liquid density, surface tension, and viscosity. There is a positive correlation between drop size and liquid density (Nuyttens, 2007). An earlier study suggested that surface tension reduction leads to production of smaller drops, and hence an increase in spray drift (Butler Ellis et al., 1997). The results were confirmed by a latter study carried out by the same research group, which recorded similar effects on spray liquid lifetime for all the hydraulic nozzles (Butler Ellis and Tuck, 1999). However, the hollow cone, and pre-orifice nozzles showed variation in droplet size. For this reason, a more recent study concluded that lower surface tension only produces smaller droplets, and hence less drift (De Schampheleire et al., 2009). An increase in viscosity increases the droplet size, and hence reduces spray drift because it causes resistance to flow (De Schampheleire et al., 2009).

The type of pesticide formulation also influences the droplet size, and hence spray drift (Carvalho et al., 2018). A pesticide formulation consists of an active ingredient which is responsible for the efficacy of the formulation, adjuvants, and surfactants (Karasali and Maragou, 2016). Adjuvants are responsible for improving the performance of the pesticide spray by increasing the droplet sizes (Akesson et al., 1994). On the other hand surfactants improve the wetting and coverage of the target surface by reducing the dynamic surface tension of the spray liquid. **Table 2-2** lists the available formulation types and their definitions. The effect of pesticide formulation on spray drift has been extensively reviewed (Hilz and Vermeer, 2013). A general trend in pesticide formulations is the inclusion of polymeric materials which reduce spray drift by increasing the coarseness of the spray, and hence the size of the droplets (Ferguson et al., 1992). For instance, in a study to determine the effect of adjuvants on spray drift using a medium quality flat fan nozzle, emulsion-based adjuvants gave larger droplets and less airborne drift, but more ground deposition (Sundaram et al., 1987, Hilz and Vermeer, 2013). Finally, the effects of changes in homogeneity of spray liquid due to formulation type or adjuvants on drift potential were studied using emulsifiable concentrate (EC) and suspension concentrate (SC) formulations of phenmedipham (Stainier et al., 2006). EC sprays were observed to increase airborne drift, and the opposite was true for SC formulations. This is in contrast to an earlier study in which airborne drift was reduced for an EC formulation 2 m downwind of the spraying through a hollow cone nozzle in a 4 $m.s^{-1}$ wind (Butler Ellis and Bradley, 2002). The differences might have been due to the sampling system and the air velocity (Stainier et al., 2006). On the other hand, off target deposition for SC, water dispersible granules, and soluble liquid (SL) was shown to be higher than that for emulsion based formulations because of reduced surface tension in these liquids (Hilz and Vermeer, 2012).

Table 2-2: Types of pesticide formulations available on the market adapted from (Knowles, 1998).

Class	Physical appearance	Chemical composition
Emulsifiable concentrate	Emulsion	Co-solvents, surfactants
Suspendable concentrate	Suspension	Surfactants, anti-foamers, antifreeze agents, thickeners, binders
Soluble liquid	Liquid	Surfactants, buffers, anti-foamers, fillers
Water-dispersible granules	Solid	Binders, surfactants, anti-foamers, fillers
Water-dispersible powder	Solid	Surfactants, stabilizers, anti-foamers

2.4.4 Meteorological factors

The meteorological factors that affect spray drift are wind speed, wind direction, atmospheric stability and turbulence, temperature and humidity. Of these factors, wind speed has been identified as a major factor affecting spray drift (Arvidsson et al., 2011). There is a direct relationship between wind speed and spray drift, with speeds less than 15 $km.h^{-1}$ reducing drift effects (Nuyttens, 2007). The trueness of the direct relationship between wind speed and spray drift was also found to depend on the distance from the treated area, as higher wind speeds were observed to increase spray drift only at longer distances, while reducing spray drift closer to the application site (Wang and Rautmann, 2008). Regarding off target deposition of pesticides, high wind speeds were found to give greater deposition in the near field (distances less than 30 m), where large droplets are deposited by gravitational forces (Miller et al., 2000). When the wind speed is low, off target deposition depends on the sprayer airflow profile (Garcerá et al., 2017). With regards to wind direction, it has been recently observed that front winds led to higher drift potential than lateral winds (Gil et al., 2015). In summary, wind speed and wind direction determine the horizontal velocity and transportation of the spray droplets during application (Caldwell, 2006).

Atmospheric stability refers to the vertical movement of air in the atmosphere (Nuyttens, 2007). It can exist in three phases namely neutral, unstable, and stable. In a neutral atmosphere, there is no change in temperature with height, winds are less mild than in an unstable condition, there is no droplet evaporation or turbulence and as result little drift is observed (Kelso et al., 1975). This is attributed to adiabatic lapse rate, a term which refers to the phenomenon whereby the air pressure drops as the temperature drops (Caldwell, 2006). In an unstable atmosphere, the ground layer has a higher temperature than the overhead layer, it is characterised by high wind velocity, and considerable vertical and horizontal air turbulence mixing which disperses the spray cloud upwards leading to creation of smaller droplets which may be deposited at farther distances than the stable condition (Kelso et al., 1975, Fritz, 2006).

A stable atmosphere occurs when the overhead air is warmer than the air at ground level (Miller and Stoughton, 2000). It is characterised by low wind velocity, small velocity gradient, and little or no vertical turbulence (Kelso et al., 1975). Movement of the spray cloud in a stable atmosphere is restricted to near ground levels (Miller and Stoughton, 2000). In an unstable atmosphere, there is mechanical turbulence, which causes mixing, and reduces buoyancy effects (Miller et al., 2000). Thus, the movement of the spray cloud depends on the turbulence, and therefore spray drift increases (Miller et al., 1996). However, it is worth noting that the effect of atmospheric stability has been mainly validated for aerial spray applications, whilst for ground applications, wind speed has been validated as the more important factor (Gil et al., 2007).

Temperature and humidity affect spray drift by influencing the droplet size. Higher temperatures and low humidity have been observed to result in the evaporation of droplets, and their consequent reduction in size, and thus increasing the spray drift distance (Briand et al., 2002). Consequently, pesticide deposition is reduced when the humidity is high because the droplets formed are large and have less drift potential (Lefrancq et al., 2013). For instance, when spraying was carried out under high temperatures of 26.2 ^{0}C, and low relative humidity of 58.5%, more spray drift was observed, as compared to when it was carried out at lower temperatures and high relative humidity of 14.7 ^{0}C and 87.6% respectively (De Schampheleire et al., 2008). Thus, the best time for spraying is in the early morning and early evening (Nuyttens, 2007).

2.5 Pesticide deposition monitoring

In order to be able to conduct a quality pesticide deposition monitoring campaign the stages listed in **Figure 2-3** may be followed. The planning stage involves identifying the analyte of interest, and the appropriate sampler that meets the objective of the study, sampling site, and quality control measures in sample collection and handling (Hewitt and Valcore, 2003). It is worth noting that the applicability of the sampler is determined by the extractability of the analyte from its surface. Hence, analyte recovery studies have to be carried out in the laboratory before it can be used in the field. As illustrated in **Figure 2-3**, after carrying out recovery studies, field sampling should follow. Before we discuss the sampling process, it is imperative to discuss the types of samplers that are used in pesticide deposition monitoring, their advantages, and disadvantages.

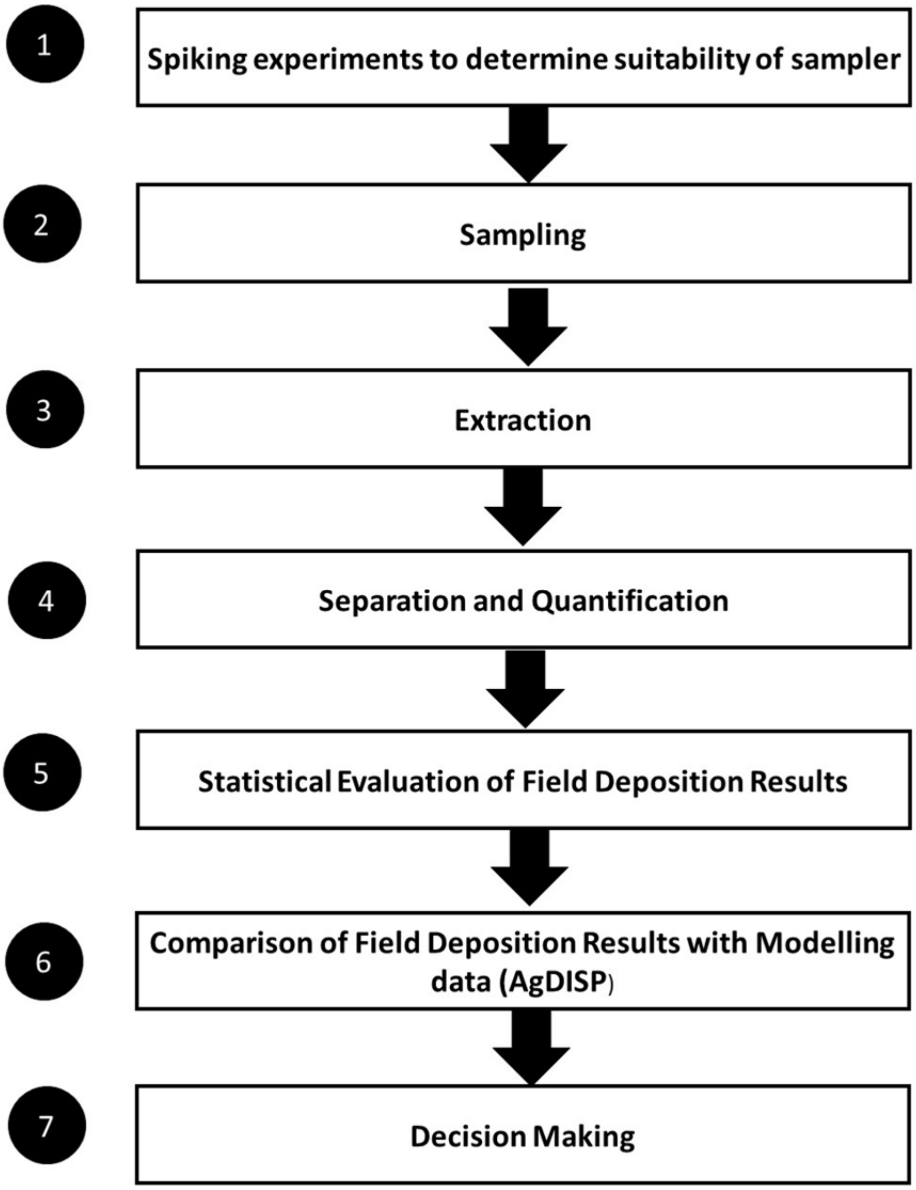

Figure 2-3: Pesticide deposition monitoring process.

2.5.1 Choice of tracers for pesticide deposition monitoring

Various tracers have been employed to monitor pesticide deposition in different parts of the world. Examples of these include water soluble metallic salts (Gil and Sinfort, 2005), metal chelates (Cross et al., 2001), colourants (Celen, 2010), and fluorescent tracers (Wolters et al., 2008). Of these tracers, fluorescent ones have been used more than other types because of the distinct advantages that they possess in pesticide deposition monitoring (Wolters et al., 2008, Garcia Santos et al., 2015, Garcerá et al., 2017). For instance, uranine has been used to quantify deposition successfully because of its low vapour pressure which stops it from volatilising once it has been deposited onto the collector surface (Garcia Santos et al., 2015). In addition, the tracer can be analysed without any difficulty, and they have high solubility in the spray mixture (García-Santos et al., 2011). Another fluorescent tracer that is widely used is Brilliant Sulfa Flavin (BSF) because of its low degradation rates (Gil and Sinfort, 2005). However, the photostability of fluorescent tracers is valid within a limited timeframe, as exemplified by Rhodamine B which was stable for only 60 minutes (Bueno et al., 2017). Another disadvantage of fluorescent tracers is that they quickly degrade in humid conditions, and when used in low concentrations (Hewitt, 2010). Finally, it is worth noting that some fluorescent tracers such as pyranine, fluorescein, and tinopal work best at an optimum pH, which is usually alkaline, and if this optimum pH is not used, pesticide deposition may be under-predicted (Zhu et al., 2005). Metal chelates have also been explored as options in deposition monitoring, but their use is limited because their analysis is complex and time-consuming, despite them being photostable, inexpensive, and water soluble (Foque et al., 2014, Nuyttens et al., 2007). However, recently studies have been carried out successfully to compare modelled and monitored data of pesticide concentrations arising from spray drift using active ingredients because they are very stable, and more representative of pesticide drift than other tracers (Hewitt, 2010). Examples of pesticides that have been studied include atrazine (Nsibande, 2015, Ravier et al., 2005), chlorpyrifos (Capri et al., 2005), and endosulfan (Ernst et al., 1991).

2.6 Sampling approaches to off-target deposition

The goal of pesticide sampling is to obtain representative samples of the application being investigated, while minimizing bias during sample collection. Various methods are available for sampling spray deposition, and the choice of technique depends largely on the data requirements of the study, cost, and availability of equipment (Donkersley and Nuyttens, 2011). In addition, the basic requirements of samplers for deposition are that they should: (1) have high collection efficiencies of small droplets in relatively low air speeds, (2) have a definable sampling volume or area, (3) be such that the captured spray drift can be recovered and quantified, (4) easy to handle under field conditions, (5) be cheap, (6) and should collect an adequate volume of drift before saturation (Miller, 1993, Hewitt et al., 2002).

The measurement of off-target deposition on deposition samplers is guided by many standards. Firstly, sampling of off-target deposition should be determined in a defined downwind area, with minimum obstructions, other than the target crop, that could influence the airflow in the region of measurement, and the topography of the area should be recorded (ISO, 2005). Most studies report the absence of obstacles around the treated field (Carlsen et al., 2006b, Capri et al., 2005). Regarding the slope of the ground, most studies are reported to be done on flat ground. Brain et al. (2019) carried out their study in a place of uniform slope whilst Capri et al. determined off-target deposition of chlorpyrifos in two fields, one was flat, and the other one was sloped. In another study, Le Francq et al. (2013) carried out deposition monitoring of kresoxim methyl in an area with a slope of 15%. It is however worth noting that some studies do not report the slope of the area where off-target deposition was made, hence making the comparison of deposition values potentially difficult.

The time lapse after spraying, and before sample collection varies, as most studies report between 10 to 30 min to allow for enough transport of the pesticide to the sampler locations and to enhance detection (Carlsen et al., 2006b, Brain et al., 2019, Nsibande, 2015). For instance, Brain et al., (2019) collected the samples 10 min after the spraying process. In another study, deposition samples were also collected after 10 min (Nsibande, 2015). However, many studies do not report the time at which the samples were collected after the spraying process (Brain et al., 2017). Thus, it is recommended that the time delay after spraying should be reported to allow for comparisons to be drawn between different studies.

2.6.1 Interaction of droplets with samplers

Before we discuss the various samplers used for deposition monitoring, it is imperative to discuss the processes that may take place when the pesticide droplets interact with the surface of the sampler. As illustrated by **Figure 2-4**, droplets can either adhere, bounce or shatter depending on the characteristics of the liquid (such as surface tension and viscosity), droplet parameters (including size and velocity), and sampler surface parameters (roughness, orientation, wettability, etc.) (Zwertvaegher et al., 2014, Celen, 2010). As a result of all these factors, the amount of kinetic energy lost by the droplets upon impaction on the sampler may vary. If less energy is lost, the droplets will rebound, but if the energy losses are high they will adhere to the sampler surface (Spillman, 1984). The high energy losses result from the spread of the droplets on the surface, and the subsequent recoiling due to surface tension (Forster et al., 2012). Shattering corresponds to the formation of a number of smaller droplets due to impact pressure (Rioboo et al., 2008).

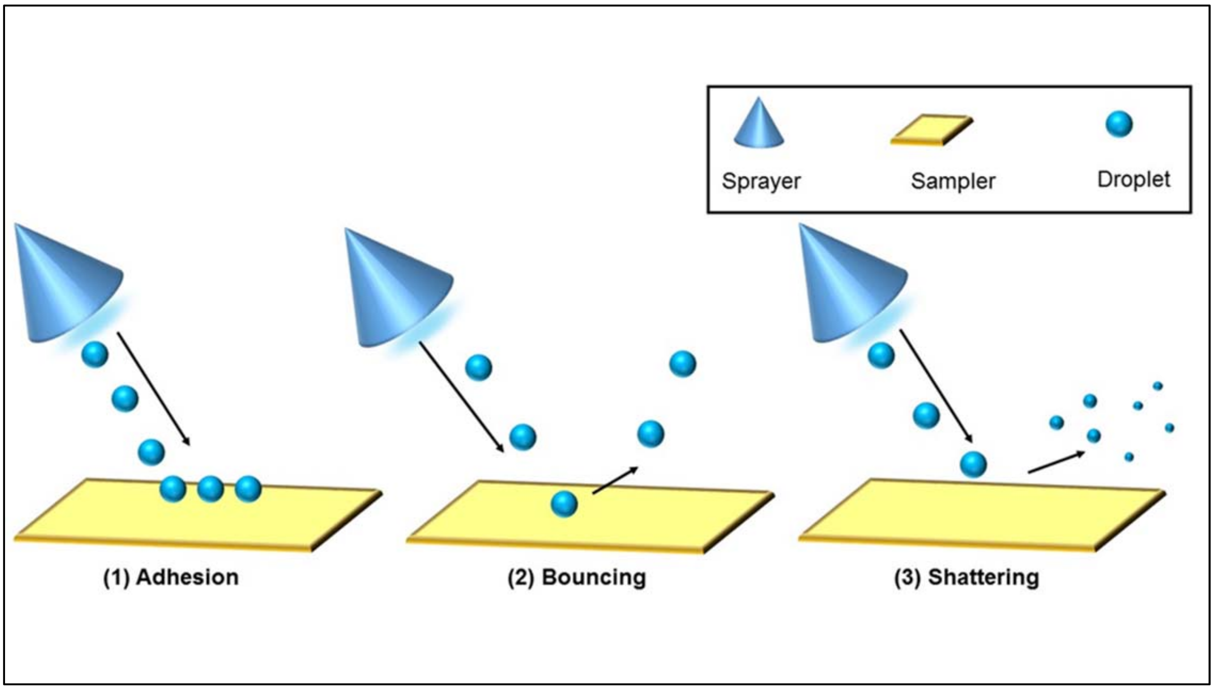

Figure 2-4: Diagram illustrating adhesion, bouncing and shattering of droplets upon interaction with a sampler surface.

2.6.2 Collection efficiency of samplers

Collection efficiency is defined as the fraction of droplet mass deposited on the surface of a sampler from the bulk air volume (Kirchner et al., 1996). This value is usually less than 100% because different collectors cause changes in air flow patterns, and this may lead to droplets going round a collector rather than impacting or sedimenting on it (Craig et al., 2000). Therefore when calculating the collection efficiency, a correction has to be made comparing the number of droplets caught by the collector to the number which would have passed through the frontal area of the collector, in the absence of the collector (Craig et al., 2000). Thus, the collection efficiency is related to the impaction parameter, defined as:

Equation 2-5

$$P = \frac{\rho_d V d^2}{18 \mu D}$$

Where P is the impaction parameter, ρ_d the droplet density (1 000 kg.m^{-3}), V is the undisturbed flow velocity (ms^{-1}), d is the droplet diameter (m), μ is the air viscosity (1.8 x 10^{-5} kg m^{-1} s^{-1}), and D is the diameter/width of the collector. Thus, the collection efficiency increases when the diameter of the sampler decreases, and the velocity and size of the droplet increases.

Several studies have been carried out to quantify the collection efficiencies of different deposition samplers. A study carried out on cylindrical samplers showed that the collection efficiencies increase as the collection surface narrowed, and as the size of the droplets increased (May and Clifford, 1967). Collection efficiencies for nylon screen collectors varied from 50-70 % for spray droplets with volume median diameter less than 45 µm for air speeds of 4 m.s^{-1} (Fox et al., 2004). Thus the collection efficiency of a sampler is affected by its shape, size, orientation to the wind, air flow through and around the sampler, meteorological conditions, and material of construction (Kirchner et al., 1996).

2.6.3 Off-target deposition of pesticides using various samplers

2.6.3.1 Glass samplers

Glass surfaces are mainly used to sample pesticide deposition because they have high capture efficiencies (Carlsen et al., 2006b) and are easily extracted. The advantages of glass petri dishes, which is the most commonly used glass sampler, is that they allow for low pesticide detection limits, they are easy to handle, and low extraction volumes are required per unit pesticide sampled (Caldwell and Wolf, 2006, Matthews, 2006). However, the presence of a raised edge may negatively affect the deposition of droplets near the edge of the petri dishes (Matthews, 2006). Another disadvantage of glass petri dishes is that volatilisation can take place from their surface resulting in an underestimation of pesticide deposition (Zhao et al., 2014). This is of concern for the more volatile pesticides.

With respect to pesticide deposition studies utilising glass petri dishes, various approaches have been used including the placement of glass fibres inside the petri dishes to collect the pesticide (Ravier et al., 2005), filling the glass petri dish with water (Dabrowski et al., 2005), or without placing any solvent or glass fibres inside the sampler (Lefrancq et al., 2013, Druart et al., 2011). The type of solvent used may contribute to the volatilization of the analyte from the surface of the sampler, as exemplified by a study where ethyl acetate caused atrazine and alachlor to volatilize more readily from the glass petri dishes, as compared to water (Ravier et al., 2005).

Glass microscope slides are another type of glass sampler that have been used to sample off-target pesticide deposition. The advantages of glass microscope slides are that deposits can be washed off easily using a relatively small volume of solvent, however the deposition amounts may be affected if the slides are not exactly horizontal (Matthews, 2006). The use of glass microscope slides has not been reported for off target deposition of pesticides in crop types such as orchards and vineyards for the last twenty years. However, they were used to sample off-target deposition of herbicides of diverse volatilities in an open field (Carlsen et al., 2006b). To investigate the effect of pesticide volatility on off-target deposition of the pesticides onto the glass microscope slides, the same research group carried out another study (Carlsen et al., 2006a). It was reported that evaporation from the surface of the glass microscope slides was not directly related to the pesticide vapour pressure, as some pesticides with low vapour pressures dissipated from the surface of the glass slides. Moreover, they underscored the need for more research into the relationship between vapour pressure and evaporation from the surface of the glass slides. Glass microscope slides have been successfully used to investigate the effect of formulation type on off-target deposition in a drift chamber (Sciumbato et al., 2005). It was reported that formulation type did not affect deposition of quinclorac and 2,4-D onto glass microscope slides. In conclusion, the behaviour of pesticides of varying volatilities, and different formulations on microscope slides is an area that still needs to be studied in order to fully understand the interaction, while keeping other conditions constant.

2.6.3.2 Paper based samplers

Samplers constructed from paper are typically used because of their flat surface which enables them to represent deposition in aquatic bodies (Hewitt, 2010). A distinct advantage of alpha cellulose samplers is that they protect the pesticides from photodegradation and volatilization (Capri et al., 2005). In addition, they have good absorbent properties which enables droplets to be captured efficiently without any bouncing off the surface, while maintaining analyte stability, and allowing efficient analytical extraction (Hewitt et al., 2002, Foque et al., 2014). The disadvantage of chromatography paper samplers is that they are less representative of an area covered with vegetation (Mathers et al., 2000). The majority of studies carried out have reported the use of patented chromatography paper such as Whatman®, and type GR512 (Proctor and Gamble, USA) filter paper or alpha cellulose strips (Nsibande, 2015, Vischetti et al., 2008, Vercruysse et al., 1999, Hewitt et al., 2002). It is important to note that both Whatman® chromatography paper and ordinary alpha cellulose strips are constructed from cotton cellulose and have thus a high degree of polymerization and crystallinity (Costa et al., 2014). However, in most of the studies, the use of Whatman® chromatography paper has been reported, excluding the grade thereof, which is an important aspect since different grades have different particle retention properties.

2.6.3.3 Other types of samplers

While several other samplers such as drinking straws, filament lines, polystyrene cords, and Teflon spheres have been used before 1999, their use has not been reported in pesticide deposition monitoring studies more recently because of some serious shortcomings. For instance with drinking straws challenges may be experienced with analyte recovery and stability prior to extraction (Hewitt, 2010, Caldwell and Wolf, 2006). Thus the materials employed in the past two decades have been carefully selected based on the fact that their collection efficiencies were known to be acceptable. Cotton cloth was successfully used to sample off-target deposition of malathion (Yarpuz-Bozdogan and Bozdogan, 2009), whilst synthetic wool yarn was found to have a collection efficiency of between 40 and 100% (Cooper et al., 1996) and it has been successfully used to sample off-target deposition of pesticides such as fenthion and permethrin (Van der Walt, 1999, Schleier III and Peterson, 2010). Another sampler that has been successfully used to sample off-target deposition of pesticides is stainless steel plates. In a study, they were used to sample off-target deposition of glyphosate and glufosinate, and no deposition of the herbicides were observed because the nozzles used for application were funnelled downwards, and hence produced large droplets that are less liable to drift (Druart et al., 2011).

Recently, circular stainless steel discs (113 cm^2) and rods (6.35 cm^2) were used to sample horizontal and vertical deposition of atrazine and mesotrione, respectively (Brain et al., 2017, Brain et al., 2019). In both studies, deposition was notably higher on the vertical rods as compared to the circular discs. For instance, as described in Brain et al. (2019), 7 to 41 times more atrazine mass was collected from vertical rods (from airborne drift) as compared to the horizontally placed stainless steel discs (reflective of ground deposition). A major difference between the two studies was that higher deposition amounts were obtained in the study carried out using atrazine (up to 21.6 $g.ha^{-1}$ for horizontal collectors, and 197 $g.ha^{-1}$ for vertical rods) compared to the one using mesotrione (up to 0.261 $g.ha^{-1}$ for horizontal collectors, and 3.969 $g.ha^{-1}$ for vertical rods). This may be attributed to the differences in the nozzles used for both studies among other factors such as wind speed, temperature, and driving speed. The nozzles employed for the atrazine study produced coarse droplets (TT11004, 40 psi) that are large and have a higher potential of off-target deposition than the ones used for the mesotrione study, which produced medium droplets (TT11025, 40 psi) with less potential for off-target deposition (Brain et al., 2019, Brain et al., 2017). **Table 2-3** summarises some of the off-target deposition monitoring studies carried out to date on active ingredients using various samplers.

Table 2-3: Summary of off-target deposition monitoring studies carried out to-date using pesticide active ingredients.

Deposition Collector	Location	Pesticide(s) sampled	Crop type	Extraction Technique	Analytical Method	References
Glass microscope slides	Denmark	Pendimethalin, metamitron, desmedipham, phenmedipham, ethofumesate, prosulfocarb, ioxynil octanoate, bromoxynil octanoate, tribenuron methyl, fluoroxypyr-1-methylheptylester		Extraction with MeOH, manual shaking and sonication	LC-MS, LC-DAD	(Carlsen et al., 2006b)
Glass petri dishes filled with distilled water	South Africa	Azinphos-methyl	Orchard	SPE	GC-ECD	(Dabrowski et al., 2005)
Glass bowls consisting of distilled water, surface area (75 cm^2, and 4 cm depth)	South Africa	Azinphos-methyl, endosulfan	Orchard	SPE using C18 columns conditioned with MeOH and water	GC-ECD-NPD	(Schulz et al., 2001)
Glass petri dishes with glass fibre soaked in ethyl acetate (8 cm diameter)	France	Alachlor and atrazine	Maize	Soxhlet using *n*-hexane and diethyl ether	GC-MS	(Ravier et al., 2005)
Glass petri dishes (9 cm diameter)	China	Imidacloprid	Wheat	Washing with MeCN followed by rotary evaporation	LC-MS/MS	(Zhao et al., 2014)
Glass petri dishes (176.71 cm^2)	France	Kresoxim methyl	Vineyard	Extraction with ethyl acetate	GC-MS/MS	(Lefrancq et al., 2013)
Stainless plates, glass petri dishes	France	Glyphosate, glufosinate, cymoxanil, folpet, tebuconazole, pyraclostrobin	Vineyard	LLE with ethyl ether, MeCN: DCM (1:1v/v)	HPLC GC-MS	(Druart et al., 2011)
Glass fibres mounted on stainless steel plates	Canada	Endosulfan	Potato	Extraction with acetone and *n*-hexane	GC-ECD	(Ernst et al., 1991)
Steel vertical rods, and steel circular	United States of America	Atrazine	Lettuce	Extraction using MeOH	HPLC-Q-Trap MS	(Brain et al., 2019)

discs						
Steel vertical rods, and steel circular discs	United States of America	Mesotrione	Lettuce, and tomatoes	Sonication in 1% formic acid in MeCN	HPLC-TripleTOF	(Brain et al., 2017)
Ground plates (929 cm^2)	New Mexico	Malathion			GC-MS	(Miller et al., 2000)
Cellulose strips (25 cm x 25 cm)	Belgium	Captan and tolylfluanide	Orchard	Sonication in *n*-hexane	GC-ECD	(Vercruysse et al., 1999)
Crepe-paper (29.5 x 4-14 cm)	Germany	Various herbicides, insecticides and fungicides		Shaking with acetone followed by evaporation in nitrogen	LC-DAD	(Epple et al., 2002)
Water sensitive paper (7.6 x 2.5 cm)	Italy	Etofenprox	Vineyard		Counting of droplets using lens	(Otto et al., 2013)
Aluminium backed silica gel chromatography sheets	United States of America	Phosmet	Orchard	Dissolving in acetone: *n*-hexane *(*1:1), followed by filtration and evaporation to dryness	GC-PFPD	(Tsai, 2007)
Chromatography paper	Australia	Endosulfan	Cotton		ELISA	(Woods et al., 2001)
Whatman chromatography paper (50×10 cm)	Italy	Chlorpyrifos and metalaxyl	Vineyard	Extraction with DCM followed by sonication	LC-DAD	(Vischetti et al., 2008)
Chromatography paper	South Africa	Atrazine	Maize	Extraction with *n*-hexane + acetone (3:1), sonication	DSA-TOFMS	(Nsibande, 2015)
Filter paper	Italy	Chlorpyrifos	Vineyard	Sonication using DCM	GC-NPD	(Capri et al., 2005)
Filter paper and filtering cloths	Belgium	Tolylfluanide			GLC	(Brusselman et al., 2004)
Cotton fabric (7×7 cm)	Turkey	Malathion		Shaking with methanol	GC-NPD	(Yarpuz-Bozdogan and Bozdogan, 2009)
Cotton wool (100 cm^2)	United States of America	Permethrin		Extraction using *n*-hexane and shaking	GC-ECD	(Schleier III and Peterson, 2010)
Wool traps	South Africa	Fenthion			GC-NPD	(Van der Walt, 1999
Plastic petri dishes	The Netherlands	Imidacloprid			R-HPLC	(Hilz and Vermeer, 2012)

Teflon targets (5.1 cm x 5.1 cm)	United States of America	Oxamyl	Citrus orchard	Adding 20 ml of MCA buffer and vortexing for 4 min	HPLC-FL	(Wilson et al.,2007)

DCM- Dichloromethane, DSA-TOFMS- Direct Sample Analyser coupled to Time of Flight Mass Spectrometer, (ELISA- Enzyme Linked Immunosorbent Assay, GC-ECD - Gas Chromatography Electron Capture Detector, GC-PFPD- Gas Chromatography Pulsed Flame Photometric Detector; GLC- Gas Liquid Chromatography, GC-MS/MS- Gas Chromatography Tandem Mass Spectrometer, GC-NPD- Gas Chromatography Nitrogen Phosphorus Detector, HPLC-FL- High Performance Liquid Chromatography Fluorescence Detector, HPLC-Q-Trap MS- High Performance Quadrupole Linear Ion Trap Mass Spectrometer, HPLC-TripleTOF- High Performance Liquid Chromatography Triple Quadrupole Time-of-Flight Mass spectrometer, LC-DAD- Liquid Chromatography Diode Array Detector, LC-MS- Liquid Chromatography Mass Spectrometer, LC-MS/MS- Liquid Chromatography Tandem Mass Spectrometer, LLE- Liquid Liquid Extraction, MCA- monochloroacetic acid, MeCN- acetonitrile, MeOH- methanol, RHPLC- Reverse Phase High Performance Liquid Chromatography, SPE- Solid Phase extraction.

In conclusion, the deposition of pesticides on various samplers is affected by numerous factors. For this reason, it may be necessary to optimize the sampling conditions for the same type of tracer or active ingredient, under similar environmental conditions. Parallel sampling using a range of samplers may also be preferable.

2.7 Extraction techniques

The extraction technique to be employed in pesticide deposition monitoring chiefly depends on the type of sampler that was used in the field. For instance, with glass petri dishes and glass microscope slides, manual shaking may be enough to extract the analyte (Zhao et al., 2014, Sundaram et al., 1987). However, in some cases when the petri dishes are used to sample deposition with distilled water placed inside them, then solid phase extraction is used as the extraction method (Schulz et al., 2001). For samplers such as chromatography paper, a more vigorous extraction technique such as ultrasonic extraction may be required (Vischetti et al., 2008). Ultrasonic extraction, also known as ultrasonic assisted extraction (UAE), uses mechanical waves to alter the physical and chemical properties of the sample matrix by cavitation, thus releasing the analyte from the matrix, leading to more contact between the solid and the solvent due to an increase in pressure and transport (Pan et al., 2008). It is carried out using either an ultrasonic probe or an ultrasonic bath, with the latter being more efficient for large scale extraction (Fenoll et al., 2011, Luque-García and Luque de Castro, 2003). The major advantage of the technique over traditional Soxhlet extraction, is the lower consumption of solvent, and shorter time (Babić et al., 1998). However, a drawback of this technique is the need for an additional clean-up step from complex matrices due to its low selectivity (Gonçalves et al., 2018). The technique has been successfully used to extract various pesticides from environmental and food matrices such as soil, animal tissue, sediments, and honey (Tor et al., 2006, Martinez and Barceló, 2001, Rezić et al., 2005). In addition it has been successfully used to extract pesticides from chromatography paper samplers in pesticide deposition monitoring (Vischetti et al., 2008, Nsibande, 2015). Based on its advantages and availability in our laboratory, ultrasonic extraction was used in this study. However, it is worth noting that it may not be the best technique, as several improvements have been made in sample preparation techniques, related to reduction of sample size, amount of solvent, and ease of automation.

2.8 Chemical analysis methods

The chemical analysis method used in deposition monitoring largely depends on the tracer used. For instance, when fluorescent dyes are used, fluorescence spectroscopy is used (Bueno et al., 2017, Longley et al., 1997). Similarly, when metal chelates are used, analytical techniques used vary, although inductively coupled plasma spectroscopy (ICP) is typically employed (Foque et al., 2014). Nowadays with the introduction of active ingredient techniques, the focus has been on chromatographic techniques which can be gas chromatographic (GC) or liquid chromatographic (LC).

Both of these techniques are based on the partitioning of an analyte between a mobile and a stationary phase. Chromatography is a powerful technique for analysing pesticides based on the differences in their physicochemical properties. In this regard, GC is used to analyse non-polar, more volatile pesticides, while the reverse is true for LC (Villaverde et al., 2016). It is worth noting that with GC-based techniques, there may be a need to carry out derivatisation (Domínguez et al., 2016). Based on availability, selective detectors may be employed such as ultraviolet visible (UV-Vis) and diode array detector (DAD) for LC, and nitrogen phosphorus detector (NPD) and electron capture detector (ECD), for GC. A recent trend nowadays is to couple these chromatographic techniques to mass spectrometers which offer better quantitative performance and confirmation of analyte composition.

Both GC-MS and LC-MS have been successfully used in pesticide deposition monitoring (Ravier et al., 2005, Carlsen et al., 2006b, Lefrancq et al., 2013, Zhao et al., 2014). GC-MS was used to successfully determine atrazine and alachlor (Ravier et al., 2005). In a different study, kresoxim methyl was determined using GC-MS/MS (Lefrancq et al., 2013). LC-MS has been used for imidacloprid, pendimethalin, desmedipham, phenmedipham, among other herbicides (Carlsen et al., 2006b, Zhao et al., 2014).

2.9 Statistical evaluation of field deposition results

The quantification of the analyte using chromatographic instruments may have some errors due to changes in the instrument or other factors during the pesticide deposition monitoring process. For this reason, statistical methods are used to provide an estimate of the likely value of the error, and to establish the uncertainty associated with measurement. For instance, with regards to deposition monitoring, the uncertainty in deposited amounts depends on the number of samples, distances between sampling locations, and the choice of interpolation methods (Lefrancq et al., 2013). In addition, there is a need to establish if bias exists in a method or whether two different methods yield similar results, or if one is more accurate or precise than the other. This is accomplished by using various significance tests such as t-tests, one and two-tailed tests, and F-tests. For instance, an independent t-test was used to examine the effect of crop height (crop stage) in an orchard on off-target deposition (Vercruysse et al., 1999). Another statistical technique that has been widely used in pesticide deposition monitoring studies is the analysis of variance (ANOVA) (Caldwell, 2006, Garcerá et al., 2017). Thus, statistical techniques are a vital component of pesticide deposition monitoring studies, as they assist in decision making.

2.10 Quality control

Quality control (QC) refers to the procedures and activities that bring the analytical process under statistical control (Galarini et al., 2017). The quality of analytical data means that it should allow reliable decision making and it should be reliable (Taverniers et al., 2004). For quality data to be obtained during pesticide deposition monitoring, certain QC procedures have to be followed from sampling up to and including the generation of the analytical results. QC procedures may deal with sample handling, collection, and storage and sampling positions. Samples should be transported to the laboratory as fast as possible and analysed in the shortest possible time to reduce the risk of pesticide losses (SANTE/11813/, 2017).

Like any other sampling technique, the reliability of the results depends on the quality control process and major variations may be observed between studies if the procedures followed in sampling of off-target deposition of pesticides are not standardised. Before deposition samplers can be used in the field, analyte extraction recovery and transit stability tests need to be carried out (Glass, 2006). According to the US EPA (2012), recoveries obtained should be between 70 and 120%, and thus most deposition samplers that have been used meet this criteria (USEPA, 2012). If the extraction recoveries obtained meet this criteria, no correction is made for the deposition amounts obtained (Vercruysse et al., 1999). For instance, analyte extraction recoveries of atrazine from stainless steel discs and rods were found to be 111 ±

7.4% (n=9), and 109 ± 3.7% (n=31) respectively (Brain et al., 2019). Extraction recovery tests have also been done for different pesticides on glass microscope slides, with high recoveries of between 74 and 121% being obtained (Carlsen et al., 2006b). Zhao et.al (2014) carried out extraction recovery tests of imidacloprid on glass petri dishes, and recovery rates were between 96.8-98.5% (Zhao et al., 2014). Extraction recoveries of atrazine and alachlor from petri dishes have also been found to be high (>84%) (Ravier et al., 2005). Extraction recoveries of four pesticides (isoproturon, terbuthylazine, metribuzin, and prosulfocarb) were determined from crepe paper, and the recoveries were between 89 and 102% (Epple et al., 2002). Extraction recovery tests of atrazine on chromatography paper were found to be > 100% (Nsibande, 2015), and for chlorpyrifos and metalaxyl were between 90 and 105% (Vischetti et al., 2008, Capri et al., 2005). Despite the importance of carrying out extraction recovery tests prior to sampling, they have been omitted from some studies, where 100% recovery from the sampler was assumed (Lefrancq et al., 2013).

It is imperative to carry out transit stability tests for various pesticides on different samplers, because their physical properties are different, and so are their interactions with the different sampler materials. For instance, when the transit stabilities of epoxiconazole, fenpropimorph, and kresoxim methyl on filter paper were determined, the recovery values were very low for epoxiconazole (27%), and fenpropimorph (17%), but were higher for kresoxim methyl (>88%), thus only deposition values for the latter were reported (Rimmer et al., 2009). Transit stability tests have also been carried out for atrazine, on both stainless steel discs and rods which gave high recoveries of 93%, and 111% respectively, showing that the samples did not degrade over the analysis time of 14 days (Brain et al., 2019).

The use of certified standards of known purity is an important practice in the analytical process. All standard solutions should be refrigerated in tightly closed containers to prevent degradation of pesticides and evaporation of solvent. Stock solutions should be prepared by weighing on an analytical balance with a high accuracy (5 decimal places), followed by dilution in an appropriate solvent (Walorczyk, 2018). Working standard solutions are prepared by further dilution of the stock standard solutions. To check the purity of existing pure standards and stock standard solution, the detector response from the freshly prepared working standard solutions of old and new stock standard solutions may be compared (Avramides, 2005).

Quantification of unknown concentrations of analytes in real samples is carried out using certified analytical standards of known concentrations. Internal standards are used to compensate for fluctuations of the detector response and improve accuracy of quantification. Good internal standards should be stable, and should represent the analytes well in the given chromatographic system. Another practice that is commonly used to compensate for fluctuations of detector response is bracketing calibration, which involves injection of standards before and after the samples.

Chapter 3 Experimental Methods

3.1 Material and reagents

3.1.1 Chemical standards

The atrazine (98.8%, Sigma-Aldrich, St. Louis, MO, USA) and terbuthylazine (98.8%, Sigma-Aldrich, St. Louis, MO, USA) certified reference standards used were of Pestanal® grade. To prepare 100 $\mu g.ml^{-1}$ stock solution of each of the pesticide standards, 2 mg of each pesticide standard was dissolved in 20 ml of acetone: *n*-hexane (1:3 v/v) in a 20 ml vial. A working standard solution of 5 $\mu g.ml^{-1}$ was prepared by adding 200 µl of 100 $\mu g.ml^{-1}$ of the respective pesticide standard to 3800 µl of *n*-hexane solvent in a 4 ml vial. Atrazine-d_5 (99.5%, LGC Standards, Augsburg, Germany) was used as the internal standard for improving the precision when quantifying atrazine and terbuthylazine in the second sampling campaign. It was prepared at a concentration of 0.5 $\mu g.ml^{-1}$ in acetone: *n*-hexane (1:3 v/v). The solutions were stored in a refrigerator away from sunlight and they were used to prepare dilute standard solutions to the required concentrations. The concentration range of the calibration standards is listed in Section 3.2.2.

3.1.2 Solvents

The solvents used in this study were *n*-hexane, dichloromethane, toluene, methanol, acetonitrile, and acetone. All of them were of analytical grade, *n*-hexane (>97.0%), and methanol (>99.5%) were purchased from Sigma-Aldrich (St.Louis, MO, USA). Dichloromethane (>99.5%), acetone (>99.5%), and toluene were purchased from ACE Chemicals (Johannesburg, South Africa). Acetonitrile (>99.5%) was purchased from Merck Chemicals (Darmstadt, Germany).

3.1.3 Pesticide deposition samplers and water sensitive paper

The chromatography paper used for this study was Whatman chromatography paper sheets (20 cm by 15 cm) (GE Grade 2 purchased from Sigma-Aldrich, Germany). The glass petri dishes (10 cm diameter by 1 cm height) and microscope slides (76 mm x 26 mm x 1 mm), were purchased from Lasec (South Africa). The plastic drinking straws (5 mm diameter) were purchased from Pick ‘n Pay, South Africa. Polyacrylic rods (6 mm diameter) were purchased from Maizey Plastics (Pretoria, South Africa). The supplier of the water sensitive paper (26 x 76 mm) was Syngenta (Basel, Switzerland).

3.2 Optimisation of sample preparation method

3.2.1 GC-MS method parameters

An Agilent gas chromatograph (GC) (7890A) with a time-of-flight mass spectrometer (TOF-MS) LECO Pegasus 4D was used for optimisation of the chromatography paper and plastic drinking straw extraction methods. The GC was fitted with an Rxi-5SilMS capillary column (Restek) (30 m x 250 µm internal diameter x 0.25 µm film thickness), and helium (UHP grade, Afrox) was used as a carrier gas at 1 ml.min^{-1} in the constant flow mode. The stationary phase used is of low polarity, and is made up of cross bonded 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane (Restek, 2017). The GC was fitted with an autosampler (Agilent® 7683 ALS), and the injection port temperature was set at 250 ^{0}C. The injection volume was 1 µl, in splitless mode for 30 seconds. MS parameters were as follows: ion source temperature, 230 ^{0}C; electron energy, -70V; detector voltage, 1750 V in the EI+ mode; acquisition rate, 10 spectra.sec^{-1}; and solvent delay 5 min. the MS mass acquisition range was 40-350 Da. The initial oven temperature was set at 60 ^{0}C for 3 min, and then increased to 300 ^{0}C at a rate of 10 ^{0}C.min^{-1}. The total run time was 27 min.

Percentage recovery experiments for the polyacrylic rods, glass microscope slides, and glass petri dishes were continued on an Agilent gas chromatograph (6890) fitted with a mass selective detector (MSD) (5975C). The GC was fitted with an HP-5 5% phenyl 95% PDMS 30 m x 320 μm internal diameter x 0.25 μm film thickness capillary column (Chemetrix, South Africa). Injection was carried out manually, and the injection port temperature was set at 250 ^{0}C. The injection volume was 1 μl in the splitless mode, and the splitless time was 1 min. MS parameters were as follows: MS quadrupole temperature, 150 ^{0}C; MS source temperature, 230 ^{0}C; transfer line temperature, 280 ^{0}C; electron energy, -70 V; electron multiplier voltage, 1750 V in the EI+ mode; scan acquisition rate, 4.51 scans/s; and solvent acquisition delay 5 min. The MS mass acquisition range in the full scan mode was 40-350 Da. For atrazine, the ions monitored in selected ion monitoring mode (SIM) were m/z 173, m/z 200, and m/z 215. In addition, for samples from the second sampling campaign, terbuthylazine was present and the ions monitored were m/z 173, m/z 214, and m/z 229, and for atrazine-d_5 the ions monitored were m/z 178, m/z 205, and m/z 220. The initial oven temperature was set at 60 ^{0}C for three min, and increased to 300 ^{0}C at a rate of 10 ^{0}C.min^{-1}. The total run time was 28 min.

3.2.2 Quantification method

The external standard method of quantification was employed in the first sampling campaign. Atrazine standards in the concentration range of 0.05 μg.ml^{-1} to 5 μg.ml^{-1} were prepared. Calibration curves (n=5) were constructed by plotting response (peak areas) for each concentration of atrazine standard. The results of the linear regression analysis are shown in **Table 4-1**. The quantitative method was based on the selected ion monitoring (SIM) technique in which the most abundant ions of m/z 200 and (m/z) 214 for atrazine and terbuthylazine respectively were used as the quantification ions respectively. For the second sampling campaign, the internal standard method of quantification was employed. Relative response factors of each analyte relative to the atrazine-d_5 internal standard were determined for the calibration standards. To all the standards and the extracts, 0.5 μg.ml^{-1} of internal standard was added. Atrazine and terbuthylazine standards in the concentration ranges of 0.l-10 μg.ml^{-1}, and 1-10 μg.ml^{-1} respectively were prepared. Calibration curves for atrazine (n=7), and terbuthylazine (n=5) were constructed by plotting relative response in terms of peak areas of each analyte relative to atrazine-d_5 internal standard for the calibration standards.

Pesticides in deposition samples were unequivocally identified if the following criteria were met: the retention time of the chromatographic peaks of the most abundant ion for atrazine (m/z 200), and terbuthylazine (m/z 214) from the unknown samples and the external standard coincided at the same retention time and the mass spectrum related to the peak of the deposition samples matched that of the atrazine standard with a mass spectral library (Wiley) match quality of > 70% in full scan mode. Non-exposed field blank samples of each of the different kinds of samplers were treated the same way as the deposition samples. To monitor if there was potential carryover, a solvent blank was periodically injected between runs.

3.2.3 Chromatography paper spiking procedure

The analyte extraction accuracy and precision were determined to establish the efficiency (% recovery), and repeatability (%RSD) of the extraction method. The method used to extract the chromatography paper was one that was previously used by our research group (Nsibande, 2015). Untreated chromatography paper strips (5 cm x 2 cm) were cut from large sheets using a clean scalpel. They were spiked using different concentrations of atrazine standard in *n*-hexane. Each chromatography paper strip was placed in a 20 ml vial (fitted with a thin foil lined cap) and spiked with 50, 25, and 12.5 μl of a 100 μg.ml^{-1} atrazine standard solution, corresponding to a final concentration of 1, 0.5, and 0.25 μg.ml^{-1} respectively when extracted with 5 ml of *n*-hexane. The paper was allowed to dry under ambient conditions, and sonication extraction was done after solvent addition under ambient conditions for 30 min. GC-MS analysis was carried out immediately after extraction. At each of the three different levels of fortification spiking was done in triplicate giving a total of nine fortified matrices. Accuracy (percentage recovery) was calculated using the formula:

Equation 3-1

$$\% \text{ recovery} = \frac{\text{peak area of fortified matrix}}{\text{peak area of atrazine standard}} \times 100\%$$

3.2.4 Plastic drinking straw spiking procedure

Plastic drinking straws were cleaned by wiping them with *n*-hexane before using them for spiking experiments. They were cut to a length of 2 cm using a clean scalpel, and placed in a 20 ml glass vial (fitted with a thin foil lined cap), and spiked with atrazine standard solution of 50, 25, and 12.5 µl of 100 µg.ml^{-1}. After the plastic drinking straws had dried under ambient conditions, 5 ml of *n*-hexane solvent was added, to give spiking concentration levels of 1, 0.5, and 0.25 µg.ml^{-1}. Sonication was done for 30 min under ambient conditions. The extraction procedure was also repeated using different solvents such as acetonitrile: *n*-hexane (1:1 v/v), dichloromethane (DCM), toluene, and acetonitrile: methanol (1:1 v/v). For each of these solvents, spiking was done at three different levels and in triplicate giving a total of nine fortified matrices for each solvent. **Equation 3-1** was used to calculate percentage recovery.

3.2.5 Polyacrylic rod spiking procedure

The first step in the spiking procedure of polyacrylic rods was to perform stability tests by immersing a 6 cm piece of polyacrylic rod in 5 ml of solvent (*n*-hexane, toluene, methanol, acetonitrile, and dichloromethane, respectively), to see in which solvents the rods dissolve. Before the polyacrylic rods were spiked, they were cleaned by wiping them with *n*-hexane. Pieces which were 2 cm long were cut from a metre long polyacrylic rod. The 2 cm long pieces were placed in 20 ml glass vials (fitted with a thin foil lined cap), and spiked with 50, 25, and 12.5 µl of 100 µg.ml^{-1} atrazine standard solution. After they had dried under ambient conditions, 5 ml of *n*-hexane solvent was added, to give spiking concentration levels of 1, 0.5, and 0.25 µg.ml^{-1}. For each concentration, triplicate spikes were made giving a total of nine fortified matrices, and the percentage recovery was calculated using **Equation 3-1**.

3.2.6 Glass petri dish spiking procedure

Glass petri dishes were first cleaned by wiping them with *n*-hexane. They were then spiked with 50, 25, and 12.5 µl of a 100 µg.ml^{-1} solution of atrazine standard, corresponding to a final concentration of 1, 0.5, and 0.25 µg.ml^{-1} respectively. The pesticide was allowed to dry under ambient conditions. Five ml of *n*-hexane was then added, and the solution was transferred to a 20 ml vial, and shaken manually. GC-MS analysis was carried out immediately after extraction. For each concentration, triplicate spikes were made; giving a total of nine fortified matrices, and **Equation 3-1** was used to calculate the percentage recovery.

3.2.7 Glass microscope slide spiking procedure

Glass microscope slides were cleaned by wiping them with *n*-hexane. They were then placed in a clean 100 ml glass beaker and spiked with 50, 25, and 12.5 µl of 100 µg.ml^{-1} atrazine standard solution. After they had dried under ambient conditions, 5 ml of *n*-hexane solvent was added, to give spiking concentration levels of 1, 0.5 and 0.25 µg.ml^{-1}. The beaker was shaken briefly, and the solution was transferred immediately to a 20 ml glass vial. The extraction technique was optimized by testing different solvents such as *n*-hexane, acetonitrile: *n*-hexane (1:1 v/v), dichloromethane (DCM), and toluene, acetonitrile: methanol (1:1 v/v). GC-MS analysis was done after extraction. For each extraction spiking was done at three different levels was done in triplicate giving a total of nine fortified matrices. To calculate percentage recovery **Equation 3-1** was used.

3.3 First atrazine spray deposition monitoring campaign

A spray deposition monitoring campaign was conducted on a commercial farm during ground application of atrazine in order to compare different deposition samplers under local conditions. During this campaign, chromatography paper, glass petri dishes, glass microscope slides, and polyacrylic rods were compared. This section presents the experimental details of the sampling campaign, during which a total of 75 downwind samplers were placed outside the field in order to collect pesticides deposited, and 5 upwind samplers were placed outside the field to establish a background value. Details of additional input parameter values required by the AgDISP model were also collected. Data analysis is described in Section 3.3.6.

3.3.1 Study area

The atrazine spray deposition monitoring campaign was conducted on the 18th of July 2018 during spraying of a ± 1.5 ha uncultivated field in Ogies, Mpumalanga (South Africa) and the meteorological conditions are described in Section 3.3.2. The GPS coordinates of the area are 26^0 01’ 50.9’’S, 28^0 53’ 21.8”E (downwind samples), and 26^0 01’ 53.7”S 28^0 53’ 32.9’’E (upwind samples). A John Deere 4630 “Hiboy” ground sprayer (**Figure 3-1**) was employed, which was fitted with 48 twin air reduction nozzles, with a 1.94 extra coarse (xc) droplet classification, which were uniformly distributed along a 24 m boom. The pesticide concentrate (Terbusien Super 600 SC, Villa Crop Protection) contained atrazine (291 $g.L^{-1}$), terbuthylazine (291 $g.L^{-1}$), and other related active triazines (18 $g.L^{-1}$). Spraying was done at a height of 1 m above the ground, for 10 min at a speed of 12 $km.h^{-1}$.

Figure 3-1: 4630 “Hiboy” ground sprayer showing 24 m boom.

3.3.2 Meteorological conditions

Meteorological conditions were monitored throughout the application and sampling period using a Kestrel 4500 portable weather station (Envirocon, South Africa).

3.3.3 Sample collection

Downwind samplers were distributed downwind of the application region, and another set of samplers was placed upwind, as shown in **Figure 3-2**. At sampling distances from 0 to 50 m, there were three sampling lines which were labelled as A (left), B (middle), and C (right). The distance between each of the sampling lines was 5 m. The samplers used were placed adjacent to each other at each sampling station as shown in **Figure 3-3**. All samplers were mounted on wooden stands at a height of 20 cm above ground level. Collection of samples began 30 min after spraying, starting with the ones furthest from the spraying area in order to minimise cross contamination. The samples were transported to the laboratory in cooler boxes, where they were refrigerated at a temperature of -18 ^{0}C prior to analysis.

Each set of samplers comprised of two 20 cm by 15 cm pieces of Whatman™ chromatography paper which were used without prior treatment, and one was oriented horizontally, and the other was oriented vertically as shown in **Figure 3-3**. Regardless of its orientation, each piece of chromatography paper was placed on an aluminium foil covered stand and was held in place with fold back clips. After spraying, the paper was collected and stored in plastic zip lock bags that were marked according to sample location, and stored in cooler boxes for transportation to the laboratory.

Polyacrylic rods of length 10 cm were used to measure vertical deposition. Before sampling, they were treated by wiping them with *n*-hexane. They were mounted onto a wooden stand with a hole drilled at the centre. The rods were collected, and stored in plastic zip lock bags that were labelled according to sample location. The plastic zip lock bags were placed in cooler boxes, and transported to the laboratory for analysis.

The glass microscope slides used to measure horizontal deposition were treated by wiping them with *n*-hexane before use. They were mounted onto a plastic stand in sets of four, and were secured using foldback clips (**Figure 3-3**). After sampling, they were removed from the stands starting with the ones furthest from the spray area. They were stored in microscope slide holders with slots labelled according to each sample name. In each slot there were two microscope glass slides, one used for sampling and another that was not used, in order to serve as a cover to minimise loss of analyte.

The glass petri dishes used to measure horizontal deposition were treated before use by wiping them with *n*-hexane. They were mounted onto a plastic stand and secured using adhesive tape (**Figure 3-3**). After sampling, they were removed from the stands and closed using the glass lids, and then the glass petri dish and its lid were secured using adhesive tape, after which they were placed in plastic zip lock bags labelled according to sampling location. The plastic zip lock bags containing the glass petri dishes were transported to the laboratory in cooler boxes and stored in the freezer at a temperature of -18 ^{0}C prior to analysis.

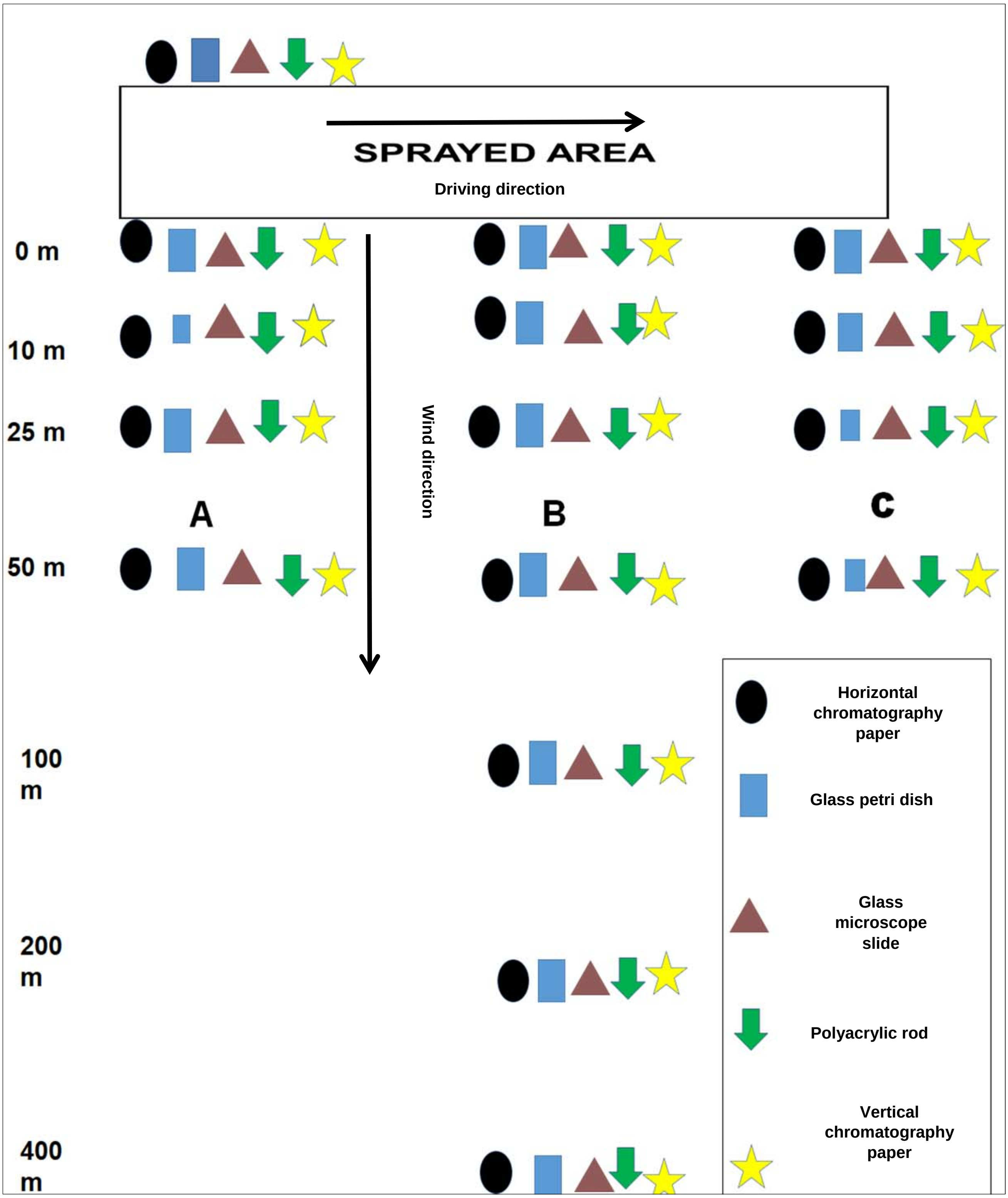

Figure 3-2: Layout of samplers in the field in the first sampling campaign. One set of samplers was placed upwind for control purposes.

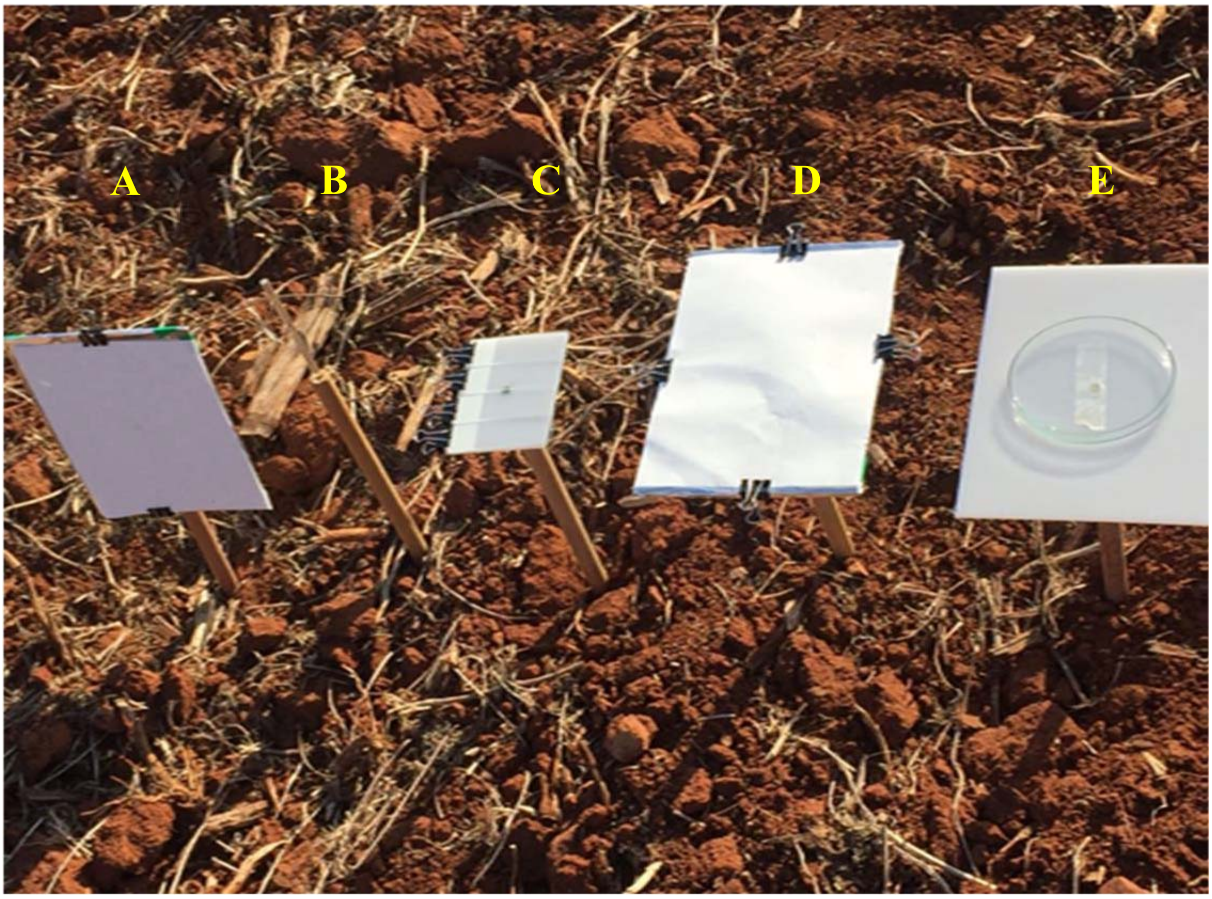

Figure 3-3: Deposition samplers employed from left to right vertical filter paper (A), polyacrylic rod (B), microscope slides (C), horizontal filter paper (D), and petri dish (E).

3.3.4 Extraction and analysis of samples

Deposition samplers were extracted using the previously optimized methods. To extract the chromatography paper samples, a 5 cm x 2 cm piece was cut from the middle of each chromatography paper sampler using a scalpel (cleaned with *n*-hexane between samples) and was placed in a 20 ml vial. Extraction was done with 5 ml of *n*-hexane in an ultrasonic bath for 30 min. The extracts were evaporated to dryness using nitrogen gas, and reconstituted was done using 1 ml of *n*-hexane. Polyacrylic rods were extracted by first cutting a 2 cm piece from the 10 cm rod sampler using a hacksaw (cleaned with *n*-hexane between samples), placed in a 20 ml vial and extracted using 5 ml of *n*-hexane for 30 min using an ultrasonic bath. The extracts were evaporated to dryness using nitrogen gas and reconstituted to 1 ml in *n*-hexane. Glass microscope slides were extracted by placing both the exposed and non-exposed slides from each sampling location in a 100 ml glass beaker and shaking them with 5 ml of *n*-hexane. The extracts were transferred to a 20 ml vial, followed by evaporation to dryness using nitrogen gas. Reconstitution was done using 1 ml of *n*-hexane. Glass petri dishes were extracted by washing both the lid and the petri dish itself with a total of 5 ml of *n*-hexane. The extracts were transferred to a 20 ml vial followed by evaporation to dryness using nitrogen gas. The extracts were reconstituted in 1 ml of *n*-hexane. The amount of atrazine that deposited on each deposition sampler (µg.cm^{-2}) was calculated using the following equation:

Equation 3-2

$$\mu g.cm^{-2}\ of\ pesticide\ deposited = \frac{ng.\mu l^{-1} found \times final\ volume\ (\mu l)}{area\ of\ deposition\ sampler\ (cm^{2}) \times 1000}$$

Where ng.µl^{-1} found = transcribed from the calibration curve; Final volume= extraction solvent used (µl), and 1000 is the conversion factor from ng to µg.

3.3.5 Modelling of spray deposition using AgDISP

The AgDISP model (v8.27) was used to predict off-target deposition of atrazine. The model's predictions are based on a set of parameters which must be consistent with those under which pesticide application was carried out. The parameters can be broadly classified as equipment conditions, nozzles, droplet size distribution (DSD), spray material properties, and ambient meteorology. These are summarised in **Table 3-1**. To determine the droplet size distribution (DSD), the nozzle diameter which was obtained from the farmer was used. According to the manufacturer of the tractor, the droplet sizes for this type of nozzle are classified using American Society of Agricultural and Biological Engineers (ASABE classification). There are other default values that were left unchanged such as the evaporation rate. This is because previous studies showed that agrochemicals in water based carriers behave approximately the same way as water in terms of evaporation (Hewitt et al., 2002, Nsibande et al., 2015).

Table 3-1: AgDISP input parameters for sampling campaigns 1 and 2.

Parameter	**Input**	
	1st sampling campaign	**2nd sampling campaign**
Application method	Ground sprayer	Ground sprayer
Boom pressure (bar)	2	2
Number of nozzles	48	54
Nozzle type	Air injection	Air injection
Nozzle interdistance (mm)	500	500
DSD	1.94 extra coarse (XC) drop size (ASABE classification)	User defined
Release height (m)	1	0.3
Spray lines	15	1
Swath width (m)	24	27
Swath displacement (m)	0	0
Wind speed ($m.s^{-1}$)	1.90	2.5
Wind direction (^{0})	-90	26.4 from North West
Temperature (^{0}C)	16.8	26.1
Spray material evaporates	Yes	Yes
Spray volume rate ($L.Ha^{-1}$)	200	200
Active fraction	0.003	0.003
Active fraction of tank mix	0.003	0.003
Evaporation rate ($\mu m^{2}\,{}^{0}C^{-1}\,s^{-1}$)	84.76	84.76
Canopy height (cm)	none	50

DSD- Droplet size distribution, ASABE- American Society of Agricultural and Biological Engineers.

3.3.6 Data analysis

Due to the small number of data points, a normal distribution was assumed. An F-test compares two experimentally observed variances, s_a^2 and s_b^2. Since variances are squared standard deviations, it may also be used to compare standard deviations. This is useful for comparing the precision of analytical methods to see if one is significantly better than the other. The F-test was carried out to compare the sample variances between two samplers of the same orientation but with different materials of construction at each sampling point for all distances where positive results were obtained. The null hypothesis, H_0 and alternative hypothesis, H_1 were stated as:

H_0: there is no significant difference between the variances of the horizontal chromatography paper and those of the glass petri dish.

H_1: there is a significant difference between the variances of the horizontal chromatography paper and the glass petri dish.

The F-test was also used to determine if the variances between the vertical chromatography paper and the polyacrylic rods were significant.

The null hypothesis H_0 was stated as H_0: there is no significant difference between the variances of the vertical chromatography paper and those of the polyacrylic rods.

H_1: there is a significant difference between the variances of the vertical chromatography paper and the polyacrylic rods.

For the two-tailed F-test, the calculation is arranged so that the value of F is always greater than 1.0. The test statistic, F_{calc} is calculated as

$$F_{calc} = \frac{s_{max}^2}{S_{min}^2}$$

Where s^2_{max} is the larger variance and s^2_{nin} is the smaller variance. The significance level for the test is α= 0.05. However, this is a two-tailed test; the correct critical value is obtained from the tables for α/2=0.025. F_{calc} is compared with F_{crit} (=$f_{DF;0.05}$) where DF= degrees of freedom= n-1. If $F_{calc} < F_{crit}$, H_0 cannot be rejected and if $F_{calc} > F_{crit}$, H_0 is rejected and H_1 is accepted.

A paired t-test is used to compare two methods of analysis by studying test samples containing different amounts of analyte. If $t_{calc} < t_{crit}$, H_0 cannot be rejected, and if $t_{calc} > t_{crit}$, H_0 is rejected and H_1 is accepted. The paired t-test was carried out since we have samplers constructed from different materials. The same techniques were applied to compare the experimental outcome from the field deposition results to the results obtained by AgDISP simulation. The null and alternative hypotheses were stated as follows:

$H_{0:}\mu_d = 0$*, meaning that there is no significant difference between the means obtained for the vertical chromatography paper and the polyacrylic rod.*

$H_1{:}\mu_d \neq 0$*, meaning that there is a significant difference between the means obtained for the vertical chromatography paper and the polyacrylic rods.*

$H_{0:}\mu_d = 0$*, meaning that there is no significant difference between the means obtained for the horizontal chromatography paper and the glass petri dish.*

$H_1{:}\mu_d \neq 0$*, meaning that there is a significant difference between the means obtained for the horizontal chromatography paper and the glass petri dish.*

$H_{0:}\mu_d = 0$*, meaning that there is no significant difference between the experimental means obtained for the field deposition and AgDISP modelled results.*

$H_1{:}\mu_d \neq 0$*, meaning that there is a significant difference between the experimental means obtained for the field deposition and AgDISP modelled results.*

$$T_{calc} = \frac{\bar{x}_{d\sqrt{n}}}{S_d}$$

Where *d = difference between each pair of results given by the two methods*

$\bar{x}_d$ = *mean of the different samples*

S_d = *standard deviation of the differences*

T_{calc} is compared with t_{crit} (=$t_{DF;0.05}$) where DF= degrees of freedom= n-1. If $t_{calc} < t_{crit}$, H_0 cannot be rejected and if $t_{calc} > t_{crit}$, H_0 is rejected and H_1 is accepted.

3.4 Second spray deposition monitoring campaign

A spray deposition monitoring campaign was conducted on a commercial farm (Section 3.4.1) during ground application of atrazine in order to validate the chromatography paper as the best deposition samplers for atrazine (and terbuthylazine when present in the formulation) under local conditions. In addition, the purpose of the second sampling campaign was done under improved sample storage conditions to maximise the amount of deposition retained on and extracted from the chromatography paper. This section presents the experimental details of the sampling campaign, during which a total of 22 downwind samplers were placed outside the spray area in order to collect pesticides deposited, one sampler placed inside the spray area and 2 upwind samplers were placed upwind of the spray area to establish a background value. Details of the additional input parameter values required by the AgDISP model were also collected. Data analysis is also described in Section 3.4.7.

3.4.1 Study area

The second spray deposition monitoring campaign was conducted to validate the chromatography paper as the best sampler, and to further compare the sampling efficiencies in both the horizontal and vertical orientation. The study was conducted at Rossgro Estates, in Delmas, Mpumalanga, South Africa on the 24^{th} of January 2019. The GPS coordinates of the area are S 26^0 8’ 44.628’’ E 28^0 37’ 55.178’’ (downwind samples), and N 26^0 8’ 44.855’’ E 28^0 37’ 19.452’’ (upwind samples). A John Deere R4023 ground sprayer was employed, which was fitted with 54 nozzles, which were uniformly distributed along a 27 m boom. The pesticide concentrate (Terbusien Super 600SC, Villa Crop Protection) contained atrazine (291 $g.L^{-1}$), terbuthylazine (291 $g.L^{-1}$), and other related active triazines (18 $g.L^{-1}$). Spraying was done at a height of 0.9 m above the ground, for one minute, at a speed of 13 $km.h^{-1}$.

3.4.2 Meteorological conditions

Meteorological conditions were monitored throughout the application and sampling period using a Kestrel 4500 portable weather station (Envirocon, South Africa).

3.4.3 Sample collection

Downwind samplers were distributed downwind of the application region, and another set of samplers was placed upwind, as shown in **Figure 3-4**. At sampling distances from 0 to 50 m there were three sampling lines which were labelled as A (left), B (middle), and C (right). The distance between the sampling lines was 5 m. The samplers used were placed adjacent to each other at each sampling station as shown in **Figure 3-5**. Each set of samplers comprised of two 20 cm by 15 cm pieces of Whatman™ chromatography which were used without prior treatment, and one was oriented horizontally, and the other was oriented vertically. Regardless of its orientation, each piece of chromatography paper was placed on an aluminium foil covered stand and was held in place with fold back clips. All samplers were mounted on wooden stands at a height of 20 cm above ground level. Collection of samples began 30 min after spraying, starting with the ones furthest from the spraying area in order to minimize cross contamination. After spraying, the paper was collected and stored in 50 ml Schott bottles fitted with aluminium foil on the inside of the lid (**Figure 3-6 (a)-(c)).** These were marked according to sampling location and stored in a cooler box for transportation to the laboratory. The samples were transported to the laboratory in the cooler box as shown by **Figure 3-6 (d)**, where they were stored in a freezer at a temperature of -18 ^{0}C prior to analysis.

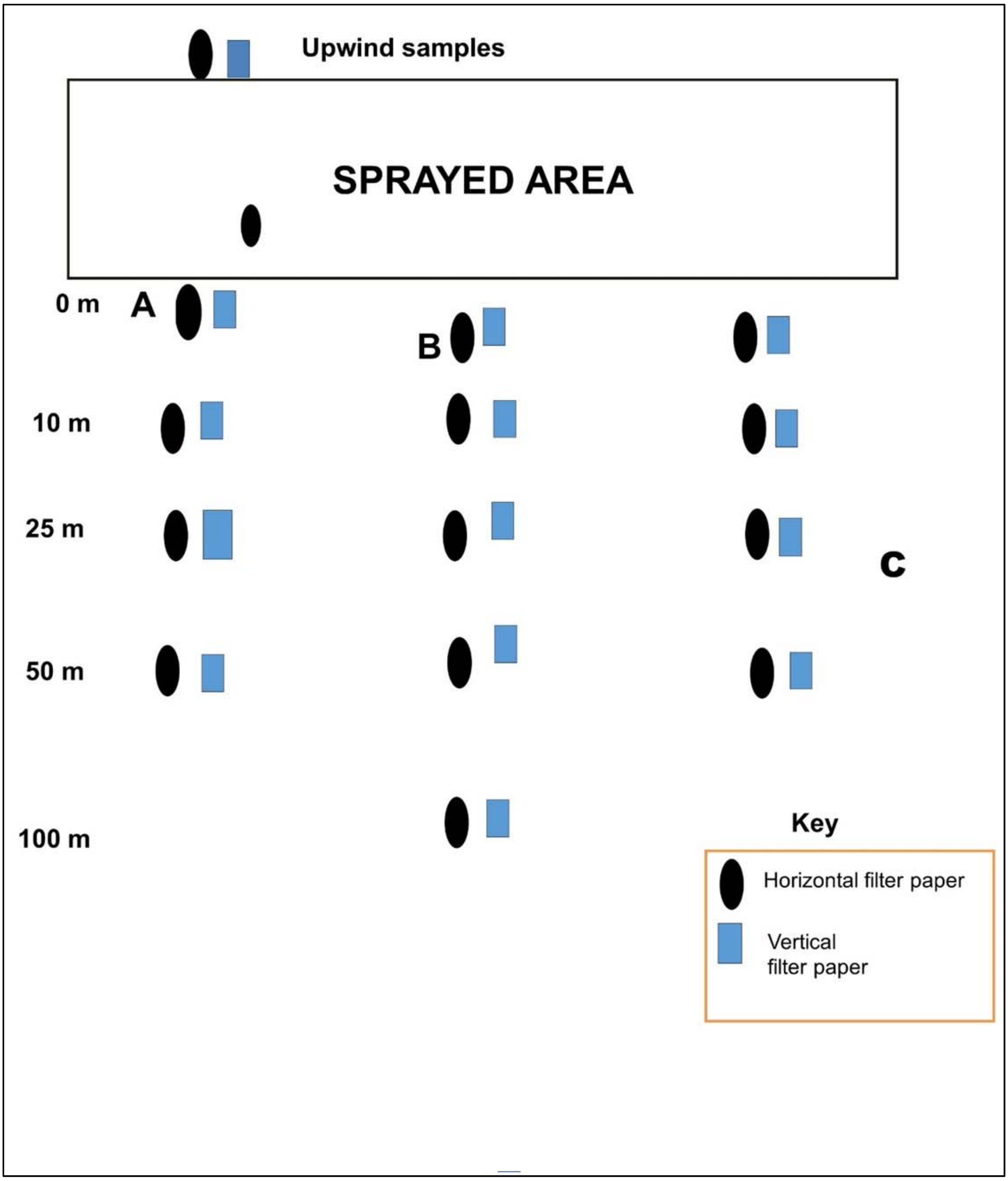

Figure 3-4: Layout of samplers in the field in the second sampling campaign. One set of samplers was placed upwind for control purposes.

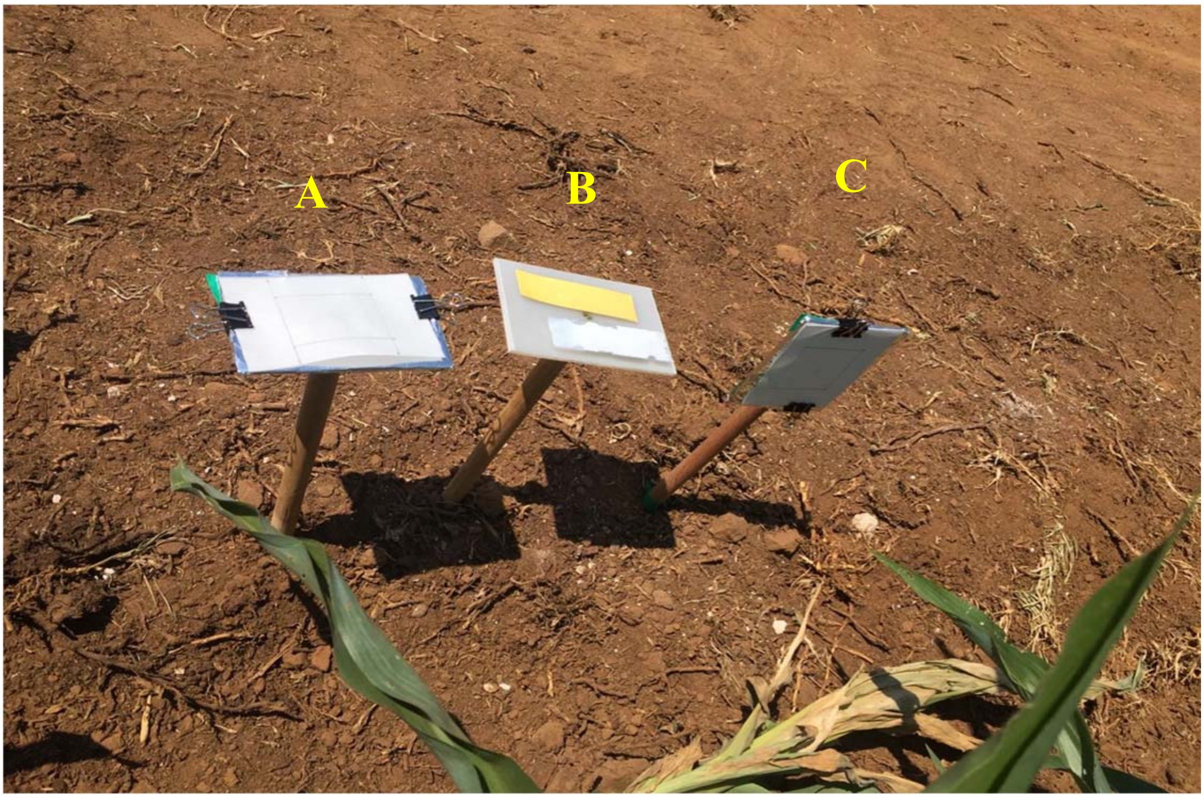

Figure 3-5: Deposition samplers employed from left to right horizontal chromatography (A), water sensitive paper (B), vertical chromatography paper (C).

Figure 3-6: (a) A 5 cm x 2 cm piece being cut from the middle of each chromatography paper sheet using a scalpel; (b) the 5 cm x 2 cm piece being separated from the rest of the chromatography paper; (c) the 5 cm x 2 cm chromatography paper inside a 50 ml Schott bottle covered with aluminium foil on top; (d) Schott bottles containing 5 cm by 2 cm chromatography paper pieces in a cooler box, awaiting transportation to the laboratory.

3.4.4 Extraction and analysis of samples

On arrival at the laboratory, 5 ml of *n*-hexane was added to each 50 ml Schott bottle where the cut 5 cm x 2 cm chromatography paper pieces had been placed. All samples were stored in a freezer, awaiting analysis at a temperature of -18 ^{0}C. Extraction was done in an ultrasonic bath for 30 min. The extracts from samples upwind, field blanks, and downwind samples at 30, 50, and 100 m were evaporated using nitrogen gas to dryness, and 100 µl of 5 $\mu g.ml^{-1}$ (giving a concentration of internal standard of 0.5 $\mu g.ml^{-1}$) was added to the Schott bottle and 900 µl of *n*-hexane added to make the total volume 1 ml. For the samples in the spray area and those at 0 m from the spray area, they were diluted by adding 2 ml of 5 $\mu g.ml^{-1}$ of atrazine-d_5, followed by an additional 13 ml of *n*-hexane added to the initial 5 ml of *n*-hexane to make a total volume of 20 ml (they were 20x more dilute than other samples). To the samples at 10 m downwind of the spray area, they were diluted by adding 1 ml of atrazine-d_5 followed by an additional 4 ml of *n*-hexane added to the initial 5 ml of *n*-hexane to make the total volume 10 ml. The concentration of atrazine-d_5 was maintained at 0.5 $\mu g.ml^{-1}$ for all extracts. Analysis of the samples was done on a GC-MSD using the parameters described in Section 3.2.1. The amounts of atrazine and terbuthylazine deposited on the deposition samplers were calculated using **Equation 3.2.**

3.4.5 Droplet size distribution

To determine the droplet size distribution (DSD) of the spray, water sensitive paper was used. The water sensitive paper is a rigid paper with a yellow surface coated with bromophenol blue which stains dark blue by droplets impinging on it as its pH changes from approximately 2.8 to 4.6 (Syngenta, 2019, Kira et al., 2018, Sies et al., 2017). The water sensitive paper was placed on plastic stands 20 cm above ground level, and adjacent to the samplers at distances of 0, 10, and 30 m to capture droplets during spray application. They were then marked according to the distance where it was placed and stored in an envelope and later analysed using an image analyser.

A Samsung J200 core smartphone was used to take images of the water sensitive paper, and transfer them to a computer. The resolution of the phone was 540 x 960 pixels. Droplet size on the water sensitive paper was measured using ImageJ software (version 1.80). However, overlap of some droplets occurred due to the high air pressure of the nozzles (Sayinci et al., 2012). Thus, elimination of unsuitable spots on the image was necessary to ensure a good result. Overlapping and non-circular spots were eliminated manually using GIMP 2.4 image manipulation software. The remaining spots were evaluated for their droplet characteristics using ImageJ software. The data was transferred to MS excel to determine the droplet sizes using specific equations. To determine the actual droplet diameter from the diameter of the spot **Equation 3-3** was used (Sayinci et al., 2012):

Equation 3-3

$$d = 0.95{d_s}^{0.910}$$

Where d is the actual diameter of the droplet, and d_s is the spot diameter.

To get the spot diameter d_s, **Equation 3-4** was used (Sayinci et al., 2012):

Equation 3-4

$$d_s = \sqrt{\frac{4A}{\pi}}$$

Where A is the area of the spot

Equation 3-5 was used to calculate the droplet diameter values that are shown in **Table 4.11** **(**Sayinci et al., 2012)**:**

Equation 3-5

$$d = 1.06A^{0.455}$$

3.4.6 Modelling of spray deposition using AgDISP

Using the AgDISP model (v8.27) off-target deposition of atrazine (and terbuthylazine when present in the formulation) was predicted. The parameters are listed in **Table 3.1**. Using the droplet sizes obtained in Section 3.4.5, modelling was done using the same method described in Section 3.3.5.

3.4.7 Data analysis

Due to the small number of data points, a normal distribution was assumed. An F-test was carried out to compare the sample variances between two samplers of different orientation at each sampling distance where positive results were obtained. The null hypothesis, H_0 was stated as:

H_0: there is no significant difference between the variances of the horizontal chromatography paper and those of the vertical chromatography paper.

H_1: there is a significant difference between the variances of the horizontal and vertical chromatography paper.

To compare the results from the AgDISP model with those from the pesticide deposition monitoring study, the paired t-test was applied.

Depending on the outcome, a paired t-test was carried out to further compare the means of the samples. The null hypothesis, H_0 was stated as:

H_0: there is no significant difference between the means of the horizontal chromatography paper and those of the vertical chromatography paper.

H_1: there is a significant difference between the means of the horizontal and vertical chromatography paper.

The same techniques were applied to compare the experimental outcome from the field deposition results to the results obtained by AgDISP simulation. The null and alternative hypotheses were stated as:

H_0: $\mu_d = 0$, meaning that there is no significant difference between the means of the modelled deposition data, and the experimental deposition data.

The alternative hypothesis, H_1 was stated as:

H_1: $\mu \neq 0$, there is a significant difference between the means of the modelled and experimental deposition data.

Chapter 4 Results and Discussion

4.1 Analytical method validation

Quantitation of samples from the first sampling campaign was carried out using the external standard method. The off-target deposition samples were quantified using the linear equations in **Table 4-1**. In the linear equation which is y=mx+c, y represents the response peak area from the analytical instrument, and x represents the amount of atrazine (µg.ml^{-1}), m is the slope of the line, and c is the intercept. Excellent linearity was observed in the concentration range of 0.08-1.0 µg.ml^{-1}. The limit of detection (LOD) was defined as that concentration which gave a signal to noise ratio of 3, and the limit of quantification (LOQ) is defined as that concentration which gave a signal to noise ratio of 10. **Table 4-1** summarises the LOD and LOQ values obtained when analysing samples from the first and second sampling campaign. Limits of detection for both atrazine and terbuthylazine were in the range of 0.006-0.0159 µg.ml^{-1}. Limits of quantitation for atrazine and terbuthylazine ranged from 0.02-0.0529 µg.ml^{-1}. The instrumental method displayed good repeatability as shown by the between-run precision (expressed as percentage relative standard deviation (%RSD) of 6.9% RSD as determined with a 1 µg.ml^{-1} atrazine standard (n=6) (**Table 4-2**). For the second sampling campaign, the internal standard method was used for quantitation. The off-target deposition samples were quantified using linear equations in **Table 4-1**. In the linear equation, y represents the ratio of the peak response of the analytical standard of the pesticide to that of the internal standard and x represents the concentration of the pesticide (µg.ml^{-1}). Atrazine-d$_5$ was added as an internal standard to the extracts to increase analytical accuracy. The precision of the method (**Table 4-2**) was 8.2 %RSD for terbuthylazine peak area relative to the peak area of the internal standard. The precision of atrazine in terms of %RSD was 6.9 and 2.4 for the first and second sampling campaign respectively. For all the calibration curves, excellent linearity was observed with R^2 values greater than 0.99. However, it is worth noting that on comparison, the external standard method gave lower detection and quantification limits relative to the internal standard method (**Table 4-1**).

During the initial stages of this research it had been decided to have both atrazine and terbuthylazine as the primary analytes of interest. However, that idea was abandoned, when it was observed that the response of terbuthylazine on the GC-TOFMS was very low at a concentration of 1 µg.ml^{-1}. However, the instrument showed excellent selectivity as both peaks were resolved (**Figure 4-1**).

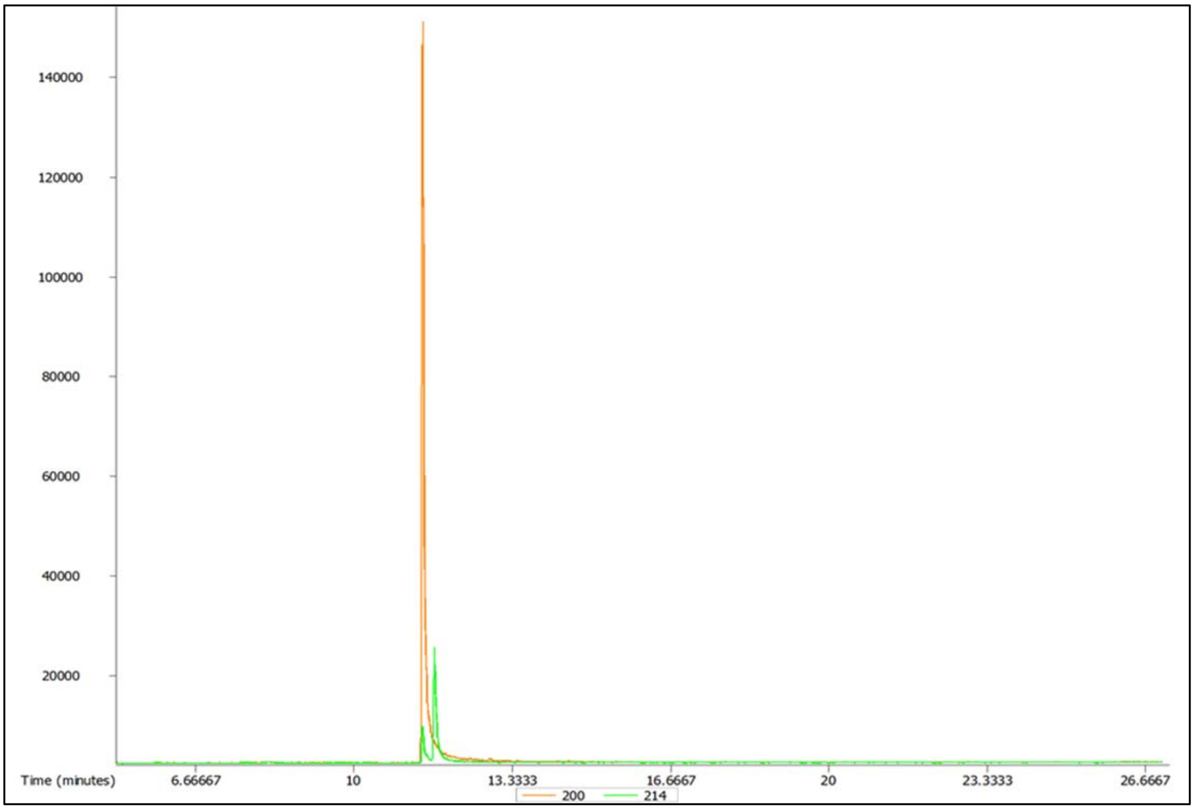

Figure 4-1: Reconstructed ion chromatogram of atrazine (200 Da) and terbuthylazine (214 Da) at a concentration of 1 µg.ml^{-1} analysed by GC-TOFMS

Table 4-1: Linear regression analysis of atrazine and terbuthylazine by GC-MSD.

Calibration curve	**Quantification ion (m/z)**	**[a] Regression equation y=mx+c**	**R^2**	**[b]LOD (µg.ml $^{-1}$)**	**[c]LOQ (µg.ml^{-1})**	**Samples analysed using this equation**
1 (external method of calibration)	200 (Atrazine)	y=112327x-2480.3	0.999	0.006	0.02	All samples from the 1st sampling campaign
2 (internal standard method of calibration)	200 (Atrazine)	y=0.8422x+0.0976	0.993	0.01	0.04	All samples from 2nd sampling campaign
3 (internal standard method of calibration)	214 (Terbuthylazine)	y=1.2775x-0.6112	0.994	0.02	0.05	All samples from 2nd sampling campaign

[a]m = gradient of line, c = intercept, [b] LOD was calculated as that concentration which gave a signal to noise ratio (S/N) of 3, [c] LOQ was calculated as that concentration which gave a signal to noise ratio of 10

Table 4-2: GC-MSD instrument precision using 1µg.ml^{-1} atrazine and terbuthylazine

Between-run precision			
Injection	Atrazine peak area (1st sampling campaign)	Atrazine peak area/internal standard peak area ratio (2nd sampling campaign)	Terbuthylazine peak area/Internal standard peak area ratio (2nd sampling campaign)
1	134472	1.02	1.10
2	136411	0.98	1.23
3	142096	1.00	1.05
4	123032	1.05	1.13
5	126336	1.03	1.08
6	118630	1.00	0.96
mean±σ	130163±8928	1.01±0.025	1.09±0.089
%RSD	6.9	2.4	8.2

σ is the standard deviation of the mean

4.2 Optimisation of the sample extraction method

The extraction method (atrazine) for plastic drinking straws was optimised according to solvent type, and the analyses were done by GC-MSD. Toluene, acetonitrile, methanol, dichloromethane, and *n*-hexane were compared. Of all the solvents, *n*-hexane gave the highest recoveries (>40%), although they were not good enough for practical implementation, as shown in **Figure 4-2.** This might have been because atrazine was not easily desorbed from the surface of the straws, especially by the more polar solvents. For this reason, the use of plastic drinking straws was discontinued for this particular study, and polyacrylic rods were used instead (Topp and Smith, 1992).

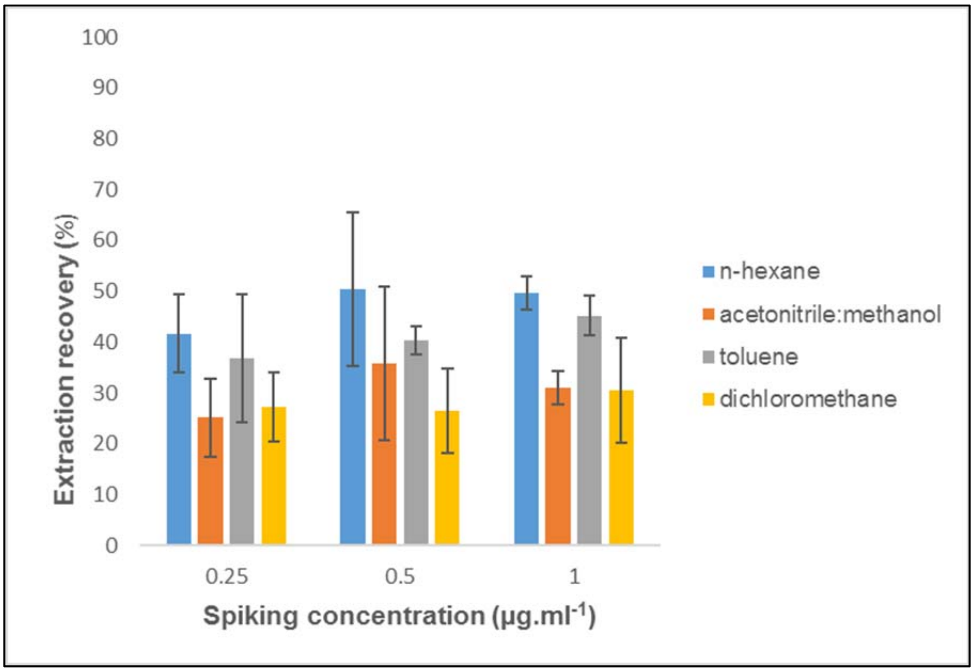

Figure 4-2: Extraction recovery (%) of atrazine from plastic drinking straws using different solvents (at three concentration levels. n=3). Error bars show ± standard deviation.

With polyacrylic rods, the choice of extracting solvent was made by immersing pieces of the rod in toluene, acetonitrile, methanol, dichloromethane, and *n*-hexane. In all of the solvents except for *n*-hexane, the polyacrylic rods dissolved, thus, *n*-hexane was chosen as the extracting solvent. In addition, *n*-hexane gave good extraction recoveries of atrazine for glass microscope slides, as compared to acetonitrile, methanol, and dichloromethane (**Figure 4-3**). Hence *n*-hexane was used as the extraction solvent for glass petri dishes as well, giving good recoveries. Excellent recoveries (>80%) were obtained for chromatography paper at concentrations of 0.25, 0.5, and 1 μg.ml^{-1}, with *n*-hexane extraction (**Figure 4.4**). Polyacrylic rods also showed very good recoveries (>75%) as did glass microscope slides and petri dishes, though they were not as high as those for chromatography paper and polyacrylic rods **(Figure 4-4**). The overall recovery mean, standard deviation, and relative standard deviation (RSD) for extraction recoveries for all the fortified deposition samplers were within the US.EPA guidelines for environmental chemistry methods (ECM) of 70-120% for mean recovery at each spiking level with RSD≤ 20% (USEPA, 2012). For all the samplers, high recoveries (>70%) (chromatography paper, glass microscope slides, glass petri dishes, polyacrylic rods) were obtained for atrazine using the GC-MSD method described in Section 3.2.1, therefore the field samples were not corrected for method recovery (Ratola et al., 2014).

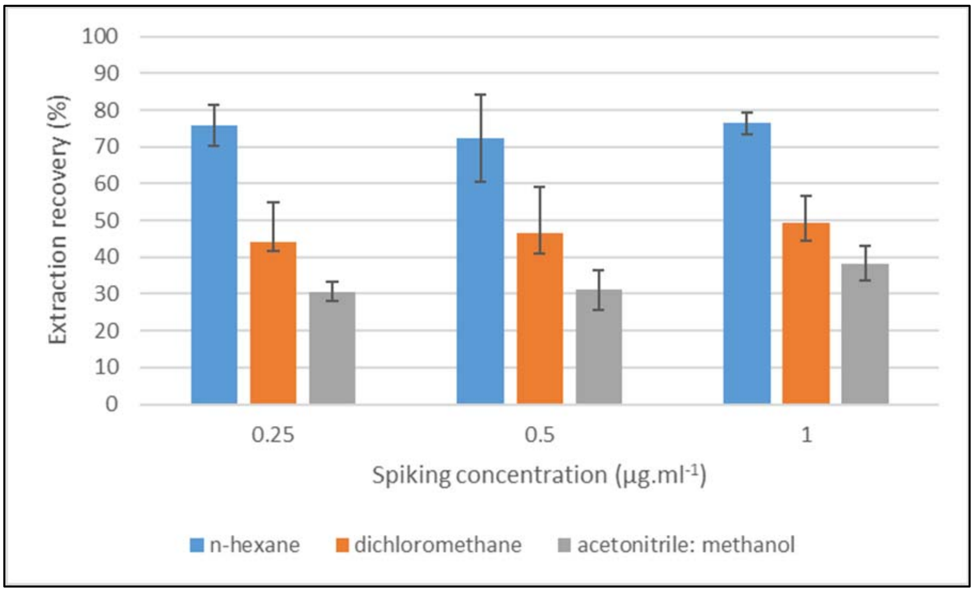

Figure 4-3: Optimisation of extraction technique for glass slides using different solvents at three concentration levels (n=3) using atrazine. Error bars represent ± standard deviation.

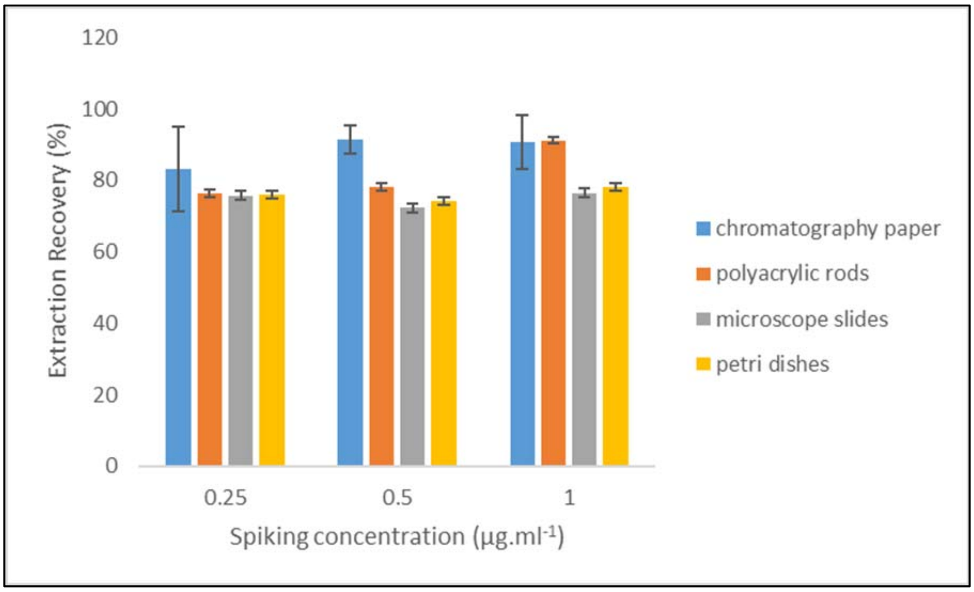

Figure 4-4: Comparison of extraction recoveries (%) of atrazine for chromatography paper, polyacrylic rods, glass microscope slides, and glass petri dishes in *n*-hexane at three concentration levels (n=3). Error bars represent ± standard deviation.

4.3 First sampling campaign

4.3.1 Field deposition results

The average wind speed for the first sampling campaign was measured at a height of 20 cm above ground level and the average wind speed was 1.9 m.s^{-1}. The wind direction shifted from north to north east, and the ambient temperature was 16.8 ^{0}C.

All samples that were transported to the laboratory from the field sampling were analysed by GC-MSD. The calibration curves that were used for quantification of deposition samples are given in **Table 4-1**. The method showed good linearity within the measured range of concentrations 0.08-1 µg.ml^{-1}.

During this sampling campaign, a general trend observed was that deposition values obtained were very low, and these results are shown in **Table 4-3**. The low deposition values may be explained by the fact that drift reducing nozzles were used to spray the crop. This is in contrast to a previous study carried out by our research group where much higher deposition values were obtained as a result of use of a flat fan nozzle (Nsibande, 2015). Flat fan nozzles produce fine droplets with high velocities, whereas, the drift reducing nozzles used in this particular study produced extra coarse droplets that have a high tendency of sedimenting, and have high inertia (Nuyttens et al., 2007). The trend in deposition amongst the different collectors was that chromatography paper, regardless of orientation, collected more atrazine relative to the other collectors. This is in agreement with a previous study that was carried out, where chromatography paper was proven to be a good deposition sampler because of its ability to protect the pesticide from photodegradation and volatilisation (Capri et al., 2005). This behaviour can be attributed to the material of construction of the chromatography paper, where the Whatman chromatography paper used in this study is made from pure cellulose. Although its interaction with atrazine is not well understood, there is a possibility that hydrogen bonds may be the dominant force of attraction between the paper and the pesticide since they both contain polar functional groups.

Table 4-3 Atrazine mean (n=3) deposition results from analysis of chromatography paper, glass microscope slides, glass petri dishes, and polyacrylic rods by GC-MSD. The peak area of atrazine (m/z 200) was used for quantitation (R^2= 0.9996, LOD=0.006 µg.ml $^{-1}$, LOQ=0.02 µg.ml $^{-1}$).

Sample location	**Sample name**	**Peak area**	**Concentration (ng.µL^{-1})**	**Concentration (pg.µL^{-1})**	**Final volume (mL)**	**Extracted amount (pg)**	**Extracted amount (µg)**	**Sampler area (cm^2)**	**Deposition (µg.cm^{-2})**
Upwind	UPW-CP	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	UPW-CP-V	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	UPW-MS	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	UPW-PR	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
	UPW-PD	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
0 m	0-CP-A	9242	0.060	60	1.00	60201	0.060	10	0.0060
	0-CP-A-V	15994	0.12	120	1.00	120312	0.12	10	0.012
	0-PD-A	12974	0.093	93	1.00	93430	0.09	75.4	0.0012
	0-MS-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	0-PR-A	7265	0.043	43	1.00	42596	0.043	11.9	0.0037
	0-CP-B	11496	0.080	80	1.00	80269	0.08	10	0.0084
	0-CP-B-V	7063	0.04	41	1.00	40798	0.04	10	0.012
	0-PR-B	4266	0.02	16	1.00	15900	0.016	11.9	0.008
	0-MS-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	0-PD-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	0-CP-C	8272	0.052	52	1.00	51567	0.052	10	0.0052
	0-CP-C-V	8508	0.054	54	1.00	53665	0.54	10	0.0053
	0-PD-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.

	0-MS-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	0-PR-C	5476	0.027	27	1.00	26669	0.0027	11.9	0.0022
10 m	10-CP-A	7911	0.048	48	1.00	48347	0.048	10	0.0048
	10-CP-A-V	5751	0.029	29	1.00	29123	0.03	10	0.0031
	10-PD-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	10-MS-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	10-PR-A	6180	0.033	33	1.00	32937	0.033	11.9	0.0027
	10-CP-B	8884	0.057	57	1.00	57009	0.057	10	0.0057
	10-CP-B-V	5957	0.031	31	1.00	30957	0.031	10	0.0031
	10-PD-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	10-MS-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	10-PR-B	3614	<LOQ	n.d.	1.00	n.d.	n.d.	11.9	n.d.
	10-CP-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	10-CP-C-V	4867	0.021	21	1.00	21253	0.02	10	0.0021
	10-PD-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	10-MS- C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	10-PR-C	5476	0.027	27	1.00	26669	0.027	11.9	0.0022
25 m	25-CP-A	3166	<LOQ	n.d.		n.d.	n.d.	10	n.d.
	25-CP-A-V	3610	<LOQ	n.d.	1.00	n.d.	n.d.	10	n.d.

	25-PD-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	25-MS-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	25-PR-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
	25-CP-B	4235	0.020	20	1.00	15624	0.016	10	0.0016
	25-CP-B-V	3174	<LOQ	n.d.	1.00	n.d.	n.d.	10	n.d.
	25-PD-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	25-MS-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	25-PR-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
	25-CP-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	25-CP-C-V	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	25-PD-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	25-MS-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	25-PR-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
50 m	50-CP-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	50-CP-A-V	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	50-MS-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	50-PD-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	50-PR-A	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
	50-CP-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	50-CP-B-V	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	50-MS-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.		n.d.

	50-PD-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	50-PR-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
	50-CP-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	50-CP-C-V	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	50-MS-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	50-PD-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	50-PR-C	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
100 m	100-CP-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	100-CP-V-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	100-MS-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	100-PD-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	100-PR-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
200 m	200-CP-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	200-CP-B-V	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	200-MS-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.

	200-PD-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	200-PR-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
400 m	400-CP-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	400-CP-B-V	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	400-MS-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	400-PD-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	400-PR-B	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.
Field blanks	CP	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	10	n.d.
	MS	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	79	n.d.
	PD	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	75.4	n.d.
	PR	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	11.9	n.d.

n.d. = not detected**;** CP- chromatography paper, MS- glass microscope slides, PD- glass petri dishes, PR- polyacrylic rods; A, B, and C are the sampling lines; H-horizontal, V-vertical. Samples are named according to the distance from the spray area, type of sampler, group of samplers to which it belongs, and orientation of the chromatography paper. For instance, 0-CP-B means a chromatography paper sampler, 0 m away from the spray area, and belonging to group B of samplers. UPW-upwind sample

In the case of polyacrylic rods, atrazine was detected in some samples up to 10 m. While the mechanism of interaction between the pesticide and the sampler is not known, it appears that the pesticide is less subject to volatilisation losses than from glass substrates and is assumed that the low deposition values may have been due to the small diameter of the sampler.

Deposition values generally decreased as the distance from the spray area increased for both horizontal and vertical deposition samplers, as expected. For the vertical deposition samplers, impaction was greater on the chromatography paper compared to the polyacrylic rods up to a distance of 25 m **(Figure 4-5).** This is because the surface of the chromatography paper had a better way of interacting with the droplets as compared to the polyacrylic rods, thus increasing the chance of impaction and thereby collection. In addition, the chromatography paper had a flat rectangular shape which is capable of collecting more droplets than the cylindrical polyacrylic rod. Further statistical analysis was conducted by first carrying out an F-test to check whether the variances in terms of standard deviations were significantly different between the vertical chromatography paper and the polyacrylic rods at the sampling points where positive results were obtained.

The null hypothesis H_0 *was stated as* H_0*:* $\sigma_1^2 = \sigma_2^2$*, where* σ_1^2 *is the variance in terms of standard deviation of the vertical chromatography paper, and,* σ_2^2*, is the variance in terms of standard deviation of the polyacrylic rods.*

The alternative hypothesis was stated as H_1*:* $\sigma_1^2 \neq \sigma_2^2$ *there is a significant difference between the variances of the vertical chromatography paper and the polyacrylic rods.*

It was found that the F-values obtained were less than the F-critical values (**Table 4.4**), therefore there were no significant differences between the variances in terms of standard deviation for the two sampler types.

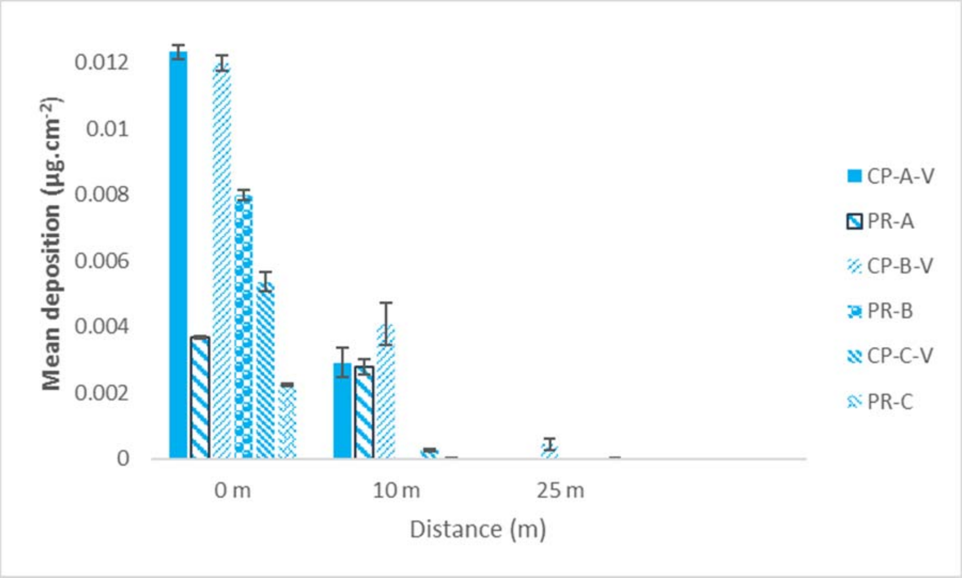

Figure 4-5: Comparison of vertical filter paper and polyacrylic rods up to 25 m from the edge of the field (no atrazine was detected at distances further than this) in the first sampling campaign. PR-A- polyacrylic rod in group A of samplers, CP-B-V- chromatography paper in type B of samplers, being vertically oriented, PR-B- polyacrylic rods of group B samplers, CP-A-V- chromatography paper of group A samplers being vertically oriented, CP-C-V chromatography paper in group C of samplers, being vertically oriented. Error bars represent ± standard deviation, (n=3).

Table 4-4: Statistical analysis (F-test) of atrazine (ATZ): comparison of variances of deposition samplers namely horizontal chromatography paper vs. glass petri dish and vertical chromatography paper vs. polyacrylic rods (1) 0-CP-A vs. 0-PD-A, (2) 0-CP-A-V vs. 0-PR-A, (3) 0-CP-B vs. 0-PR-B, (4) 0-CP-C-V vs. 0-PR-C, (5) 10-CP-A-V vs. 10-PR-A, (6) 10-CP-C-V vs. 10-PR-C.

Deposition samplers	**F-Test** **Null hypothesis: $\sigma_1^2 = \sigma_2^2$.**						**Reject H_0?** *
	Variance in terms of standard deviation (n=3)				$F_{calculated}$	$F_{critical}$	
	CP	CP-V	PD	PR			
0-CP-A vs 0-PD-A	8.8E-09		3.7E-09		2.4	19	No
0-CP-A-V vs 0-PR-A		1.4E-08		1.1E-09	12		No
0-CP-B-V vs 0-PR-B		9.5E-08		2.5E-08	3.8		No
0-CP-C-V vs 0-PR-C		4.9E-09		1.8E-09	2.8		No
10-CP-A-V vs 10-PR-A		3.9E-08		2.6E-08	1.5		No
10-CP-C-V vs 10-PR-C		1.8E-09		1.3E-09	1.3		No

*$F_{calculated} < F_{critical}$, we accept the null hypothesis, and there is no significant difference between the precision obtained for the two sampler types. PR-C- polyacrylic rod in sampling line C, PR-B- polyacrylic rod in sampling line B, PR-A- polyacrylic rod in sampling line A, CP-C-V- vertically oriented chromatography paper in sampling line C, CP-B-V- vertically oriented chromatography paper in sampling line B, CP-A-V- vertically oriented chromatography paper in sampling line A, CP-A- horizontally oriented chromatography paper in sampling line A, PD-A- glass petri dish in sampling line A.

A paired t-test was done on the samples to test whether the difference between the mean deposition values (**Table 4-5**) of the two methods, μ_d, is zero, or not.

The null hypothesis was stated as H_0: $\mu_d = 0$*, meaning that there is no significant difference between the mean deposition values (***Table 4.5***) obtained for the vertical chromatography paper, and the polyacrylic rod.*

The alternative hypothesis was stated as H_1: $\mu_d \neq 0$*, meaning that there is a significant difference between the means obtained for the vertical chromatography paper and the polyacrylic rods.*

At 95% confidence interval, all the calculated t-values for all sets of data were greater than the critical (t) values (**Table 4.5**). Hence, the null hypothesis was rejected, and the alternative hypothesis, H_1 was accepted and the mean deposition values obtained for the vertical chromatography paper and the polyacrylic rods differed significantly.

The results of the paired t-test are in agreement with the expectation that deposition samplers with different materials of construction capture droplets differently, although the differences in shape would also have contributed to the observed differences. The differences between the vertical chromatography paper and the polyacrylic rods are statistically significant.

Table 4-5: Statistical analysis (paired t-test) of atrazine (ATZ): comparison of mean deposition values of samplers (1) 0-CP-A vs. 0-PD-A, (2) 0-CP-A-V vs. 0-PR-A, (3) 0-CP-B vs. 0-PR-B, (4) 0-CP-C-V vs. 0-PR-C, (5) 10-CP-A-V vs. 10-PR-A, (6) 10-CP-C-V vs. 10-PR-C.

Deposition samplers	**Paired t-test** **Null hypothesis: $\mu_d = 0$**						**Reject H_0?** *
	Mean deposition (µg.cm^{-2}) n=3				$t_{calculated}$	$t_{critical}$	
	CP	PD	CP-V	PR			
0-CP-A vs 0-PD-A	0.0060	0.0012			60	4.3	Yes
0-CP-A-V vs 0-PR-A			0.012	0.0037	107		Yes
0-CP-B-V vs 0-PR-B			0.0041	0.00085	18		Yes
0-CP-C-V vs 0-PR-C			0.005	0.002	48		Yes
10-CP-A-V vs 10-PR-A			0.0031	0.0010	10		Yes
10-CP-C-V vs 10-PR-C			0.00026	0.0022	44		Yes

*$t_{calculated} > t_{critical,}$ we reject the null hypothesis, and the mean deposition values differ significantly.

PR-C- polyacrylic rod in sampling line C, PR-B- polyacrylic rod in sampling line B, PR-A- polyacrylic rod in sampling line A, CP-C-V- vertically oriented chromatography paper in sampling line C, CP-B-V- vertically oriented chromatography paper in sampling line B, CP-A-V- vertically oriented chromatography paper in sampling line A, CP-A**-** horizontally oriented chromatography paper in sampling line A, PD-A- glass petri dish in sampling line A

For the horizontal deposition samplers, the chromatography paper collected the most pesticide deposition, and the glass petri dish only collected deposited pesticide at values above LOD once at 0 m, while atrazine was not detected on the glass microscope slides **(Figure 4-6).** This may be ascribed to the fact that atrazine might have volatilised from the surface of the glass microscope slides prior to extraction and analysis (Hubbs and Lavy, 1990). For glass petri dishes, atrazine was only detected in one sample, at 0 m. However, some of the samples gave a mass spectrum of atrazine, but the peak area was very low, and these were reported to be below the instrumental detection limit. This might also have been due to volatilisation taking place from the surface of the glass petri dishes prior to extraction, since their material of construction is similar to that of the glass microscope slides. This may be the reason why a previous study that used glass petri dishes immediately extracted the pesticides with solvent in the field before transporting the extracts to the laboratory for analysis (Lefrancq et al., 2013).

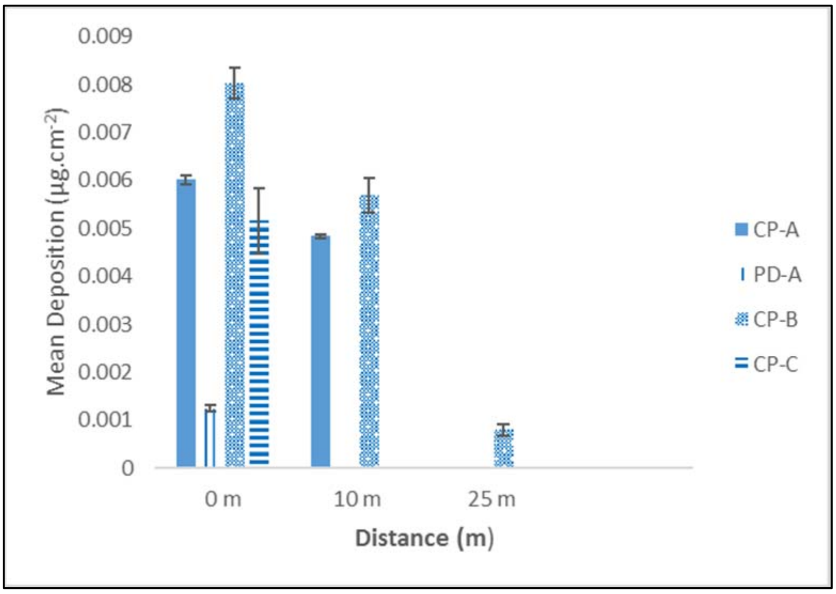

Figure 4-6: Comparison of horizontal deposition samplers up to 25 m from the edge of the field (no atrazine was detected at distances further than this) in the first sampling campaign. CP-A- chromatography paper in group A of samplers, CP-B- chromatography paper in group B of samplers, CP-C- chromatography paper in group C of samplers, PD-A- petri dish in group A of samplers. Error bars represent ± standard deviation (n=3).

Statistical analysis was also carried out to compare the horizontal chromatography paper and glass petri dishes at one sampling location. An F-test was carried out to check whether the variances in terms of standard deviation were significantly different between the horizontal chromatography paper and the petri dish at one sampling point.

The null hypothesis, H_0, was stated as: H_0: there is no significant difference between the variances of the horizontal chromatography paper and those of the glass petri dish.

The alternative hypothesis: H_1: there is a significant difference between the variances of the horizontal chromatography paper and the glass petri dish.

It was found that the F-values obtained were less than the F-critical values (**Table 4.4**), therefore there were no significant differences between the variances in terms of standard deviation of the two methods. A paired t-test was carried out on the samples to test whether any differences between mean deposition values (**Table 4.5**) obtained by the horizontal chromatography paper and the glass petri dishes were significant, or not.

*The null hypothesis was stated as H_0: $\mu_d = 0$, meaning that there is no significant difference between the mean deposition values obtained for the horizontal chromatography paper (**Table 4.5**), and the petri dish.*

The alternative hypothesis H_1 was stated as $\mu_d \neq 0$, meaning that there is a significant difference between the means obtained for the horizontal chromatography paper and the glass petri dish.

At 95% confidence interval, the calculated t-values for all sets of data were greater than the critical value (**Table 4.5**), hence the null hypothesis was rejected, and the alternative hypothesis, H_1 was accepted. This agrees with the experimental results obtained because the horizontal chromatography paper and the glass petri dish have different materials of construction, and hence they interact differently with the pesticide droplets.

Regarding the distribution of deposition amongst the three sampler lines, A, B, and C (**Figure. 3-2**) up to 25 m it can be deduced that more deposition was observed amongst B group samplers for both vertical and horizontal deposition samplers. This trend shows that the wind direction was more biased towards that direction more than the others.

The upwind and field blank samples did not record any deposition value, therefore no cross contamination took place, and there was no detectable concentration of atrazine in the background air. Finally, the trend regarding which orientation of chromatography paper collects more deposition was not very clear. Owing to the low deposition amounts reported in the first sampling campaign, it was decided to improve the sample storage technique for chromatography paper from plastic zip lock bags to glass Schott bottle, in order to further minimise the loss of target analytes. Thus, a second sampling campaign was carried out to determine which orientation of the chromatography paper collects pesticide droplets more droplets than the other. Moreover, the second sampling campaign was carried out to further improve the storage conditions of deposition samples from the field by replacing the plastic zip lock bags with glass Schott bottles.

4.3.2 Comparison between AgDISP model and field deposition results obtained from the first sampling campaign

Estimated atrazine deposition results as predicted by the AgDISP model are given in **Figure 4.7**. It was found that the model under-predicted deposition of atrazine onto chromatography paper by an order of up to 3 for horizontal deposition samplers at 0 m. This agrees with the previous study carried out by our group where deposition values for chromatography paper were higher than those predicted by the AgDISP model by an order of up to 10 (Nsibande, 2015). For the vertical chromatography paper, the model under-predicted deposition by an order of 5. It is therefore appears that the model tends to under-predict deposition under local conditions.

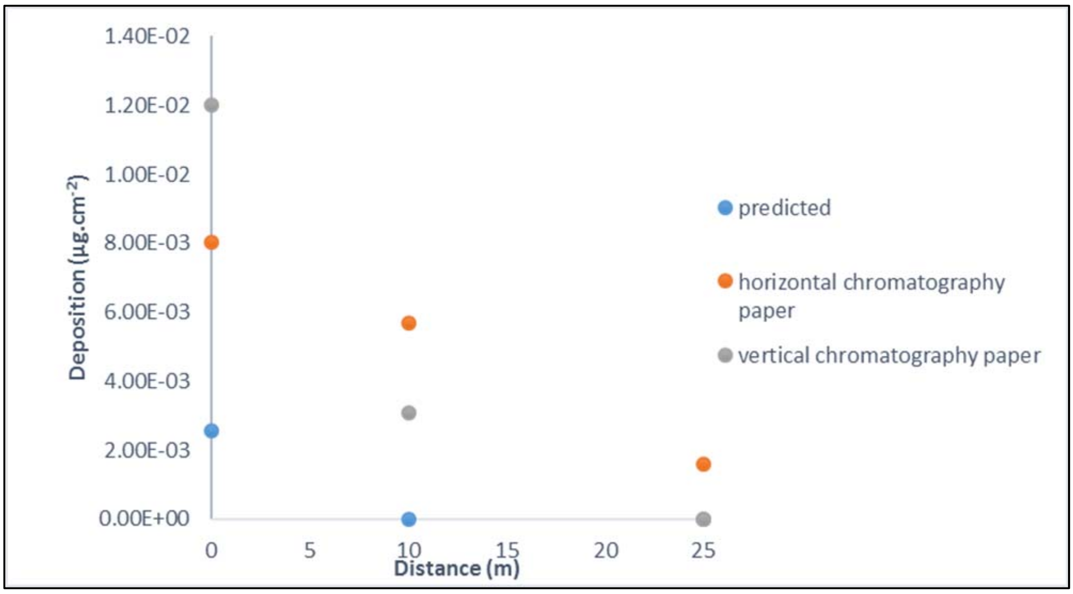

Figure 4-7: Comparison of model predicted deposition for atrazine (blue dots) with experimental deposition on horizontal chromatography paper (orange dots), and vertically oriented chromatography paper (grey dots) in the first sampling campaign.

To compare the results from the AgDISP model with those from the pesticide deposition monitoring study, the paired t-test was applied to test whether the difference between the experimental means and the AgDISP output values, μ_d, is zero.

Therefore, the null hypothesis was stated as, H_0*:* $\mu_d = 0$*, meaning that there is no significant difference between the mean deposition values obtained in the field, and those predicted by AgDISP.*

H_1*: there is a significant difference between the variance obtained in field deposition and the AgDISP model.*

At 95% confidence interval, the calculated t-values (**Table 4.6**) for the horizontal chromatography paper was greater than the critical value, hence the null hypothesis was rejected, and the alternative hypothesis, H_1 was accepted and there is a significant difference between the deposition predicted by the AgDISP model and the experimentally obtained deposition results. Therefore, this is in agreement with the trend observed in **Figure 4.7** whereby the AgDISP under-predicts the amount of atrazine deposition by orders of up to 3. However, for the vertical chromatography paper, at 95% confidence level, the calculated t-values were less than the critical value; hence the null hypothesis was accepted, meaning that there is no significant difference between the modelled deposition data and the experimental deposition data.

Table 4-6: Statistical analysis (paired t-test) of atrazine: comparison of mean deposition values obtained by AgDISP vs horizontal chromatography paper field deposition, and (2) AgDISP vs vertical chromatography paper from field.

Comparison of AgDISP vs deposition sampler	**Paired t-Test Null hypothesis: $\mu_d = 0$**					**Reject H_0?** *
	Mean deposition values (n=3) as predicted by AgDISP vs those obtained by deposition samplers in field			$t_{calculated}$	$t_{critical}$	
	AgDISP	Horizontal chromatography paper	Vertical chromatography paper			
AgDISP vs horizontal chromatography paper	0.00127	0.00686		50.7	12.7	Yes
AgDISP vs vertical chromatography paper			0.00755	1.97		No

*$t_{calculated} > t_{critical}$, we reject the null hypothesis, and the mean deposition values differ significantly.

4.4 Second sampling campaign

4.4.1 Field deposition results

The average wind speed for the second sampling campaign was measured at a height of 1 m above ground level, and it was approximately 2.5 m.s^{-1}. The wind direction was from north west, and the ambient temperature was 26.1 ^{0}C.

The use of stable isotope labelled analyte analogues as internal standards is a common practice in quantitative mass spectrometric methods. Atrazine-d5 is one such internal standard that is used to correct for any potential variations in extraction efficiency, when added to the sample prior to extraction, whereby it is called a surrogate standard), ionisation efficiency, and GC-MSD detection (Walorczyk, 2001). In this study, the atrazine-d_5 was added to the final extract. Using m/z =205 as the quantification ion for atrazine-d_5 atrazine, m/z 200 for atrazine, and m/z 214 for terbuthylazine, quantification was carried out by means of the signal ratio of the analyte to that of the internal standard. The calibration curve that was used for the deposition samples is shown in **Table 4-1** (Curves 2 and 3). Excellent linearity was obtained in the concentration ranges of 0.1-10 μg.ml^{-1} (R^2=0.999) and 1.0-10 μg.ml^{-1} for atrazine (R^2 =0.993) (**Figure 4-8**) and terbuthylazine (R^2 = 0.994) (**Figure 4-9**) respectively. The limit of detection was 0.0125 μg.ml^{-1} and 0.0159 μg.ml^{-1} for atrazine and terbuthylazine respectively. The limit of quantitation was 0.0414 μg.ml^{-1}, and 0.0459 μg.ml^{-1} for atrazine and terbuthylazine respectively. Atrazine, terbuthylazine, and atrazine-d_5 eluted at almost the same retention time of approximately 15 min. Hence the chromatogram appears as two peaks that are not baseline separated (**Figure 4-10**). However, peak deconvolution is achieved by extracted ion chromatograms as shown in **Figure 4-11**.

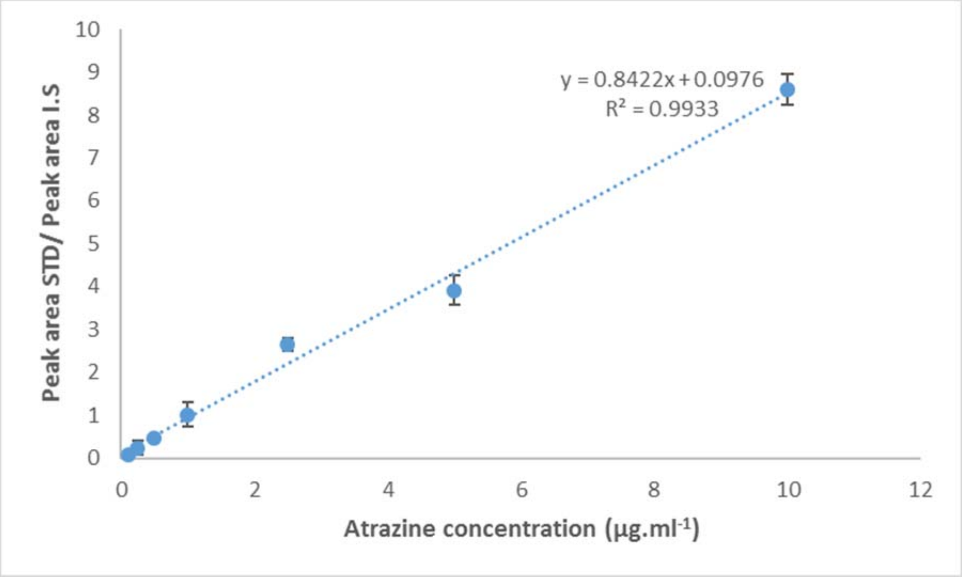

Figure 4-8: Calibration curve (internal standard method) for atrazine (LOD=0.0125 μg.ml^{-1}). Error bars represent ± standard deviation (n=3).

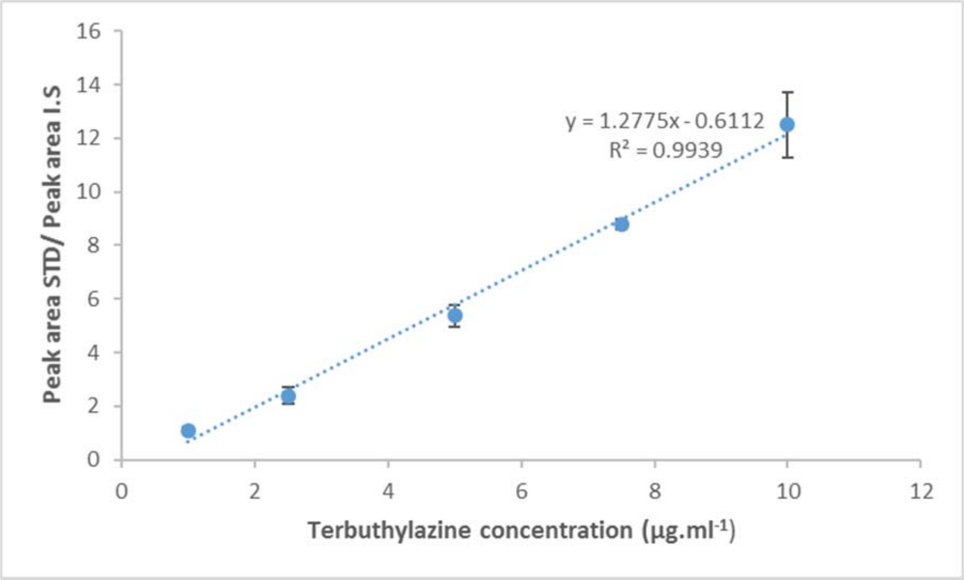

Figure 4-9: Calibration curve (internal standard method) for terbuthylazine (LOD= 0.01592 µg.ml^{-1}). Error bars represent ± standard deviation (n=3).

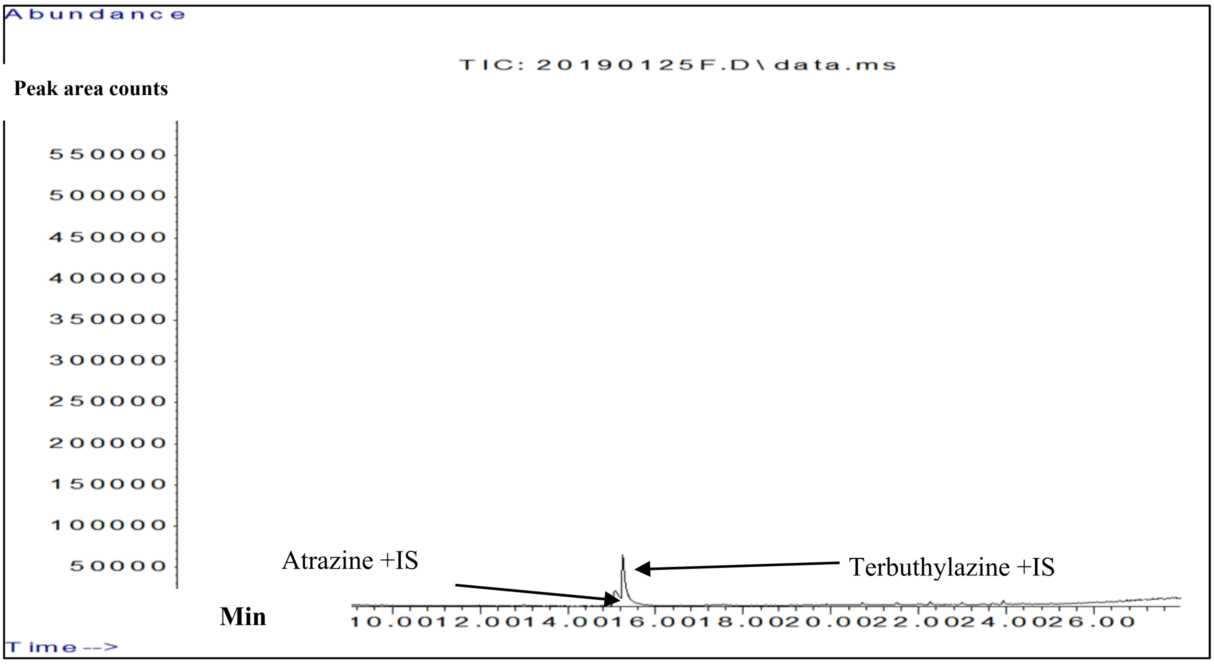

Figure 4-10: Total Ion chromatogram of atrazine, terbuthylazine sample and atrazine-d5 (internal standard) of concentration 0.5 µg.ml^{-1}.

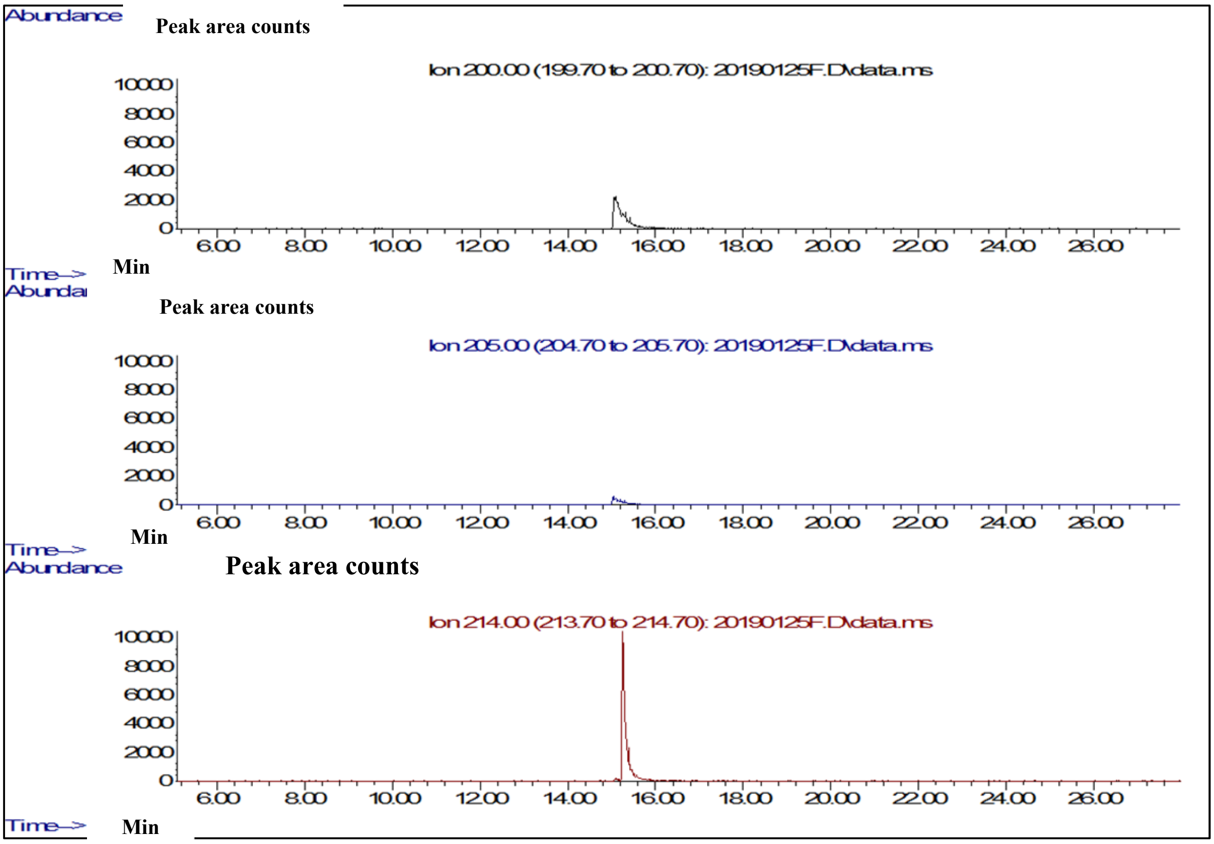

Figure 4-11: Reconstructed Ion chromatograms of sample at 0 m from spray area from top to bottom (a) atrazine m/z 200, (b) atrazine-d5 m/z 205, (c) terbuthylazine m/z 214

Off-target deposition values generally decreased as the distance from the spray area increased, for both horizontal and vertical deposition samplers, as expected. Both atrazine and terbuthylazine were only detected up to 10 m (**Table 4-7** and **Table 4-8**). This might be attributed to the fact that the deposition samplers were positioned in a grass field as compared to open soil in the first sampling campaign. The deposition values were almost similar for atrazine and terbuthylazine on the horizontal deposition samplers up to 10 m. This is expected because the concentrations of the two pesticides in the formulation are equal. However, for the vertical deposition samplers up to a distance of 10 m, these two concentrations varied by a factor of up to 10, with terbuthylazine being higher. This may be due to the fact that atrazine (vapour pressure 3.82×10^{-5} Pa) has a lower volatility than terbuthylazine (vapour pressure 9×10^{-5} Pa). The trend is similar to another study in which off-target deposition of alachlor and atrazine were determined using glass petri dishes with glass fibres, and the deposition amounts were higher for alachlor, the more volatile pesticide (Ravier et al., 2005). A similar trend was also observed at distances greater than 300 m, when off-target deposition of diazinon, the more volatile pesticide, was greater than that of malathion, when sampling was done using alpha cellulose sheets (Hewitt et al., 2002). On the other hand, when glass petri dishes were used, tebuconazole, the less volatile pesticide, was deposited more than folpet, the more volatile pesticide. Thus, off-target deposition of pesticides with different volatilities is a subject that still needs further investigation under different climatic conditions, pesticide application conditions, as well as for different deposition samplers.

Table 4-7: Atrazine (ATZ) deposition results from analysis of chromatography paper by GC-MSD. The ratio of the peak area of atrazine (m/z 200) to that of the internal standard was used for quantitation (R^2= 0.9933, LOD= 0.0125 µg.ml$^{-1,}$ LOQ= 0.0414 µg.ml^{-1}). Samples are named according to the distance from spray area, group of samplers to which it belongs, and orientation for chromatography paper. For instance, 0-B-V means a vertically oriented chromatography paper sampler, 0 m away from spray area, and belonging to group B of samplers. Field sample refers to the horizontal chromatography paper that was placed between the rows of the maize plants to intercept the droplets that fell to the ground. FLB-BLK refers to field blanks. UPW refers to upwind samples

Sample location	Sample name	Peak area ATZ	Peak area I.S.	Response factor ATZ/ I.S.	ATZ concentration (µg.ml^{-1})	ATZ concentration (pg.µl^{-1})	Final volume (ml)	ATZ extracted amount (pg)	ATZ extracted amount (µg)	Area of sampler (cm)	ATZ deposition (µg.cm^{-2})
Upwind	UPW-H	n.d.	51765	0.00	n.d.	n.d.	1.00	n.d.	n.d.	20	0.000
	UPW-V	n.d.	49887	0.00	n.d.	n.d.	1.00	n.d.	n.d.	20	0.000
Field sample	FLD-H	267734	56456	4.7	5.5	5515	20.00	110301141	110	20	5.5
0 m	0-A-H	483943	52890	9.2	11	10749	20.00	214971582	215	20	11
	0-A-V	124960	52879	2.4	2.7	2690	20.00	53800000	54	20	2.7
	0-B-H	359596	54671	6.6	7.7	7694	20.00	153880300	154	20	7.7
	0-B-V	95200	52432	1.8	2.0	2040	20.00	40800000	41	20	2.0
	0-C-H	236866	56549	4.2	4.9	4828	20.00	97152361	97	20	4.9
	0-C-V	83778	52790	1.6	1.8	1769	20.00	35369541	35	20	1.8
10 m	10-A-H	15907	52808	0.3	0.24	242	10.00	241766	2.4	20	0.12
	10-A-V	7954	53369	0.15	0.064	61	10.00	61068	0.61	20	0.031
	10-B-H	14514	52046	0.28	0.22	215	10.00	215223	2.2	20	0.11
	10-B-V	8080	53630	0.15	0.063	63	10.00	630005	0.63	20	0.032
	10-C-H	11321	54992	0.21	0.13	129	10.00	128543	1.29	20	0.064
	10-C-V	n.d.	50879	n.d.	n.d.	n.d.	10.00	n.d.	n.d.	20	n.d.
30 m	30-A-H	n.d.	56924	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-A-V	n.d.	54113	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-B-H	n.d.	54345	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-B-V	n.d.	57880.	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-C-H	n.d.	55334	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.

	30-C-V	n.d.	50211	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
50 m	50-B-H	n.d.	56190	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	50-B-V	n.d.	57093	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
100 m	100-B-H	n.d.	53308	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	100-B-V	n.d.	49943	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
Field blanks	FLD-BLK1	n.d.	51167	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	FLD-BLK2	n.d.	57729	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	FLD-BLK3	n.d.	56123	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.

Table 4-8: Terbuthylazine (TERB) deposition results from analysis of chromatography paper by GC-MSD. The ratio of the peak area of terbuthylazine (m/z 214) to that of the internal standard was used for quantitation (R2=0.9939, LOD=0.0159 $\mu g.ml^{-1}$, LOQ= 0.0529 $\mu g.ml^{-1}$). Samples are named according to the distance from spray area, group of samplers to which it belongs, and orientation for chromatography paper. For instance, 0-A-H means a horizontally oriented chromatography paper sampler, 0 m away from spray area, and belonging to group B of samplers. FLD-BLK refers to field blanks. UPW refers to upwind samples

Sample location	**Sample name**	**Peak area TERB**	**Peak area I.S.**	**Response factor TERB/I.S.**	**TERB concentration ($\mu g.ml^{-1}$)**	**TERB concentration ($pg.\mu l^{-1}$)**	**Final volume (ml)**	**TERB extracted amount (pg)**	**TERB extracted amount (µg)**	**Area of sampler (cm)**	**TERB deposition ($\mu g.cm^{-2}$)**
Upwind	UPW-H	n.d.	51765	0.00	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	UPW-V	n.d.	49887	0.00	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
Field	FLD-H	530342	56456	9.4	7.8	7828	20.00	156558249	157	20	7.8
0 m	0-A-H	757931	52890	15	12	12006	20.00	240114972	240	20	12
	0-A-V	460922	52879	8.8	2.4	2430	20.00	48596092	49	20	2.4
	0-B-H	582868	54671	11	8.3	8343	20.00	166862873	167	20	8.3
	0-B-V	344365	52431.67	6.6	7.4	7069	20.00	70693970	71	20	3.5
	0-C-H	409517	56459	7.3	6.2	6158	20.00	123162496	123	20	6.2
	0-C-V	130703	52790	2.5	3.5	3463	20.00	69258992	69	20	3.5

10 m	10-A-H	33837	52808	0.64	0.98	979.8	10.00	9797306	13	20	0.49
	10-A-V	11730	53369	0.22	0.65	650.8	10.00	6508882	6.5	20	0.33
	10-B-H	25375	51713	0.49	0.87	865.1	10.00	8651206	8.7	20	0.43
	10-B-V	12204	53630	0.23	0.66	657.2	10.00	6571733	6.6	20	0.33
	10-C-H	13069	54992	0.24	0.66	660.4	10.00	660430	0.66	20	0.033
	10-C-V	n.d.	50879	n.d.	n.d.	n.d.	10.00	n.d.	n.d.	20	n.d.
30 m	30-A-H	n.d.	56924	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-A-V	n.d.	54113	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-B-H	n.d.	54345	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-B-V	n.d.	57880	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-C-H	n.d.	55334	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	30-C-V	n.d.	50211	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20.	n.d.
50 m	50-B-H	n.d.	56190	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	50-B-V	n.d.	57093	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
100 m	100-B-H	n.d.	53308	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	100-B-V	n.d.	49943	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
Field blanks	FLD-BLK1	n.d.	51167	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	FLD-BLK2	n.d.	57729	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.
	FLD-BLK3	n.d.	56123	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	20	n.d.

For both analytes, deposition was higher for the horizontally oriented chromatography paper relative to the vertically oriented chromatography paper (**Figures 4-12 to 4-15**) at distances of 0 m and 10 m. This can be explained by the fact that the warm temperatures caused lofting of droplets higher above ground level, thus favouring sedimentation of droplets, and not impaction. This is in contrast to a recent study that was carried out to determine off-target deposition of atrazine using horizontally oriented stainless steel discs (113 cm^2), where the vertically oriented steel rods (6.35 cm^2) collected more atrazine than the horizontally oriented ones (Brain et al., 2019). Similarly, a study comparing horizontal alpha cellulose cards (2500 cm^2), and vertical alpha cellulose cards (100 cm^2), at various wind speeds reported that the latter had higher collection efficiencies (Hewitt, 2010). This can be explained using **Equation 2-1**, the smaller the diameter of the sampler, the higher its collection efficiency. However in our study, both the horizontal and the vertical deposition samplers had the same dimensions. The difference in the deposition trend between the two studies can be explained by the differences in the materials of construction, and not much is known about the mechanisms of capture of droplets for both chromatography paper and stainless steel.

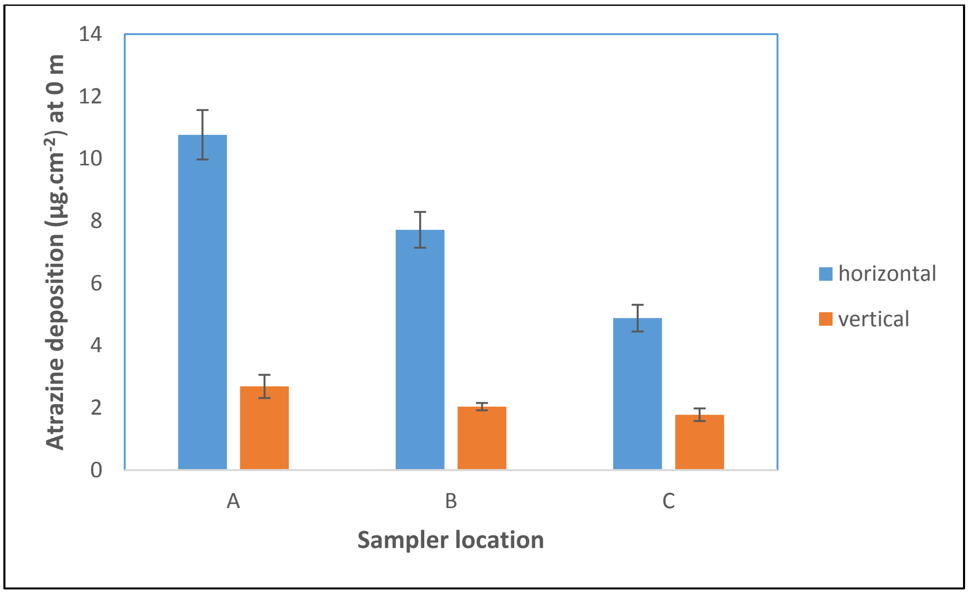

Figure 4-12: Off-target deposition of atrazine at 0 m on both horizontal and vertical deposition samplers in the second sampling campaign. Error bars represent ± standard deviation (n=3).

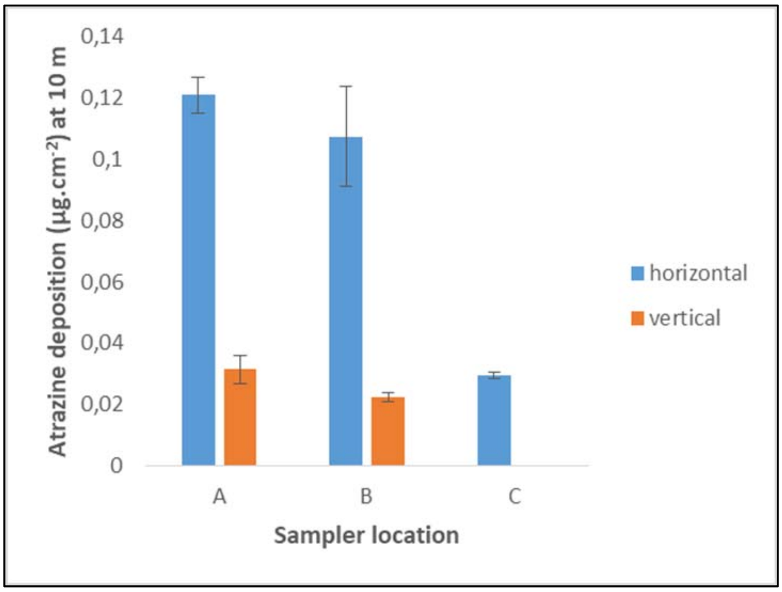

Figure 4-13: Off-target deposition of atrazine at 10 m on both horizontal and vertical deposition samplers in the second sampling campaign. Error bars represent ± standard deviation (n=3).

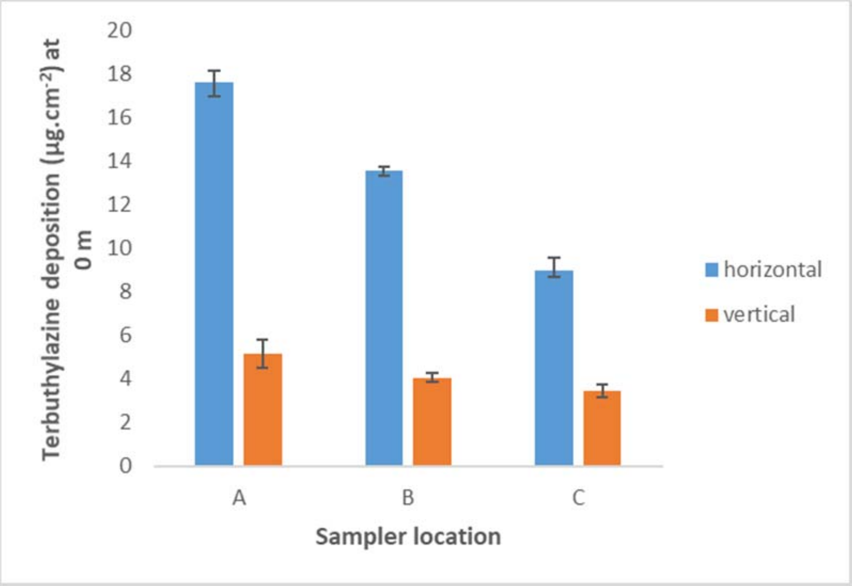

Figure 4-14: Off-target deposition of terbuthylazine at 0 m on both horizontal and vertical deposition samplers in the second sampling campaign. Error bars represent ± standard deviation (n=3).

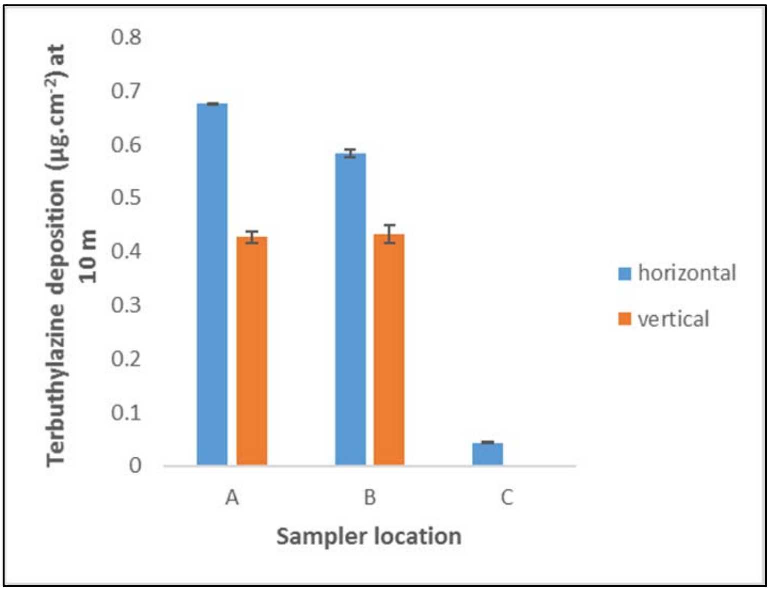

Figure 4-15: Off-target deposition of terbuthylazine at 10 m on both horizontal and vertical deposition samplers in the second sampling campaign. Error bars represent ± standard deviation (n=3).

Regarding the distribution of deposition amongst the three groups of samplers, it was observed that most deposition was collected among sampling line A samplers for both horizontal and vertical deposition samplers, and the least deposition was collected among the group C samplers. This suggests that while the wind direction was in the direction of the sampler locations, it was more towards the sampling line A, and least towards C samplers as no deposition was observed at 10 m for the vertical deposition sampler at that distance.

A paired t-test was carried out to compare the means of the horizontal chromatography papers and the vertical chromatography papers. Prior to carrying it out, the F-test was carried out to compare variations (precision) of the two samplers at 95% confidence interval. The null hypothesis, H_0 was stated as:

H_0: there is no significant difference between the variances of the horizontal chromatography paper and those of the vertical chromatography paper.

H_1: there is a significant difference between the variances of the horizontal and vertical chromatography papers.

The F-values obtained were less than the critical values (**Table 4-9**); hence there were no significant differences between the variances in terms of standard deviation (precision) of the horizontal and vertical chromatography paper. Thus, the null hypothesis was accepted.

Table 4-9: Statistical analysis (F-test) of atrazine (ATZ) and terbuthylazine (TERB): comparison of variances of samplers (1) 0-A-H vs. 0-A-V, (2) 0-B-H vs. 0-B-V, (3) 0-C-H vs. 0-C-V, (4) 10-A-H vs. 10-A-V, (5) 10-B-H vs. 10-B-V (6) 10-C-H vs. 10-C-V.

Deposition samplers	**F-Test Null hypothesis: $\sigma_1^2 = \sigma_2^2$**							**Reject H_0 ?***
	Variance in terms of standard deviation				$F_{calculated}$		$F_{critical}$	
	ATZ		TERB		ATZ	TERB	19	
	Horizontal	Vertical	Horizontal	Vertical				
0-A-H vs. 0-A-V	0.63	0.11	0.13	0.036	5.9	3.6		No
0-B-H vs. 0-B-V	0.33	0.027	0.025	0.010	12	2.3		No
0-C-H vs. 0-C-V	0.030	0.0030	0.12	0.030	9.8	4.4		No
10-A-H vs. 10-A-V	4.1E 10^{-5}	2.1E10^{-5}	5.2E 10^{-5}	4.9E10^{-5}	2.0	1.1		No
10-B-H vs. 10-B-V	8.8E 10^{-5}	5.1E10^{-6}	2.8E 10^{-6}	2.8E 10^{-5}	17	10		No

*$F_{calculated} < F_{critical}$, we accept the null hypothesis, and there is no significant difference between the standard deviations of the two sampler types. 0, and 10 m are the sampling distances, A, B, and C are the sampling lines, H and V represent horizontal and vertical orientation respectively.

The paired t-test was used to compare the mean deposition values (**Table 4-10**) of the horizontal and vertical chromatography paper.

H_0: $\mu_d = 0$, where μ_d is the difference between the mean deposition values (**Table 4.10**). *There is no significant difference between the mean deposition values of the horizontal chromatography paper and those of the vertical chromatography paper.*

H_1: there is a significant difference between the mean deposition values of the horizontal and vertical chromatography papers.

Table 4-10: Statistical analysis (paired t-test) of atrazine (ATZ) and terbuthylazine (TERB): comparison of mean deposition values of deposition of samplers (1) 0-A-H vs. 0-A-V, (2) 0-B-H vs. 0-B-V, (3) 0-C-H vs. 0-C-V, (4) 10-A-H vs. 10-A-V, (5) 10-B-H vs. 10-B-V.

Deposition samplers	**Paired t-Test Null hypothesis: $\mu_{d=0}$**						**$t_{critical}$ ATZ and TERB**	**Reject H_0^***
	Mean deposition ($\mu g.cm^{-2}$) n=3				$t_{calculated}$			
	ATZ		TERB		ATZ	TERB		
	H	V	H	V				
0-A	11	2.7	12	2.4	22	68	4.3	Yes
0-B	7.7	2.0	8.3	3.5	15	88		Yes
0-C	4.9	1.8	6.8	3.5	26	9.0		Yes
10-A	0.12	0.031	0.49	0.33	24	27		Yes

$^*t_{calculated} > t_{critical,}$ we reject the null hypothesis, and the mean deposition values differ significantly.

At 95% confidence interval, the t-values obtained for both atrazine and terbuthylazine were greater than the critical value. Hence, the null hypothesis was rejected, and the alternative hypothesis was accepted and there is a significant difference between the deposition means of the horizontal and vertical chromatography papers. It is to be expected that there is a significant difference between the deposition values on these two samplers, because they capture droplets differently. The horizontal chromatography paper captures droplets by sedimentation, while the vertical chromatography paper captures droplets by impaction.

4.4.2 Droplet size analysis

Water sensitive paper was mounted in the field, at 0, 10, 30, 50, and 100 m. However, the one at 0 m was the only one that was used for droplet size analysis because no droplets were observed on the others. This serves as a good qualitative analysis of off-target deposition because on quantitation of deposition samplers, at distances greater than 10 m, no deposition of atrazine and terbuthylazine was detected. As for the water sensitive paper mounted in the field, it could not be used because it was spoilt, and fell to the ground after it was run over by the sprayer.

Table 4-11 provides the droplet size distribution generated from image analysis of the water sensitive paper, which are represented graphically in **Figure 4-16**, upon entry into the AgDISP model. The volume median diameter (VMD) was 37.65 μm which corresponded to an average diameter of 36.88 μm. According to the American Society of Agricultural Engineers (ASAE), the sprayer nozzles used thus produce an extremely fine spray consisting of small droplets which would have excellent retention on leaves but would increase airborne spray drift, although decreasing off-target deposition due to settling (ASAE, 2009). However, the droplet size produced may also have been as a result of other factors such as pressure, spray angle, and the specific gravity of the pesticide mix (Schick, 2015). The applicability of the water sensitive paper for measuring droplet size distribution was demonstrated in this study. However, it may also be interesting to compare the droplet size distribution (DSD) with newer, more advanced methods that are now available such as laser diffraction, in a future study.

Table 4-11: Area of droplets and diameters determined from water sensitive paper from the second sampling campaign. Ds is the spot diameter, and D is the actual diameter of the droplet. Dv0.5 is the volume median diameter.

$D_{v0.5}$ =37.65 µm			
Droplet number	**Area**	**D_s (µm)**	**D (µm)**
1	2112	52	35
2	2250	54	36
3	6970	94	59
4	1928	50	33
5	10579	116	72
6	4151	73	47
7	3260	64	42
8	2681	58	38
9	781	32	22
10	1965	50	33
11	3939	71	46
12	2856	60	40
13	4656	77	49
14	1093	37	26
15	882	34	23
16	3122	63	41
17	1451	43	29
18	1304	41	28
19	1148	38	26
20	3609	68	44
21	46	8	6
22	2938	61	40
23	1175	39	26
24	5152	81	52
25	6244	89	57
26	2433	56	37
27	46	8	6

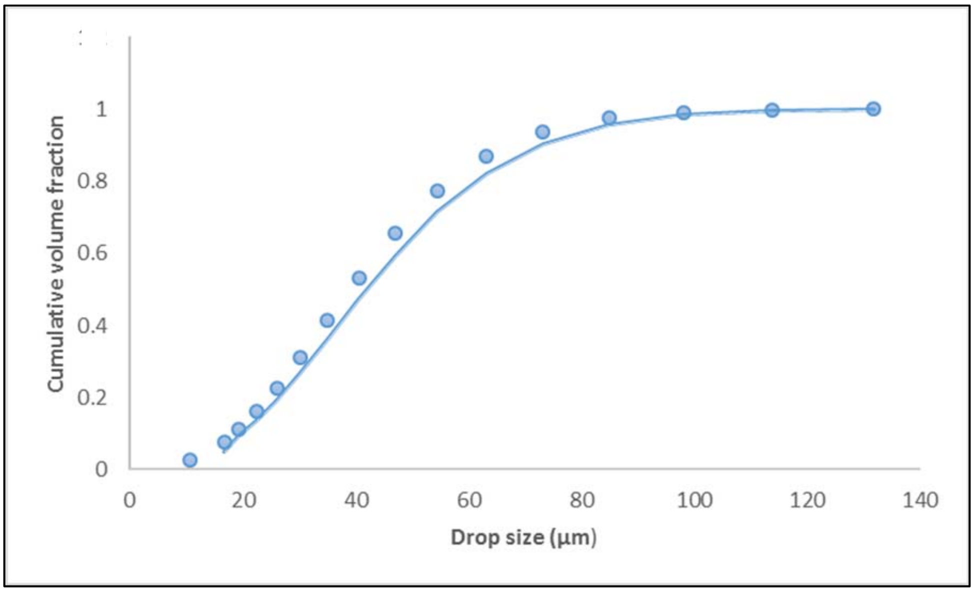

Figure 4-16: Cumulative volume fraction for droplet size distribution generated by AgDISP.

4.4.3 Comparison between AgDISP model and field deposition results obtained from the second sampling campaign

Figures 4-17 and **4-18** illustrate the comparison between the experimentally determined downwind deposition rates which were measured using GC-MSD and the model predicted deposition rates for the group of samplers with the highest value, which in this case was group A (**Figure 3.4**). At 0 m, the model under-predicted the concentrations of both atrazine and terbuthylazine by orders of 14 and 22 respectively for the horizontally oriented chromatography paper. The results are in agreement with a previous study carried out by our research group where the atrazine deposition was under-predicted by the same rate (Nsibande, 2015). However, this is in direct contrast to a study carried out which found that the AgDISP model over-predicted downward deposition by order of up to 100 (Woodward et al., 2008). However, it is worth noting that this study used metal ions as tracers, and it was not under local conditions, which could account for the difference.

The vertically oriented chromatography paper also had higher levels of deposition for terbuthylazine and atrazine at 0 m. As the distance increased, there was no longer under-prediction by the model, as the amounts obtained in the field deposition study agreed with those of the AgDISP model. This might be attributed to the fact that the samplers experienced some interception from the grass in their vicinity at this distance. Hence, the model may not be able to predict deposition accurately. However, further studies may need to be carried out where there is no interception of droplets from surrounding vegetation in order for this assertion to be tested.

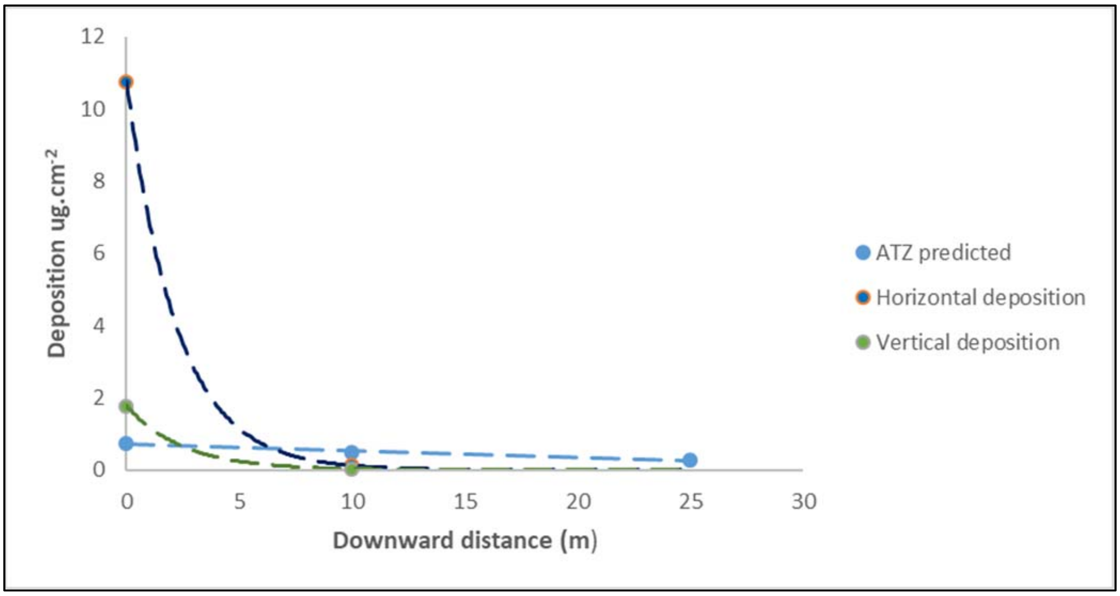

Figure 4-17: Comparison of model predicted deposition for atrazine (ATZ) blue dotted line) with experimental deposition on horizontal chromatography paper (navy blue dotted line), and vertically oriented chromatography paper (green dotted line) in the second sampling campaign.

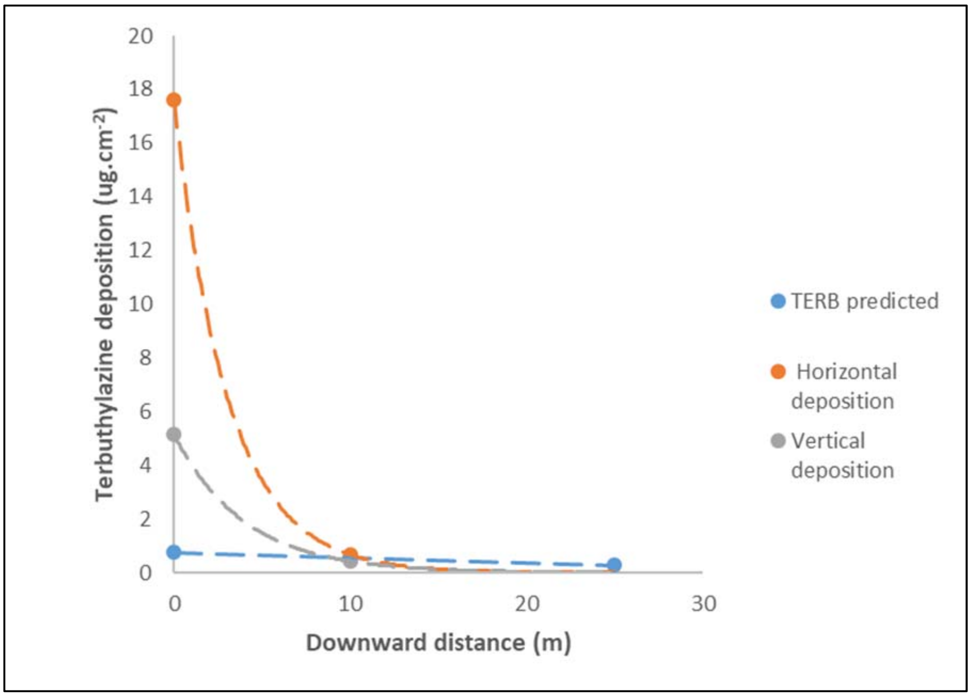

Figure 4-18: Comparison of model predicted deposition for terbuthylazine ((TERB) blue dotted line) with experimental deposition on horizontal chromatography paper (orange dotted line), and vertically oriented chromatography paper (grey dotted line) in the second sampling campaign.

To compare the results from the AgDISP model with those from the second pesticide deposition monitoring campaign, the paired t-test was applied.

For the paired t-test, the null hypothesis was defined as:

H_0: $\mu_d = 0$, meaning that there is no significant difference between the means of the modelled deposition data, and the experimental deposition data.

The alternative hypothesis, H_1 was stated as:

H_1: $\mu \neq 0$, there is a significant difference between the means of the modelled and experimental deposition data.

The calculated t-values (**Table 4-12**) were less than the critical value for both atrazine and terbuthylazine on horizontal and vertical deposition samplers, hence the null hypothesis was accepted, and the alternative hypothesis was rejected and there is no significant difference between the means of the modelled and experimental deposition data. This may be explained by the fact that as the distance increases from 0 m, there is agreement between the modelled data and the field deposition results.

Table 4-12: Statistical analysis (paired t-test) of atrazine (ATZ) and terbuthylazine (TERB): comparison of mean deposition values obtained by AgDISP vs. horizontal chromatography paper field deposition, and (2) AgDISP vs. vertical chromatography paper from field deposition.

Comparison of AgDISP vs deposition sampler	**Paired t-Test Null hypothesis: $\mu_d = 0$**						**Reject H_0?**[*]
	Mean deposition values (n=3) as predicted by AgDISP vs those obtained by deposition samplers in field			$t_{calculated}$		$t_{critical}$	
	AgDISP	ATZ	TERB	ATZ	TERB		
AgDISP vs horizontal chromatography paper	0.616	5.45	9.14	0.93	1.02	12.7	No
AgDISP vs vertical chromatography paper		0.904	2.78	0.39	0.97		No

[*] $t_{calculated} > t_{critical,}$ we reject the null hypothesis, and the mean deposition values differ significantly between the AgDISP modelled data and the field deposition results.

4.5 Comparison between the first and second sampling campaigns

The off-target deposition of pesticides in both the first and the second sampling campaign exhibited a similar pattern whereby the different samplers captured droplets in the near-field only. This might be ascribed to the use of drift reducing nozzles in both sampling campaigns, which are less affected by variations in wind speed, as compared to conventional nozzles (Grella et al., 2017). The atrazine mean deposition during the second sampling campaign was much greater, for both horizontal and vertical chromatography paper, ranging from 10 to 1833 times, than that from the first sampling campaign, up to a distance of 10 m downwind. This is despite the fact that the application rates were the same. One possible explanation could be that the droplet size distribution during both applications were quite different. In the first sampling campaign, the droplet size was determined from the nozzle size to be extra coarse, whereas in the second sampling campaign droplet size was determined from the water sensitive paper and was found to be extremely fine (ASAE,2009). It would be expected that higher deposition amounts would be obtained in the first sampling campaign because the droplets had larger diameters (extra coarse droplet classification), which should contain more dissolved pesticide than smaller droplets, and should therefore sediment easily onto horizontal samplers because of gravity and air resistance (Wilson et al., 2007, Stover et al., 2003). However, the opposite trend was observed between the two sampling campaigns. This can be attributed to the different meteorological conditions (air temperature, relative humidity, and wind speed), that existed when each sampling campaigns took place. The mean value of temperature during the first sampling campaign was 16.8 ^{0}C, whereas it was 26.1 ^{0}C during the second sampling campaign. When the temperature is lower it is expected that off-target deposition of pesticides is higher than when the temperature is higher, because the evaporation rate of the droplets decreases as the temperature decreases (Lefrancq et al., 2013). Contrary to this, off-target deposition values were higher on both horizontal and vertical chromatography paper in the second sampling campaign when the temperature was higher than that in the first sampling campaign, and the droplets were deposited up to 10 m, which is greater than 0.5 m, the theoretical value for deposition of small droplets (Zhu et al., 1994). This was attributed to the higher wind speed experienced in the second sampling campaign (2.5 m.s^{-1}) compared to 1.90 m.s^{-1} in the first sampling campaign. Moreover, the wind direction in the second sampling campaign was more stable, unlike in the first sampling campaign where it varied. The influence of the wind direction could also account for the uniform trend of deposition of atrazine and terbuthylazine onto horizontal and vertical chromatography paper, unlike in the first sampling campaign when the deposition trend was not as clear as the wind direction was constantly changing. The findings in our study are in agreement with previous studies that have been carried out, where increasing wind speed increased off-target deposition by factors of between 2 to 7 (Carlsen et al., 2006b). The findings in our study indicate an even greater increase of deposition than the increase that was recorded by Carlsen et.al (2006b), because the distance of the ground sprayer from where the deposition samplers were located was less than that in the first sampling campaign. The distance of the deposition samplers from the edge of the boom affects their relative sampling efficiencies (Rimmer et al., 2009). The two sampling campaigns also employed different sample storage techniques, with the first sampling campaign making use of plastic zip lock bags, while the second sampling campaign the chromatography paper was transported to the laboratory in glass Schott bottles, and on arrival at the laboratory the extraction solvent was added, before refrigeration, as the samples awaited analysis. This might be one of the reasons why the deposition amounts obtained in the second sampling campaign were significantly higher than the first sampling campaign, because loss of analytes was greatly minimised. To minimise analyte loss when plastic zip lock bags are used to store the chromatography paper samples, extraction could be done directly in the plastic zip lock bags, as reported by a recent publication (Li et al., 2018). This approach should also be compared to the extraction method used in our study, so as to determine the optimal extraction technique for chromatography paper samples.

The difference between the amounts of pesticide deposited at 0 m and 10 m for both experiments can be explained by the different fields where the sampling took place. In the first sampling campaign, spraying was done in an open field, whereas in the second sampling campaign, sampling was done in a cultivated maize field with some grass outside it. In the second experiment, the grass may have filtered the spray drift. Drift capture by surrounding vegetation is said to occur by gravity driven sedimentation on upward facing surfaces or by inertial impaction onto the vegetation carried by air currents (Brain et al., 2017, Marrs and Frost, 1997). Hence according to Marrs and Frost (1997) the interception by vegetation is a complex interaction between wind speed, sprayer droplet size spectrum, and the orientation of the vegetation (surface texture, shape, size, leaf waxiness, etc.).

The empirical deposition data for both sampling campaigns were compared with the model output of the AgDISP model, which is used in the regulatory process in some countries to determine buffer zones. The model under-predicted deposition of atrazine in the first sampling campaign, at all distances. For the second sampling campaign, the model under-predicted the amounts of atrazine and terbuthylazine for both horizontal and deposition samplers at 0 m, but as the distance increased, there was some agreement. Thus, regulators of pesticide use should take caution in using the model to estimate environmental concentrations of pesticides downwind of an application. The findings of this study make it apparent that field deposition studies are still important to arrive at buffer distances that accurately reflect environmental concentrations of pesticides from a pesticide application.

4.6 Comparison of the different pesticide deposition samplers

In this study, various samplers have been utilised to sample off-target deposition of atrazine. In the first sampling campaign, three horizontal deposition samplers, and two vertical deposition samplers were compared. However, not all samplers successfully captured droplets in the field, despite the fact that good extraction recoveries had been obtained in the laboratory. This might have been attributed to easy volatilisation of atrazine droplets from their surfaces, for instance in the case of the glass petri dishes and the glass microscope slides. **Table 4-13** summarises the advantages and limitations of the various samplers used as experienced in this study.

Table 4-13: Advantages and disadvantages of different pesticide deposition samplers

Sampler	Cost (ZAR) per sampler	Advantages	Disadvantages
Chromatography paper	0.03	Excellent retention and absorptive properties for target analytes. Good extraction efficiencies. Low extraction solvent volume. Cheapest compared to all the samplers used in this study.	
Glass microscope slides	2	Degradation of analyte (less likely if extraction of glass microscope slides is done in the field). Low cost.	Some analytes like atrazine evaporate quickly from the surface. Extraction may require large volume of solvent if they are placed in bottles in the field. Loss by volatilisation can occur from the surface. Easy to break when transporting from the field.
Glass petri dishes	17	Easy to extract. Cheaper than chromatography paper and polyacrylic rods. Low cost.	Easy to break when transporting from the field. Loss by volatilisation can occur from the surface.
Polyacrylic rods	25	Comes in a range of sizes. Low cost.	Limitations in terms of solvents that can be used to extract analytes, as it dissolves in some organic solvents.

In the second sampling campaign, the horizontal and vertical chromatography paper samplers were compared, and the horizontal chromatography paper exhibited higher sampling efficiency than the vertical chromatography paper of the same size. Even though terbuthylazine is more volatile than atrazine, the deposition rates on both horizontal and vertical chromatography paper were comparable, although terbuthylazine was slightly higher.

Finally from this study, the horizontal chromatography paper was found to be the best sampler.

Chapter 5 Conclusion and Recommendations

In this study, off-target deposition of atrazine (and terbuthylazine when present in the formulation) upon ground-based spray application of this pesticide was first sampled using various samplers such as chromatography paper, glass microscope slides, glass petri dishes, plastic drinking straws and polyacrylic rods, then analysed with GC-MS. These samplers were chosen based on availability, cost, and their suitability to study off-target deposition as reported in literature. To establish their applicability, recovery tests were conducted in the laboratory. Excellent recoveries (>70%) were achieved, with the exception of the plastic drinking straws, which were therefore not used in the field.

Two sampling campaigns were conducted, and the GC-MSD was used to analyse the deposition samples. For the first sampling campaign, in which chromatography paper, glass microscope slides, glass petri dishes, and polyacrylic rods were deployed, low deposition values were reported for atrazine up to 25 m downwind of the spray area, and no terbuthylazine was detected. The chromatography paper proved to be the best deposition sampler for both the horizontal and vertical orientations and the atrazine ranged collected was up to 0.008 $\mu g.cm^{-2}$ atrazine was collected. According to literature, this has been attributed to ability of the paper to protect analytes from photodegradation. For the second sampling campaign, using horizontal and vertically oriented chromatography paper, high deposition values, up to 11 $\mu g.cm^{-2}$, and up to 12 $\mu g.cm^{-2}$ were obtained for atrazine and terbuthylazine respectively, up to 10 m downwind of the spray area.

Slightly higher deposition values were obtained for terbuthylazine, which is more volatile than atrazine. Different trends in off-target deposition of pesticides with different volatilities have been reported in literature. Hence, further work should be done to ascertain the trend in off-target deposition of different classes of pesticides, with varying volatilities, under standardised conditions. Lastly, deposition values for both pesticides were higher on the horizontally oriented chromatography paper than the vertically oriented chromatography paper. Further work is needed to validate the correlation of deposition levels of various pesticides occurring on both horizontal and vertical deposition samplers of a range of materials of construction. Knowledge of this information may lead to a better understanding of deposition onto ground surfaces and human dermal exposure, by using horizontal and vertical deposition samplers respectively. Further studies should be done on the interactions that exist between pesticide deposition samplers and different types of pesticides so that the optimum sampler for each pesticide class can be determined. In addition, different pesticide mixtures have different adjuvants and surfactants, and these may affect the way in which the pesticide interacts with the sampler. On-site analysis of deposition samplers using portable GC-MS may reduce analyte loss and provide a useful future alternative monitoring option.

The field deposition data from both sampling campaigns in this study was compared to AgDISP modelled data. In the first sampling campaign, the model under-predicted the deposition values for atrazine, whilst in the second sampling campaign the model under-predicted deposition values at 0 m only. As the distance from the spray area increased, there was better agreement between the model and the field deposition data. The findings of this study make it apparent that field deposition studies are still important to arrive at buffer distances that accurately reflect environmental concentrations of pesticides arising from off-target deposition during pesticide applications.

In this study, a range of pesticide deposition samplers with different materials of construction were successfully directly compared in the collection of off-target deposition of atrazine (and terbuthylazine when present in the formulation) and chromatography paper was found to be the best deposition sampler for this application under local conditions. The findings of this study reveal that several knowledge gaps still exist in the determination of off-target deposition using pesticide active ingredients.

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Appendix

Published Review Article:

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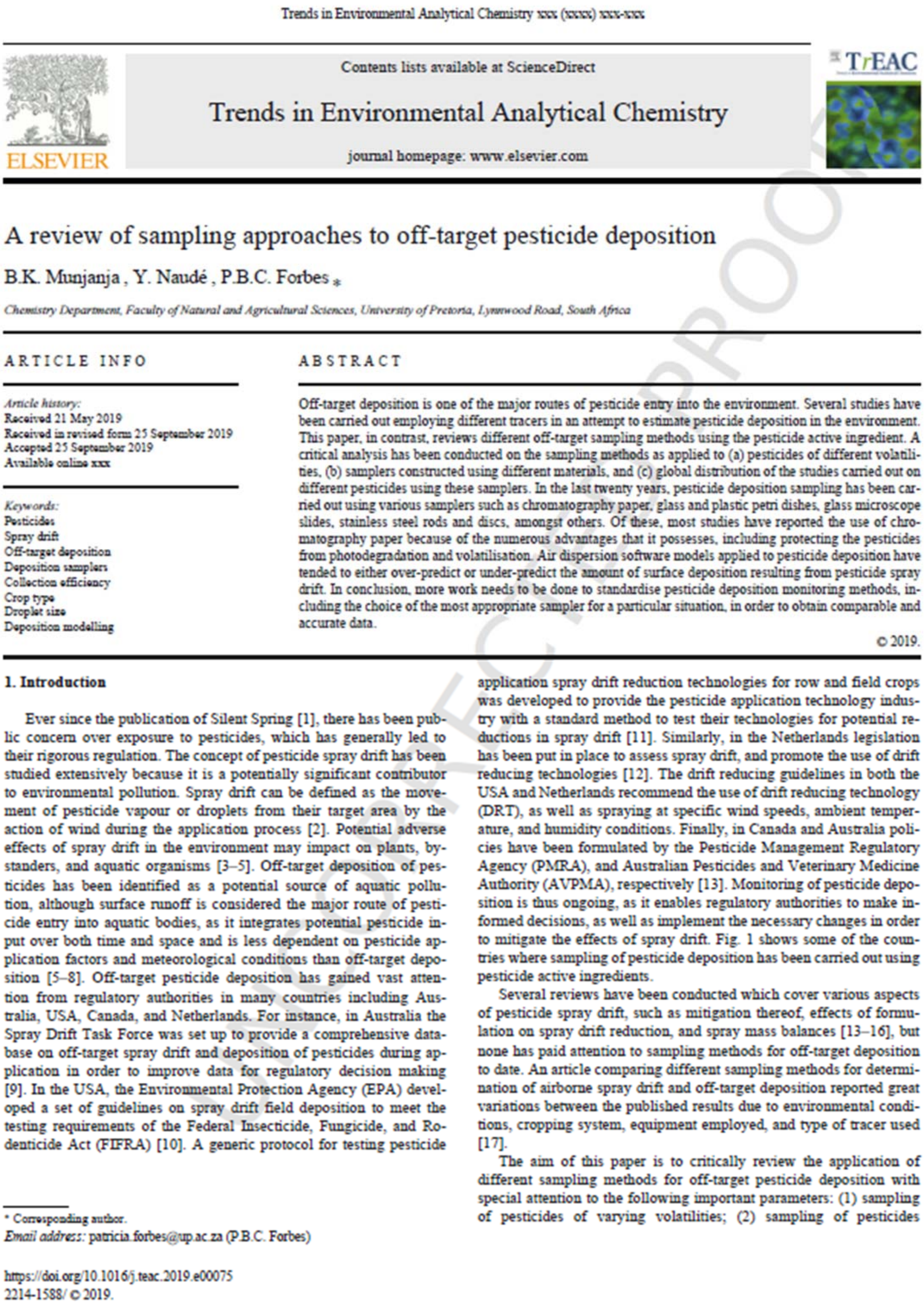

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A review of sampling approaches to off-target pesticide deposition

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ABSTRACT

Off-target deposition is one of the major routes of pesticide entry into the environment. Several studies have been carried out employing different tracers in an attempt to estimate pesticide deposition in the environment. This paper, in contrast, reviews different off-target sampling methods using the pesticide active ingredient. A critical analysis has been conducted on the sampling methods as applied to (a) pesticides of different volatilities, (b) samplers constructed using different materials, and (c) global distribution of the studies carried out on different pesticides using these samplers. In the last twenty years, pesticide deposition sampling has been carried out using various samplers such as chromatography paper, glass and plastic petri dishes, glass microscope slides, stainless steel rods and discs, amongst others. Of these, most studies have reported the use of chromatography paper because of the numerous advantages that it possesses, including protecting the pesticides from photodegradation and volatilisation. Air dispersion software models applied to pesticide deposition have tended to either over-predict or under-predict the amount of surface deposition resulting from pesticide spray drift. In conclusion, more work needs to be done to standardise pesticide deposition monitoring methods, including the choice of the most appropriate sampler for a particular situation, in order to obtain comparable and accurate data.

1. Introduction

Ever since the publication of Silent Spring [1], there has been public concern over exposure to pesticides, which has generally led to their rigorous regulation. The concept of pesticide spray drift has been studied extensively because it is a potentially significant contributor to environmental pollution. Spray drift can be defined as the movement of pesticide vapour or droplets from their target area by the action of wind during the application process [2]. Potential adverse effects of spray drift in the environment may impact on plants, bystanders, and aquatic organisms [3–5]. Off-target deposition of pesticides has been identified as a potential source of aquatic pollution, although surface runoff is considered the major route of pesticide entry into aquatic bodies, as it integrates potential pesticide input over both time and space and is less dependent on pesticide application factors and meteorological conditions than off-target deposition [5–8]. Off-target pesticide deposition has gained vast attention from regulatory authorities in many countries including Australia, USA, Canada, and Netherlands. For instance, in Australia the Spray Drift Task Force was set up to provide a comprehensive database on off-target spray drift and deposition of pesticides during application in order to improve data for regulatory decision making [9]. In the USA, the Environmental Protection Agency (EPA) developed a set of guidelines on spray drift field deposition to meet the testing requirements of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) [10]. A generic protocol for testing pesticide application spray drift reduction technologies for row and field crops was developed to provide the pesticide application technology industry with a standard method to test their technologies for potential reductions in spray drift [11]. Similarly, in the Netherlands legislation has been put in place to assess spray drift, and promote the use of drift reducing technologies [12]. The drift reducing guidelines in both the USA and Netherlands recommend the use of drift reducing technology (DRT), as well as spraying at specific wind speeds, ambient temperature, and humidity conditions. Finally, in Canada and Australia policies have been formulated by the Pesticide Management Regulatory Agency (PMRA), and Australian Pesticides and Veterinary Medicine Authority (AVPMA), respectively [13]. Monitoring of pesticide deposition is thus ongoing, as it enables regulatory authorities to make informed decisions, as well as implement the necessary changes in order to mitigate the effects of spray drift. Fig. 1 shows some of the countries where sampling of pesticide deposition has been carried out using pesticide active ingredients.

Several reviews have been conducted which cover various aspects of pesticide spray drift, such as mitigation thereof, effects of formulation on spray drift reduction, and spray mass balances [13–16], but none has paid attention to sampling methods for off-target deposition to date. An article comparing different sampling methods for determination of airborne spray drift and off-target deposition reported great variations between the published results due to environmental conditions, cropping system, equipment employed, and type of tracer used [17].

The aim of this paper is to critically review the application of different sampling methods for off-target pesticide deposition with special attention to the following important parameters: (1) sampling of pesticides of varying volatilities; (2) sampling of pesticides

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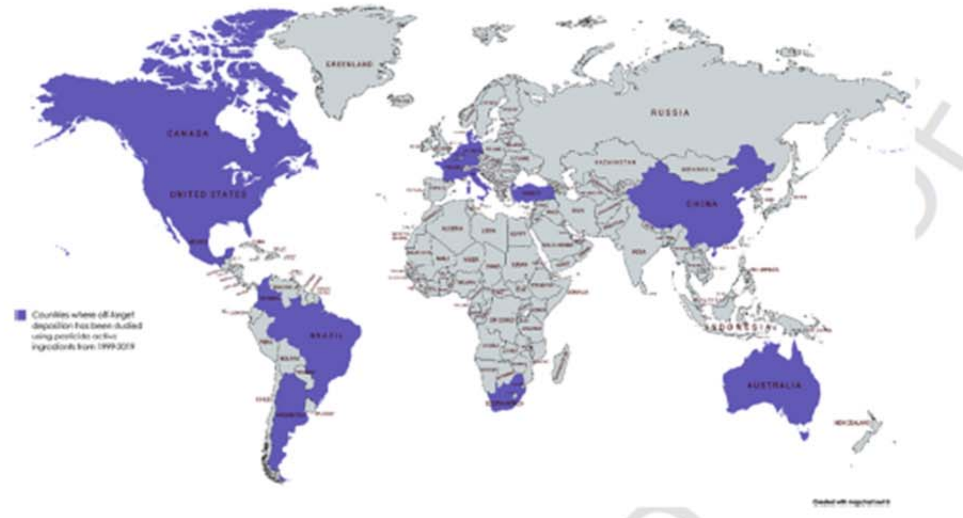

Fig. 1. .

using samplers of various materials of construction ; (3) global distribution of studies carried out to date on the various pesticides, and (4) comparison of pesticide deposition estimations obtained from software models with the monitoring results obtained from various deposition samplers. Moreover, the scope of this review is limited to deposition sampling of pesticide active ingredients in the period from 2000 to 2018, and excludes deposition sampling utilising tracers such as dyes and metal cations.

2. Deposition samplers

The goal of pesticide sampling is to obtain representative samples of the application being investigated, while minimizing bias during sample collection. Various methods are available for sampling spray deposition, and the choice of technique depends largely on the data requirements of the study, cost, and availability of equipment [17]. In addition, the basic requirements of samplers for deposition are that they should: (1) have high collection efficiencies of small droplets in relatively low air speeds, (2) have a definable sampling volume or area, (3) to be such that the captured spray drift can be recovered and quantified from the sampler, (4) easy to handle under field conditions, (5) cheap, (6) and should collect an adequate volume of drift before saturation [18].

2.1. Interaction between droplets and deposition samplers

Before we discuss the various samplers used in deposition monitoring, it is imperative to discuss the processes that may take place when the pesticide droplets interact with the surface of the sampler. The droplets can either adhere, rebound or shatter (Fig. 2), depending on the characteristics of the liquid (such as surface tension and viscosity), droplet parameters (including size and velocity), and sampler surface parameters (roughness, orientation, wettability, *etc.*) [19,20]. As a result of all these factors, the amount of kinetic energy lost by the droplets upon impaction on the sampler may vary. If less energy is lost, the droplets will rebound, but if the energy losses are high, the droplet will adhere to the sampler surface [21]. The high energy losses result from the spread of the droplets on the surface, and the subsequent recoiling due to surface tension [22]. Shattering corresponds to the formation of a number of smaller droplets due to impact pressure [23] .

2.2. Types of samplers

Pesticide deposition samplers are typically classified according to their orientation that is, either horizontal or vertical [9]. Horizontal deposition samplers such as filter paper [24–26], petri dishes [27,28], and Mylar cards [29] are used when information on spray deposition on an aquatic or ground surface is required. They capture droplets by sedimentation, which takes place when droplets falling under gravity reach a constant velocity known as the sedimentation velocity, the value of which depends on the droplet size [30,31]. Vertical deposition samplers such as alpha cellulose cards oriented perpendicular to the ground, strings made of cotton, cylinders, plastic drinking straws, or Teflon spheres provide information on relative drift of one field trial compared to another [30,32–34]. These capture droplets by impaction, and this refers to the collection of particles present in an airstream on the vertical surface of the sampler [35]. However, in real life, droplets tend to follow a divergent flow round the target and not impact [35]. For this reason, it is important to calculate the collection efficiency of both horizontal and vertical deposition samplers.

3. Collection efficiency

Collection efficiency is defined as the fraction of droplet mass deposited on the surface of a sampler from the bulk air volume [36]. This value is usually less than 100% because different collectors cause changes in air flow patterns, and this may lead to droplets going around a collector rather than impacting or sedimenting on it [37]. Therefore when calculating the collection efficiency, a correction has to be made comparing the amount of droplets caught by the collector to the amount which would have passed through the frontal area of the collector, in the absence of the collector [37]. Thus, the collection efficiency is related to the impaction parameter, defined

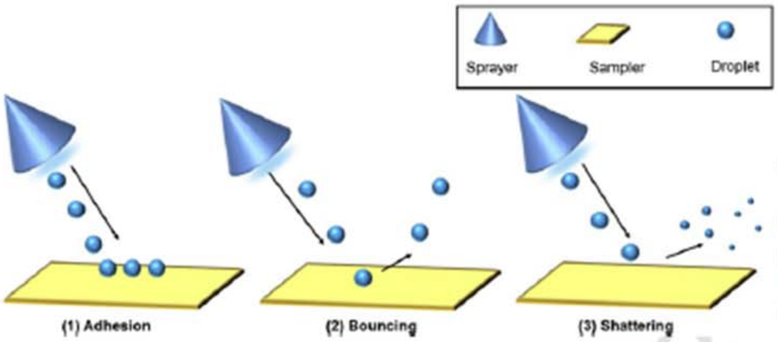

Fig. 2. Diagram illustrating adhesion, bouncing and shattering of droplets upon interaction with a sampler surface.

as:

$$P = \frac{\rho_d V d^2}{18 \mu D} \quad (1)$$

Where P is the impaction parameter, ρ the droplet density ($1000\,kg\,m^{-3}$), V is the undisturbed flow velocity (ms^{-1}), d is the droplet diameter (m), μ is the air viscosity ($1.8 \times 10^{-5}\,kg\,m^{-1}s^{-1}$), and D is the diameter/width of the collector. Thus, the collection efficiency increases when the diameter of the sampler decreases, and the velocity and size of the droplet increases.

Several studies have been carried out to quantify the collection efficiencies of different deposition samplers. A study carried out on cylindrical samplers showed that the collection efficiencies increase as the collection surface narrowed, and as the size of the droplets increased [38]. Collection efficiencies for nylon screen collectors varied from 50 to 70% for spray droplets with volume median diameter less than 45 µm for air speeds of $4\,ms^{-1}$ [39]. Thus the collection efficiency of a sampler is affected by its shape, size, orientation to the wind, air flow through and around the sampler, meteorological conditions, and material of construction [36].

4. Sampling of pesticides

4.1. The sampling process

The measurement of off-target deposition using deposition samplers is guided by many standards. Firstly, sampling of off-target deposition should be determined in a defined downwind area, with minimum obstructions, other than the target crop, that could influence the airflow in the region of measurement, and the topography of the sampling site should be recorded [2]. Most studies report the absence of obstacles around the treated field [40,41]. Regarding the slope, Brain et.al (2019) carried out their study in an area of uniform slope [42], whilst Capri et.al determined off-target deposition of chlorpyrifos in two fields, where one was flat, and the other one was sloped [41]. In another study, Le Francq et.al carried out deposition monitoring of kresoxim methyl in an area with a slope of 15% [43]. It is however worth noting that some studies do not report the slope of the area where off-target deposition was made, hence making the comparison of deposition values potentially difficult.

Wind direction is another important aspect when conducting deposition monitoring, where frontal winds lead to higher drift potential than lateral winds [44]. Samplers should be placed downwind of the treated field, and spraying is carried out perpendicular to the wind direction. The mean angle between the horizontal wind direction and the sampling line should not exceed 30^0 [11]. In some cases, the wind direction may change during the sampling event, and this may lead to variations in the amount of pesticide deposited at each sampling position. For this reason, sampling of off-target deposition should be carried out when the wind direction is constant. Wind speed is another major factor that affects off-target deposition of pesticides. High wind speeds have been found to give greater deposition in the near field (distances less than 30 m), where large droplets are deposited by gravitational forces [45]. Most pesticide deposition monitoring studies have been carried out at wind speeds less than $15\,ms^{-1}$ [40,41,43], however in some cases the wind speeds have been higher than this [42,46].

After spraying has been carried out, the samplers need to be collected prior to transportation to the laboratory for analysis. Various sample collection times have been reported, but most of them report times of between ten to thirty minutes to allow for enough transport of the pesticide to the sampler locations and to enhance detection [40,42,47]. For instance, Brain et.al collected the samples ten minutes after the spraying process [42]. In another study, deposition samples were also collected after ten minutes [47]. However, many studies do not report the time at which the samples were collected after the spraying process [48]. Thus it is recommended that the time delay after spraying should be reported to allow for comparisons to be drawn between different studies.

4.2. Glass samplers

Glass surfaces are mainly used to sample pesticide deposition because they have high capture efficiencies [49] and are easily extracted. The advantages of glass petri dishes, which is the most commonly used glass sampler, is that they allow for low pesticide detection limits, they are easy to handle, and low extraction volumes are required per unit pesticide sampled [32,50]. However, the presence of a raised edge may negatively affect the deposition of droplets near the edge of the petri dishes [51]. Another disadvantage of glass petri dishes is that volatilisation can take place from their surface resulting in an underestimation of pesticide deposition [27]. This is of concern for the more volatile pesticides.

With respect to pesticide deposition studies utilising glass petri dishes, various approaches have been used including the placement of glass fibres inside the petri dishes to collect the pesticide [27], filling the glass petri dish with water [52], or without placing any solvent or glass fibres inside the sampler [43,53]. The type of solvent used may contribute to the volatilisation of the analyte from the surface of the sampler, as exemplified by a study where ethyl acetate caused atrazine and alachlor to volatilise more readily from the glass petri dishes, as compared to water [27].

Various crops have different crown shapes, crown size, foliage density and planting arrangement or configuration, all of which affect the amount of off-target deposition [54]. However, regardless of all these factors, glass petri dishes have been successfully applied to sample pesticides in field crops, vineyards, and orchards [27,28,43,52,53]. Fifty one glass petri dishes were successfully used to sample deposition of kresoxim methyl in vineyard catchments, for example [43]. The variations obtained in the deposition values were explained by the interception of the spray by the vine plants, and the variations in exposure time according to the application period at each plot. In orchards, off target deposition rates can be affected by orchard structure (spacing between rows), among other factors [55]. Glass petri dishes have been successfully used in orchards to sample off target deposition of azinphos-methyl, with predicted deposition rates comparing very well with measured deposition rates [52].

The volatility of a pesticide is an important property that may determine the extent to which it drifts off-target during application. [56]. Generally, it is expected that off-target deposition will be higher for the more volatile pesticides. A study for example was carried out to determine off-target deposition of atrazine (vapour pressure 3.85×10^{-5} Pa) and alachlor (vapour pressure 2.1×10^{-3} Pa) using glass petri dishes containing glass fibres outside a maize field [27]. Deposits of both atrazine and alachlor were very low at around 100 μgm^{-2}. However, deposits of alachlor, the more volatile pesticide, were slightly higher than those of atrazine. In contrast, a study was carried out to determine off-target deposition of cymoxanil (vapour pressure 1.5×10^{-4} Pa), folpet (vapour pressure 2.1×10^{-4} Pa), and tebuconazole (vapour pressure 1.3×10^{-6} Pa), where off-target deposits followed the order tebuconazole > folpet > cymoxanil, whilst in the second application the order was folpet > tebuconazole > cymoxanil [53]. The authors thus concluded that pesticide deposition trends were difficult to account for due to variations in climatic parameters during each spray event. Furthermore, the deposition trends for pesticides of different volatilities are summarised in Table 1.

Glass microscope slides are another type of glass sampler that have been used to sample off target pesticide deposition. The advantages of glass microscope slides are that deposits can be washed off easily using a relatively small volume of solvent, however the deposition amounts may be affected if the slides are not exactly horizontal [50]. The use of glass microscope slides has not been reported for off-target deposition of pesticides in crop types such as orchards and vineyards for the last twenty years. However, they were used to sample off-target deposition of herbicides of diverse volatilities in an open field [40]. To investigate the effect of pesticide volatility on off-target deposition of the pesticides onto the glass microscope slides, the same research group carried out another study [49]. It was reported that evaporation from the surface of the glass microscope slides was not directly related to the pesticide vapour pressure, as some pesticides with low vapour pressures dissipated from the surface of the glass slides. Moreover, they underscored the need for more research into the relationship between vapour pressure and evaporation from the surface of the glass slides. Glass microscope slides have been successfully used to investigate the effect of formulation type on off-target deposition in a drift chamber [57]. It was reported that formulation type did not affect deposition of quinclorac and 2,4-D onto glass microscope slides. In conclusion, the behaviour of pesticides of varying volatilities, and different formulations on microscope slides is an area that still needs to be studied in order to fully understand the interaction, while keeping other conditions constant.

4.3. Paper based samplers

Samplers constructed from paper are typically used because of their flat surface which enables them to represent deposition in aquatic bodies [59]. A distinct advantage of alpha cellulose samplers is that they protect the pesticides from photodegradation and volatilization [41]. In addition, they have good absorbent properties which enables droplets to be captured efficiently without any bouncing off the surface, and allowing efficient analytical extraction [9,26]. The disadvantage of chromatography paper samplers is that they are less representative of an area covered with vegetation [60]. The majority of studies carried out have reported the use of patented chromatography paper such as Whatman®, and type GR512 (Proctor and Gamble, USA) filter paper or alpha cellulose strips [9,46,47,61]. It is important to note that both Whatman® chromatography paper and ordinary alpha cellulose strips are constructed from cotton cellulose and have thus a high degree of polymerization and crystallinity [62]. However, in most of the studies, the use of Whatman® chromatography paper has been reported, but its grade is not specified even though knowledge of the grade gives an idea about the particle retention properties of the chromatography paper. In some studies, chromatography paper is also referred to as filter paper or ground plates [45,63].

Chromatography paper samplers may be mounted very close to the ground in order to represent pesticide deposition on the soil, however where there is vegetation that may obstruct the samplers, the height may be increased. Chromatography paper samplers have been mounted on wooden boards, plastic platforms, or in some cases circular filter paper has been mounted in petri dishes [46].

Whatman® chromatography paper and ordinary alpha cellulose strips have been successfully used to sample pesticides in field crops, vineyards, and orchards [46,47,61,64]. The crop type together

Table 1
Comparison of off-target deposition of pesticides of differentvolatilities.

Pesticides and vapour pressures	Deposition sampler	Trend in deposition	Reference
Atrazine (3.85×10^{-5} Pa), alachlor (2.1×10^{-3} Pa)	Glass petri dishes	Deposition was higher for alachlor than atrazine	[27]
Cymoxanil (1.5×10^{-4} Pa), folpet (2.1×10^{-4}Pa), tebuconazole (1.3×10^{-6} Pa)	Glass petri dishes	In the first application deposition was tebuconazole > folpet > cymoxanil. In the second application deposition was folpet > tebuconazole > cymoxanil	[53]
Diazinon (1.2×10^{-2} Pa), malathion (5.3×10^{-3} Pa)	Alpha cellulose sheets	No significant differences at distances <300 m. deposition was higher for diazinon at distance >300 m	[9]
Metribuzin (5.33×10^{-5} Pa), prosulforcarb (9.33×10^{-5} Pa)	Crepe paper	Deposition was higher for prosulforcarb the more volatile pesticide	[58]
Glyphosate (1.3×10^{-5} Pa), glufosinate (3.1×10^{-5} Pa)	Stainless steel plates	Spray deposits were lower for glyphosate in two different applications	[53]

with other application and meteorological factors influences the maximum distance at which deposition is observed. Whatman® chromatography paper (50 × 10 cm) was successfully used to sample off-target deposition of chlorpyrifos and metalaxyl in a vineyard catchment [61]. The maximum deposition distance was around 24 m, being further reduced to 18 m with the presence of a tree row around the agricultural field. Cellulose strips have been used to sample off-target deposition of captan and tolylfluanide in orchards [46]. Deposition of the pesticides was observed up to 40 m, and the values were lower when the crops had fully developed crop foliage [61]. It is imperative to note that another study carried out using chromatography paper to sample off-target deposition of chlorpyrifos methyl in citrus orchards, showed the importance of sprayer type [8]. The same sampler has been used to sample off-target deposition of atrazine in a maize field, with detection up to 400 m from the application site [47].

Alpha cellulose sheets (type GR512, Proctor and Gamble, USA) were successfully used to evaluate the effect of pesticide volatility on deposition rates [9]. Differences in deposition between the two pesticides, diazinon (vapour pressure 1.2×10^{-2} Pa) and malathion (vapour pressure 5.3×10^{-3} Pa) were only observed beyond 300 m from the edge of the field, because diazinon is more volatile than malathion and hence produces more airborne droplets than malathion.

Water sensitive paper (WSP) is one type of sampler that has been greatly used to indicate off-target deposition of pesticides. It is coated with a yellow surface which turns dark blue in contact with aqueous droplets, due to the reaction of the water with the bromophenol-blue indicator present in the paper, which changes to blue in the pH range 2.8–4.6 [65]. The amount of area covered on the WSP which has changed colour thus reflects the amount of drift [66]. This type of sampler was used to sample off-target deposition of etofenprox in Italian vineyards [67]. The major limitation of the WSP is that droplets less than 50 μm are unable to create a detectable stain [68]. Moreover, a limitation of this technique is that the active ingredient is not analysed, it only qualitatively shows us that off-target deposition has taken place, and estimates the fraction of the droplet size distribution that contributed to the off-target drift [69]. Crepe-paper was used to sample off-target deposition of various herbicides, fungicides, insecticides, and their metabolites [58]. In this study, the area of the sampling paper was varied according to the amount of pesticide applied per hectare, and the distance from the application site. The findings of the study showed that off-target deposition was higher for the more volatile pesticides as shown in Fig. 3. For instance for measurement 3, metribuzin (vapour pressure 5.33×10^{-5} Pa) showed lower deposition than prosulforcarb (vapour pressure 9.33×10^{-5} Pa) under similar application and environmental conditions.

4.4. Other samplers

While several other samplers such as drinking straws, filament lines, polystyrene cords, and Teflon spheres have been used before 1999, their use has not been reported in pesticide deposition monitoring studies more recently because of some serious shortcomings. For instance with drinking straws challenges may be experienced with analyte recovery and stability prior to extraction [32,59]. Thus the materials employed in the past two decades have been carefully selected based on the fact that their collection efficiencies were known to be acceptable. Cotton cloth was successfully used to sample off-target deposition of malathion [70], whilst synthetic wool yarn was found to have a collection efficiency of between 40 and 100% [71] and it has been successfully used to sample off-target deposition of pesticides such as fenthion and permethrin [72,73]. The disadvantages of wool are that they are less suitable for volatile pesticides, as evaporation may take place leading to underestimation of deposition [71]. Moreover, for wool traps made by winding wool in between the grooves of an aluminium frame in a zig zag manner, the major disadvantage is the high solvent consumption resulting from purification of the wool prior to use [47].

Nalgene Versi-Dry lab soakers, which are used in spill containment are composed of paper with a skid-resistant, waterproof chemical resistant polyethylene backing that makes absorption easy [74]. They were recently used to determine off-target deposition of imidacloprid and beta-cyfluthrin in a vineyard [75]. It was observed that the deposition values were affected by vegetation and trellising stakes throughout the downwind sampling area past the 7.5 m sampling position. The authors were unable to calculate the collection

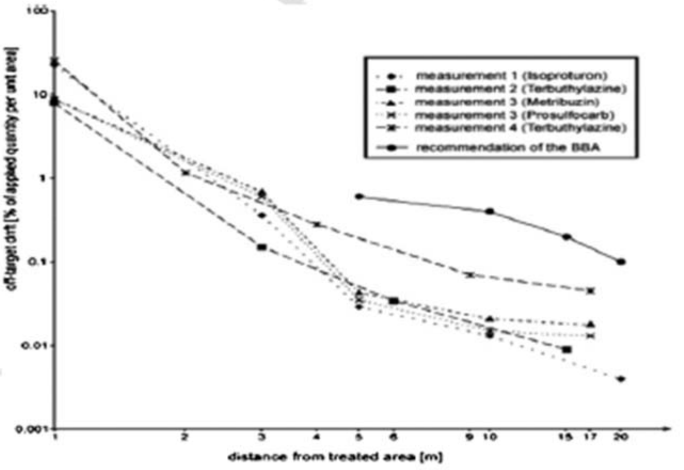

Fig. 3. Off- target drift of pesticides as a function of distance from the treated area [58] (Reproduced with permission from Elsevier). BBA- Federal Biological Research Center for Agriculture and Forestry.

efficiency of the Nalgene Versi-Dry lab soakers because there was insufficient data to do so.

Other samplers that have been successfully used to sample off-target deposition of pesticides in different crop types include stainless steel plates, Teflon targets and plastic petri dishes [53,76,77]. In a study to evaluate the effect of formulation type on off-target deposition of imidacloprid, for example, plastic petri dishes were successfully used as the samplers [77]. Stainless steel plates were used to determine off-target deposition of glyphosate (vapour pressure 1.3×10^{-5} Pa) and glufosinate ammonium (3.1×10^{-5} Pa), and less deposition was obtained for the less volatile glyphosate under different climatic conditions [53].

Recently, circular stainless steel discs ($113\,\text{cm}^2$) and rods ($6.35\,\text{cm}^2$) were used to sample horizontal and vertical deposition of atrazine and mesotrione, respectively [42,48]. In both studies, deposition was notably higher on the vertical rods as compared to the circular discs. For instance, as described in Brain et al. (2019), 7 to 41 times more atrazine mass was collected from vertical rods (from airborne drift) as compared to the horizontally placed stainless steel discs (reflective of ground deposition). A major difference between the two studies was that higher deposition amounts were obtained in the study carried out using atrazine (up to $21.6\,\text{g}\,\text{ha}^{-1}$ for horizontal collectors, and $197\,\text{g}\,\text{ha}^{-1}$ for vertical rods) compared to the one using mesotrione (up to $0.261\,\text{g}\,\text{ha}^{-1}$ for horizontal collectors, and $3.969\,\text{g}\,\text{ha}^{-1}$ for vertical rods). This may be attributed to differences in wind speed, temperature, application rate and driving speed between the two studies, as well as the use of different nozzles [42,48].

Table 2 summarises some of the off-target deposition monitoring studies carried out to date on active ingredients using various samplers

5. Comparison of monitored deposition on samplers with results from modelling studies

Spray drift models are an important tool for understanding the phenomenon of off-target deposition. To date several studies have been carried out to simulate droplet movements in the air using either plume or droplet trajectory models [87]. The difference between the two is that plume models calculate the droplet cloud displacement and chemical agent concentration from environmental conditions [88], while droplet trajectory models estimate the movement and positions of the droplets under individual physical forces. The Agricultural DISPersal (AgDISP) model, which was developed by the Spray Drift Task Force, is based on Lagrangian calculations, and can be used to simulate deposition during both aircraft and ground application. AgDRIFT is a commercial spin-off of AgDISP and uses similar algorithms to AgDISP [47]. AgDRIFT® is a near-field empirical curve fitting model at Tiers I and II, but mechanistic (Lagrangian dispersion model) at Tier III [89,90]. AGDISP is linked to a Gaussian extension module to estimate far-field drift, and the model has been verified with field observation data up to 300 m [91]. However, AgDRIFT over-predicts deposition fractions in the far- field (>50 m) by a factor as high as 4-fold [92].

For instance, in a study carried out to compare AgDRIFT model simulations of aerially applied pesticides (diazinon, malathion, and carbaryl) to monitored field deposition onto horizontal alpha cellulose cards, the model over-predicted deposition rates relative to field data for far-field distances [93]. The authors attributed the lower sample collection at the far-field to wind deviations and to limitations of the algorithm, but sampling efficiencies of the samplers for the different pesticides were not considered.

Conversely, a comparison of deposition rates predicted by AgDISP for atrazine against field deposition data on chromatography paper showed that the model under-predicted the field deposition data by up to an order of 10 [47]. This may be due to differences in the application technique, with the former study having been carried out using aerial application and the latter study involving ground based application. In addition, the physical properties of the spray solutions might have been different. It is of paramount importance to note that both AgDISP and AgDRIFT® have the limitation of assuming a flat terrain, and the absence of vegetative barriers [13]. For this reason, when carrying out exposure assessments using modelled data, regulators should be aware of these limitations.

Another model that has been compared to field deposition data is the Fugitive Dust Model (FDM) [94]. The performance of this model was evaluated in the aerial application of methamidophos. The usefulness of this model could not be verified as results were limited by the sparse distribution of the deposition samplers although the type of deposition sampler was not mentioned. A discussion of the various models for predicting off-target deposition has been done by Craig [95] in which he acknowledged the agreement between aircraft wake models such as Forest Service Cramer, Barry and Grim (FSCBG), AgDRIFT, and Gaussian Diffusion Sedimentation (GDS) for downwind distances greater than 50 m. However, most of the models do not calculate deposition of droplets on a solid surface, rather they calculate the flux of particles through an imaginary plane at height zero. This is not always the case as the ground deflects the droplets and the air. Hence the authors suggested that the models should be refined to incorporate the collection efficiencies of the different samplers [95]

6. Quality control techniques

Like any other sampling technique, the reliability of the results depends on the quality control process and major variations may be observed between studies if the procedures followed in sampling of off-target deposition of pesticides are not standardised. Before deposition samplers can be used in the field, analyte extraction recovery and transit stability tests need to be carried out [96]. According to the US EPA (2012), recoveries obtained should be between 70 and 120%, and thus most deposition samplers that have been used meet this criteria [97]. If the extraction recoveries obtained meet this criteria, no correction is made for the deposition amounts obtained [46]. For instance, analyte extraction recoveries of atrazine from stainless steel discs and rods were found to be 111 ± 7.4% (n = 9), and 109 ± 3.7% (n = 31) respectively [42]. Extraction recovery tests have also been done for different pesticides on glass microscope slides, with high recoveries of between 74 and 121% being obtained [40]. Zhao et.al (2014) carried out extraction recovery tests of imidacloprid on glass petri dishes, and recovery rates were between 96.8–98.5% [28]. Extraction recoveries of atrazine and alachlor from petri dishes have also been found to be high (>84%) [27]. Extraction recoveries of four pesticides (isoproturon, terbuthylazine, metribuzin, and prosulfocarb) were determined from crepe paper, and the recoveries were between 89 and 102% [58]. Extraction recovery tests of atrazine on chromatography paper were found to be >100% [47], and for chlorpyrifos and metalaxyl were between 90 and 105% [41,61]. Despite the importance of carrying out extraction recovery tests prior to sampling, they have been omitted from some studies, where 100% recovery from the sampler was assumed [43].

It is imperative to carry out transit stability tests for various pesticides on different samplers, because their physical properties are different, and so are their interactions with the different sampler materials. For instance, when the transit stabilities of epoxiconazole,

Table 2
Summary of the application of different samplers in sampling the monitoring of off-target deposition of pesticides.

Deposition sampler type, and dimensions	Country of study	Type of crop	Pesticides	Average wind speed m/s	Average temperature ^{0}C	References
Glass petri dishes (150 ID × 25 mm)	France	Vineyard	Kresoxim methyl	1.9	24	[43]
Glass slides (17.7 × 11.5 cm	Denmark	Field	Pendimethalin, metamitron, desmedipham, phenmedipham,ethofumesate, prosulfocarb, ioxynil octanoate, bromoxynil octanoate, tribenuron methyl, fluoroxypyr-1-methylheptylester	4.4	13.1	[40]
Whatman chromatography paper (50 × 10 cm)	Italy	Vineyard	Chlorpyrifos, metalaxyl	2.6	20	[61]
Stainless steel plates, glass petri dishes	France	Vineyard	Glyphosate, glufosinate, cymoxanil, folpet, tebuconazole, pyraclostrobin	3.1	21.4	[53]
Glass petri dishes (9 cm ID × 1.3 cm)	China	Wheat	Imidacloprid	1.8		[28]
Water sensitive paper (76 × 25 mm)	Italy	Vineyard	Etofenprox	Still wind	31	[67]
Filter paper	Italy	Vineyard	Chlorpyrifos	2.8	28.8	[41]
Glass petri dishes (15 cm ID)	South Africa	Orchards	Azinphos-methyl	–		[52]
Filter paper (27 × 15 cm)	South Africa	Sorghum field	Atrazine	5.17	26.57	[47]
Glass petri dishes with glass fibre (8 cm ID)	France	Maize field	Atrazine, alachlor	2.2	24.2	[27]
Aluminium backed silica gel chromatography sheets (10 cm × 20 cm)	United States of America	Orchard	Phosmet	5.0	21.3	[78]
Teflon targets (5.1 cm × 5.1 cm)	United States of America	Citrus orchard	Oxamyl	–	–	[76]
Teflon targets (5.08 × 5.08 cm)	United States of America	Foliage plant nursery	Methiocarb	–	–	[79]
Plastic petri dishes	Netherlands	–	Imidacloprid	4.3	7.4	[77]
Crepe paper (29.5 × 4-14 cm)	Germany		Various herbicides, insecticides and fungicides	–	–	[58]
Cellulose strips (25 cm × 25 cm	Belgium	Orchard	Captan and tolylfluanide	21.5	2.8	[46]
Wool traps	South Africa	–	Fenthion	–	–	[72]
Filter paper and filtering cloths	Germany	–	Tolylfluanide	6.5		[80]
Cotton wool (100 cm^2)	United States of America	Open field	Permethrin	3.6	21.5	[73]
Glass bowls consisting of distilled water, surface area of 75 cm^2, and 4 cm depth	South Africa	Orchard	Azinphos-methyl, endosulfan	1.7	20.9	[6]
Paper tape 5 cm wide	Italy	Citrus orchard	Chlorpyrifos methyl	0.9	32.2	[81]
Petri dishes	Argentina	Apple orchards	Azinphos-methyl		29.5	[82]
9 cm diameter glass microfiber filter discs (Whatman 934-AH, 1.5 μm pore size) placed in polystyrene petri dishes	United States of America	Engelman spruce and lodge pole pine trees	Carbaryl	3.5	10.6	[83]
Glass plate collectors (10 × 20 cm), and adsorbent gauze pads	United States of America	Corn	Chlorpyrifos, permethrin, carbaryl	4.4	23.7	[84]
Water sensitive paper	Costa Rica	Banana plantation	Chlorothalonil			[85]
Water sensitive paper		Cotton	Glyphosate	3.1	28.5	[86]
Steel vertical rods, and steel circular discs	United States of America		Atrazine	15	30	[42]
Steel vertical rods, and steel circular discs	United Kingdom	Lettuce and tomato	Mesotrione	5.1	19.1	[48]

fenpropimorph, and kresoxim methyl on filter paper were determined, the recovery values were very low for epoxiconazole (27%), and fenpropimorph (17%), but were higher for kresoxim methyl (>88%), thus only deposition values for the latter were reported [98]. Transit stability tests have also been carried out for atrazine, on both stainless steel discs and rods which gave high recoveries of 93%, and 111% respectively, showing that the samples did not degrade over the analysis time of 14 days [47].

Each time a sampling campaign for pesticide deposition monitoring is carried out, different quality control procedures are employed to ensure reporting of accurate results, and to avoid contamination of samples. Quality control steps must be taken during sample handling, mounting of samplers, and collection of samplers after spraying [2,10,99]. A useful technique that is carried out is the use of upwind controls as a way of checking if there has been a change in wind direction [100,101]. In addition, field blanks are also an integral component of the sampling campaign. These are samplers that are taken to the field but are not mounted [47]. Most pesticides have, by design, very short half-lives thus they degrade quickly to avoid persistence in the environment. To ensure that the correct amount of deposition is measured, samples must be transported to the laboratory under refrigerated conditions immediately after sampling [27]. It is worth noting that some samplers, such as the microscope slides, may cause volatilisation of pesticides faster than others for example atrazine has been reported to volatilise quickly from the surface of glass slides, hence in order to report the correct amount of pesticide deposited, microscope slides should be immediately soaked in the extraction solvent in the field [40]. Finally, with regards to sample collection post spray application it is always advisable to start by collecting the samples furthest from the application site to prevent contamination [96]. An additional quality control measure that is recommended is the use of internal standards when quantifying the amount of deposition during chromatographic analysis in order to normalise the response of the analyte, as well as to compensate for variations that may take place during the analytical process [102]. The most common internal standards are deuterium-labelled pesticides, which have a high degree of stability, although they may be very expensive [103].

7. Conclusion and future perspectives

While considerable work has been done on sampling off-target pesticide deposition for the past two decades, a lot still needs to be understood regarding optimisation of the samplers employed, and their interaction with the various pesticides. Specifically:

- Studies need to be carried out on the interaction between different pesticides and different types of samplers in terms of their material of construction. That is, it still remains to be determined which sampler is the most ideal in measuring off-target deposition for various pesticides mixes, taking into account any adjuvants and surfactants that may be present, including the pesticide active ingredient itself. A better knowledge of how particular pesticides interact with a particular type of sampler would lead to further validation of deposition monitoring approaches. Consequently, it may lead to some coherence between certain types of samplers, and deposition models, and hence a better understanding of how much deposition has taken place. Importantly, such information will allow regulatory bodies to have more information available to make informed decisions on the management of potential impacts of off-target pesticide deposition.
- The collection efficiencies of various samplers should be known, and more studies are required to validate pesticide deposition models. Several updates have been made to the AgDISP model [104], hence further studies may be needed to compare field deposition data with the modelled data in order to ascertain whether previously observed over-prediction or under-prediction persists.
- Off-target deposition samplers should be standardised for particular applications (such as for a specific pesticide).
- For standardisation of the deposition monitoring process, it is recommended that the US EPA generic verification protocol for testing pesticide application spray drift reduction technologies for row and field crops be adopted, as it contains guidelines on many important aspects. This improves comparability of the sampling process for different studies.
- Relative sampling efficiency of different deposition samplers is dependent on their distance from the edge of the spray boom [98]. Therefore it is recommended that further studies be carried out and the effect of distance of the deposition sampler from the spray boom be evaluated.
- Once the interaction between the different nozzle type and pesticide mixes have been clearly understood, studies should be carried out under standardized conditions to determine which sampler is most appropriate for which nozzle type (based on the droplet sizes produced).
- Standardised deposition sampling should be carried out in field crops, orchard crops, and vineyard crops under more or less similar conditions using various samplers to come up with an ideal sampler for a particular spray application, rather than adopt the one size fits all approach.
- Quality control procedures should allow for correction of any losses during storage and transportation. For example, the sampler packaging material may adsorb some of the pesticide mix post sampling. In addition, extraction recovery and transit stability studies should be a common feature of deposition monitoring studies in order to improve the reliability of the results.
- Further studies are required to compare horizontally and vertically oriented pesticide deposition samplers for different sampler types with different materials of construction.
- The different samplers need to be applied for pesticide deposition monitoring studies in other countries where the climate is different, and where no such studies have been carried out, in order to fully validate them.
- Nozzles may also need to be optimised before spraying, since some variability may be observed in this respect during a particular spray event due to poor maintenance, leading to uncertainty of deposition measurements.

In conclusion, off-target deposition of various pesticides has been studied using different samplers. Chromatography paper has been cited as the best pesticide deposition sampler [41]. The use of glass based deposition samplers such as petri dishes and microscope slides has also been reported, although their collection efficiency does not match that of chromatography paper. Variations have been observed in the deposition trends for pesticides of varying volatilities for various samplers, and some of these patterns have been attributed to the prevailing climatic conditions during the spray events. More work still needs to be done to better understand pesticide deposition using various samplers that have been previously used, for different pesticide classes and the introduction of new samplers made from materials that favour efficient capture of droplets is encouraged.

Declaration of Competing Interest

The authors declare no conflict of interest.

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