EVALUATION OF TWO PESTICIDE SAMPLERS & EXPOSURE ASSESSMENT OF IOWA PESTICIDE APPLICATORS

by

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A thesis submitted in partial fulfillment
of the requirements for the Master of Science
degree in Occupational and Environmental Health in the
Graduate College of
The University of Iowa

May 2023

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To Kandace

My greatest supporter, confidant, and friend

ACKNOWLEDGMENTS

I am very grateful for the opportunity to perform this project, and I could not have done it without the abundance of help that I received. I would like to thank my advisor, Dr. Patrick O'Shaughnessy for his guidance and support with this project; in addition, thank you for valuing my research interests and aspirations. I would like to thank Dr. T. Reneé Anthony and Dr. Thomas Peters for their guidance and expertise both as committee members and professors. To my classmates and former professors, thank you for the fun memories and for creating an exemplary environment to learn, teach, and grow. Thank you to my friends and family members for your encouragement throughout this process. Finally, a special thank you to my wife Kandace for all that you have sacrificed so that I can achieve my goals (including a cross-country move to ~~Heaven~~ Iowa 😊). Your unconditional love and support mean more than you will ever know.

This research was funded by the National Institute of Environmental Health Sciences through the University of Iowa Environmental Health Science Research Center. Student financial support was granted by the Heartland Center for Occupational Health and Safety, a NIOSH/CDC Education and Research Center.

ABSTRACT

Chronic exposure to pesticides has been associated with numerous adverse health effects including cancer, cognitive impairment, and endocrine system disruption. Because of their occupations, pesticide applicators may be at higher risk of illness from pesticide exposure.

Due to their semi-volatile nature, pesticides can exist both as particles and gases (vapors) in the air. Many pesticides have been assigned an inhalable fraction and vapor (IFV) endnote by the American Conference of Governmental Industrial Hygienists (ACGIH), indicating a need to sample for both their particle and vapor phases. The National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Association (OSHA) methods recommend the OSHA Versatile Sampler (OVS) when sampling for both phases simultaneously (NIOHS Method 5600 & 5601; OSHA Method 62 & 63). Unlike the OVS, the IFV Pro (SKC Inc) was designed to be an inhalable sampler and has been identified in one study to have a higher mass collection efficiency than the OVS in a laboratory setting (Alex et al., 2021).

The aims of this study were to: 1) assess the particle and dual-phase relative efficiencies of the OVS and IFV Pro in a simulated and real-world pesticide spraying operation; and 2) perform an exposure assessment of pesticide applicators from three Iowa companies. It was hypothesized that the IFV Pro would sample higher particle and vapor mass concentrations than the OVS and that participating pesticide applicators would not be exposed to significant levels of pesticide. Under the conditions in which the two samplers were compared in this study, results indicate an insignificant difference in the particle-phase collection efficiencies between the OVS (M=5.80 mg/m^3, SD=1.77) and IFV Pro (M=5.56 mg/m^3, SD=1.55) (t=1.48, p=0.11). Descriptive statistics did not prove that the OVS and IFV Pro relative dual-phase sampling efficiencies were different under the same conditions. Six applicators in this study experienced low exposure to glyphosate, dicamba, and MCPA herbicides. Exposure monitoring results indicate that the subjects are not at an increased risk of pesticide-induced illness and disease. Further research should assess the influence of directional drafts and other environmental conditions on the OVS, IFV Pro, and pesticide applicator exposure. Additional efforts should also be made to standardize an analysis method for the IFV Pro.

PUBLIC ABSTRACT

Chronic exposure to pesticides has been associated with numerous adverse health effects including cancer, cognitive impairment, and endocrine system disruption. Because of their occupations, pesticide applicators may be at higher risk of illness from pesticide exposure.

Due to their evaporative nature, pesticides can exist both as particles and gases (vapors) in the air. Many pesticides have been assigned an inhalable fraction and vapor (IFV) endnote by the American Conference of Governmental Industrial Hygienists (ACGIH), indicating a need to sample for both their particle and vapor phases. Industry standards recommend the OSHA Versatile Sampler (OVS) when sampling for both phases simultaneously. Unlike the OVS, the IFV Pro (SKC Inc.) was designed to be an inhalable sampler and has been identified in one study to have a higher collection efficiency than the OVS in a laboratory setting (Alex et al., 2021).

This study aimed to: 1) assess the particle and dual-phase sampling characteristics of the OVS and IFV Pro in a simulated and real-world pesticide spraying operation; and 2) perform an exposure assessment of pesticide applicators from three Iowa companies to evaluate their occupational exposure. It was hypothesized that the IFV Pro would sample higher particle and vapor mass concentrations than the OVS and that participating pesticide applicators would not be exposed to significant levels above the pesticide. Under the conditions in which the two samplers were compared in this study, results indicate an insignificant difference in the particle-phase collection efficiencies between the OVS (M=5.80 mg/m^3, SD=1.77) and IFV Pro (M=5.56 mg/m^3, SD=1.55) (t=1.48, p=0.11). Descriptive statistics did not prove that the OVS and IFV Pro relative dual-phase sampling efficiencies were different under the same conditions. Six applicators in this study experienced low exposure to three different herbicides. Exposure monitoring results indicate that the subjects are not at an increased risk of pesticide-induced illness and disease. Further research should assess the influence of directional drafts and other environmental conditions on the OVS, IFV Pro, and pesticide applicator exposure. Additional efforts should also be made to standardize an analysis method for the IFV Pro.

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1.1. Pesticide Industry

1.1.1. Pesticide Types

Pesticides have revolutionized how pest and weed populations are controlled. When used properly, pesticides can increase crop yield, kill noxious pests, and improve the quality of life. The term pesticide is used to describe any combination of chemical agents that kill or inhibit a pest’s ability to survive. Various pesticide subcategories target specific plants and animals, including herbicides, insecticides, fungicides, rodenticides, and arachnicides.

Herbicides are the most common type of pesticide. First developed in the 1890s, their primary objective is to disrupt metabolic processes that allow plants to reproduce and grow (Institute of Medicine (US) Committee, 1994). Herbicides are widely used in agriculture and farming. In 2012, 59% of U.S. market pesticide expenditures in the agricultural sector were for herbicides (Atwood & Paisley-Jones, 2017).

Glyphosate, the active ingredient in RoundUp®, is a common herbicide used primarily on traditional crops such as soybeans, corn, and cotton. In 2012, approximately 115,000 metric tons of glyphosate were applied in the United States and 635,000 metric tons worldwide, making it one of the most globally used herbicides (Van Buggen, 2018; Baer & Marcel, 2014). Glyphosate has also been attributed to widespread groundwater contamination in the Midwest (USDA, 2008).

Insecticides are a type of pesticide that targets bugs and insects. They are commonly used to control insect populations in private homes and buildings. In the United States home and garden sector, insecticides comprise 80% of U.S. pesticide expenditures (Atwood & Paisley-Jones, 2017). They have been used for thousands of years. Many early insecticides were composed of hazardous chemicals such as sulfur, tobacco, lead arsenate, mercury, and hydrogen cyanide gas.

For centuries, pyrethrins, a class of organic compounds found in chrysanthemum flowers, have been used as an insecticide; these organic compounds are relatively low in toxicity compared to other pesticides (Bond, Buhl, & Stone, 2014). Throughout the 20th century, scientists invented synthetic versions of pyrethrins called pyrethroids. The behavioral characteristics are very similar between the two organic and synthetic insecticides; however, pyrethroids are generally more toxic (ATSDR, 2014). Dichloro-diphenyl-trichloroethane (DDT), a chlorinated hydrocarbon insecticide, was invented in 1847. Despite its efficiency in preventing malaria, typhus, and other insect-borne diseases among civilian populations, it was banned in 1972 citing environmental and toxicological concerns (EPA, DDT-A brief history and status, 2022).

Organophosphates were first synthesized during the 19th century and were primarily used as nerve agents during WWII. It was not until the 1960s that this insecticide type began to be used for residential and agricultural pest control (Dyro, 2003). Organophosphates deactivate acetylcholinesterase between neurons, causing the rapid firing of synapses. Due to its high toxicity in humans, this category of insecticide was banned in the United States in 2001 from residential use. Many organophosphates are still used in agriculture, despite public health concerns.

1.1.2. U.S. Regulation

Per the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), all pesticides must be registered by the Environmental Protection Agency (EPA) to be sold and used in the United States. Under the legislation, pesticides must prove that they will not cause unreasonable adverse effects and irreparable harm to the economy, environment, and society. In addition, chemicals classified by the EPA as “Restricted-Use Pesticides” (RUPs) are not to be made available to the public and should only be used by licensed applicators (EPA, Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and Federal Facilities, 2022).

1.1.3. U.S. Employment Characteristics

The EPA estimates that there are approximately one million pesticide applicators in the United States (2022). There are 25,820 employed (excluding self-employed) vegetation-related pesticide handlers, sprayers, and applicators nationwide. In Iowa, Minnesota, and Illinois, there are 520, 1410, and 1180, respectively (BLS, 2022). The EPA approximates that one million pesticide applicators are certified to use RUPs, and 930,000 pesticide applicators are not (EPA, Certification Standards for Pesticide Applicators, 2022).

Pesticide handler wages vary across the United States. The national average wage in 2021 was $40,500. In Iowa, Minnesota, and Illinois, the average wages were $40,390, $42,630, and $45,070, respectively (BLS, 2022).

1.2. Pesticide Spraying Methods

Pesticide spraying units vary in size and shape. Portable units such as backpack sprayers are used in the U.S. for the direct spraying of cracks, weeds, and other site-specific locations. Most backpacks and handheld sprayers hold between 5 and 20 liters of chemicals. Portable units generally have a hand pump to pressurize the tank, although electric pumps are becoming more available in industry. Boom sprayers allow for the application of higher quantities of pesticides to properties such as fields and pastures. They are operated on or pulled by utility terrain vehicles

(UTVs) or tractors. Aerial application methods including crop dusting via airplanes and drones can replace and/or supplement land application methods.

Hydraulic nozzles used for spraying pesticides generally fit into three categories: flat fan, cone, and stream. Flat fan nozzles exhibit a narrow, elliptical, inverted ‘V’ pattern and are widely used with pesticide boom sprayers. Cone nozzles exhibit either a hollow or full pattern. Cone nozzles generate coarser droplets; however, both are used for specialty and direct “spot” spraying. Stream nozzles exhibit a steady stream and are used to spray site-specific locations on a plant or surface.

Factors such as total sprayer output, field application speed, and nozzle spacing must be considered to select the optimal nozzle. Equation 1 may be used to select the spray rate in gallons per minute (GPM) of each nozzle when operating a boom sprayer when GPA is the total sprayer output in gallons per acre, MPH is the field speed in miles per hour, and W is the nozzle spacing in inches (Montana St. University, 2022).

Equation 1: $\text{GPM} = (\text{GPA} \times \text{MPH} \times \text{W}) / 5940$

Droplet sizes may vary depending on the nozzle and tank pressure. Some studies have found that the aerosol droplet median aerodynamic diameter can vary from 25 to 543 µm when sprayed at ejection speeds of 0.5 to 12 m/s (Minov, et al., 2016); others have found that sprayers can eject “very fine” droplets ranging from 4 to 15 µm (Minov, et al., 2016; ASABE, 2020; Bémer, et al., 2007).

Meteorological conditions such as temperature and wind can influence pesticide performance efficiency. The ideal temperature for post-emergence herbicides is 65°- 85°F (Jhala & Rees, 2017; NDSU, 2022). Herbicides may be applied in temperatures of 40°- 60°F, but herbicide absorption and translocation are hindered in lower temperatures; thus, adjuvants should be added to herbicides in cooler temperatures to increase their efficiency (Jhala & Rees, 2017). Temperatures exceeding 85°F can increase the volatility of the herbicide, causing it to “evaporate” before it absorbs or translocates into the plant (Hanson, Bond, & Buhl, 2016).

Pesticide spray drift is the quantity of pesticide carried away from the treated area by meteorological phenomena in the application process (ISO, 2005). It is influenced by equipment and application techniques, spray characteristics, operator care and skill, and environmental and meteorological conditions (Arvidsson, Bergström, & Krueger, 2011; Gil, 2014). Drift increases when spraying at incorrect heights above plants and in windy conditions (Arvidsson, Bergström, & Kreuger, 2011). When applied under less-than-ideal conditions, over 90% of applied pesticides can drift away from the intended target and up to 90 km from the source (Harnley, et al., 2005; Van den Berg, et al., 1999). Hence, it is recommended to follow pesticide label directions and spray in low wind conditions (i.e., 5-11 km/hr for glyphosates and 3-16 km/hr for MCPA and dicamba).

1.3. Pesticide Exposure Health Effects

The potential adverse health effects of pesticides on workers rely on two factors: toxicity and exposure. Acute exposures are typically one-time occurrences of higher doses, whereas chronic exposures occur gradually in smaller doses.

Herbicides are normally low in toxicity because they target plant metabolic processes. Acute herbicide exposure can irritate the skin, eyes, nose, and throat (Fishel & Andre, 2002). Chronic exposure may cause endocrine disruption and increase the risk of developing various cancers such as soft-tissue sarcoma, stomach cancer, lung cancer, liver cancer, and lymphoma (Stradtman & Freeman, 2021; Sterling & Arundel, 1986).

Some insecticides such as organophosphates are highly toxic which can cause adverse health effects after small exposure doses. Adverse muscarinic and nicotinic effects such as bradycardia, diarrhea, muscle cramps, and paralysis can occur from acute exposure (Peter, Sudarsan, & Moran, 2014). Chronic exposure can cause cognitive decline and neurodegenerative diseases; in addition, there has been an indication of carcinogenic and endocrine-disrupting effects (Peter, et al., 2014; Li, et al., 2020; Astroff, Freshwater & Eigenberg, 1998; Mnif, et al., 2011). Other insecticides such as pyrethrins and pyrethroids are less toxic to humans but may still cause dermal irritation, nausea, and dizziness (Agency for Toxic Substances and Disease Registry, 2003).

1.4. Occupational Pesticide Exposures

Workers may be exposed to pesticides in three routes: dermal, inhalation, and ingestion. Dermal absorption through the cutaneous membrane is the most common route. Activities in which the possibility of dermal exposure may occur include touching contaminated surfaces, walking/driving through recently treated areas, and mixing, loading, and applying pesticides. The inhalation route accounts for less than 10% of pesticide exposure (Dowling & Seiber, 2002). Ingestion is the least common exposure route but can occur via direct (e.g., accidental consumption) or indirect (e.g., fomite) transmission.

Because agricultural workers use 90% of the nearly 499,000 metric tons of pesticide that are nationally consumed each year, they experience a higher probability of pesticide exposure and poisoning than other groups (Atwood & Paisley-Jones, 2017). From 2007-2011, the acute occupational pesticide-related illness incidence rates of agricultural workers were significantly higher than that of non-agricultural workers (18.6 per 100,000 full-time equivalent workers (FTEs) and 0.5 per 100,000 FTEs, respectively (Calvert, et al., 2016). In the state of Iowa, approximately 61 occupation-related pesticide poisonings occur annually, the majority of which occur during pesticide application (Walker, 2013).

Factors such as pesticide application technique (spray pressure, spray flow rate, spray height, and nozzle type), and chemical and physical properties of pesticides (vapor pressure, concentration, and viscosity) should be considered when evaluating the inhalation pesticide exposure of agricultural workers (Alex, S, 2018; Dorr, et al., 2013).

1.5. Environmental Factors Affecting Occupational Exposures

Meteorological conditions such as temperature, wind speed/direction, and humidity contribute to the fate and transport of volatile pesticides. These conditions have the potential to limit or increase occupational pesticide exposure. For example, pesticide droplets may evaporate into smaller droplets or into a vapor at higher rates when applied at high temperatures and low relative humidities. As a result, the smaller pesticide droplets and/or vapor can drift further off target (Hanna, 2009).

Extreme temperatures and humidity can influence workers' decisions and abilities to wear personal protective equipment (PPE) properly. Working in high temperatures/humidity while wearing PPE often causes psychological and physical strains on the body (Holmer, 1995). A study on Brazilian tomato farmers identified that farmers did not use adequate PPE while spraying herbicides because of PPE-related thermal discomfort (Coutinho, et al., 1994).

Windy conditions are not ideal for spraying pesticides as they can transport pesticides to both the applicator and off-target populations. Pesticide drift caused by high winds can damage nearby plants and water life. Because 90% of Iowa public school districts have buildings within 2,000 feet of an agricultural field, wind conditions often put students and teachers at risk of exposure (Ward, et al., 2006; Schmid, Schillinger, & Martin, 2018).

Arcury et al. (2007, 2019) identified four nontraditional pathway routes in which non-pesticide applicators are exposed to pesticides: paraoccupational take-home, environmental, residential, and residual pathways. Paraoccupational take-home involves pesticide applicators inadvertently bringing pesticides into the home via contaminated clothing, cell phones, and other objects. The environmental pathway includes the unwanted transfer of pesticides from farms to households via food, animals, and/or air. The residential pathway involves the application of pesticides within the home. Residual pathway includes pesticides previously deposited in the home. All four exposure pathways indicate manners in which populations not working in the pesticide industry may be exposed (Arcury, et al., 2007, 2019).

1.6. Particle and Vapor Theory

1.6.1. Inhalable Sampling Criterion

Because particle deposition relies on particle size, particles with small aerodynamic diameters can deposit deeper in the respiratory system. The respiratory system consists of three regions to help identify a particle's destination: nasopharyngeal, tracheobronchial, and pulmonary regions. The American Conference of Governmental Industrial Hygienist (ACGIH) has identified sampling criterion of the inhalable, thoracic, and respirable fractions to describe their size-selective sampling characteristics.

The inhalable fraction (IF) consists of all particles that enter through the mouth or nose during inhalation. The mathematical definition of the inhalable fraction is described in Equation 2, in which IF is the inhalable fraction collection efficiency and d_{ae} is the particle aerodynamic diameter in μm (European Committee for Standardization (CEN), n.d.). This definition is based on the results of studies in which aspiration efficiencies of mannequin torsos in a wind tunnel were collected (Vincent & Ambruster, 1981; Vincent & Mark, 1990). Mannequins were connected to a mechanical breathing device and angled or rotated inside of the tunnel. A series of aerosolized dusts with specific aerodynamic diameters ranging from 5 to 100 um were released into the tunnel. The dusts were collected by a filtering media in the mannequin's nose/mouth while isokinetic samplers near the mannequin head provided reference samples. The ratio of the sample mass to the isokinetic samplers is the inhalable fraction, for a given particle size and condition (Hinds, 1999).

Equation 2: $IF(d_{ae}) = 0.5[1+ \exp(-0.06d_{ae})]$

Traditional studies used wind speeds from 1 to 8 m/s to determine the inhalable fraction (Armbruster & Breuer, 1982). Other studies have been conducted with varying wind speeds (Ogden & Birkett, 1977; Vincent, et al., 1990). Vincent et al. assessed the inhalable fraction in a simulated outdoor environment (wind speed: 4-10 m/s). The mathematical definition of the inhalable fraction in environments in which air velocities surpass 4 m/s is given in Equation 3, in which d_{ae} represents the particle aerodynamic diameter and U_0 represents winds speed (Vincent, et al., 1990).

Equation 3: $IF(d_{ae},U_0) = 0.5(1+\exp(-0.06d_{ae})) + 10^{-5}(U_0^{2.75}\exp(0.055d_{ae}) \quad \text{for } U_0>4\text{m/s}$

Inhalable samplers are designed to capture and measure the concentration of particles that deposit anywhere in the respiratory system, especially within the nasopharyngeal and tracheobronchial regions. The design of these samplers relies on the mechanisms of interception, inertial impaction, sedimentation, diffusion, and electrostatic attraction to collect aerosolized particles on fiber filters. Typically, the filters are analyzed gravimetrically but may also be analyzed using mass spectrometry, gas chromatography, or flame ionization detection.

Analytical sampling methods from the Occupational Safety & Health Association (OSHA) and the National Institute for Occupational Safety and Health (NIOSH) disagree on the type of fiber filters that ought to be used when sampling pesticides. OSHA recommends using glass fiber filters while NIOSH suggests quartz fiber filters. Both filters are adequate. However, quartz filters can have a higher collection efficiency with compounds of high polarity (Reynolds, 2020).

1.6.2. Vapor Sampling Criterion

The terms vapor and gas are often used synonymously in the pesticide industry. While they often behave similarly in the environment, they are indeed different. A vapor is the gaseous state of an evaporated liquid by altering the environment's temperature and/or pressure conditions. A gas remains in a gaseous state under normal temperature (20°C) and pressure (1 atm) conditions (NTP).

As opposed to inhalable samplers, vapor samplers use adsorbents or resins to collect and measure vapor concentrations. As air passes through the resin, the vapor adheres to the resin. Most AMBERLITE® resins (Rohm and Haas Company, Philadelphia, PA) such as the XAD-2 are hydrophobic polyaromatic compounds. The XAD-2 has a surface area of 330 sq. m/g and is widely used in removing hydrophobic compounds (e.g., pesticides) up to 20,000 MW. The XAD-7, composed of acrylic ester, has a surface area of 450 sq. m/g and adsorbs organic compounds, dry waste, and metal ions up to 60,0000 MW (SIGMA-ALDRICH, 1998). Resins can be analyzed using gas chromatography or high-performance liquid chromatography with detector (OSHA, OSHA Analytical methods Manual, 1991).

1.6.3. Dual-Phase Sampling/IFV Endnote

Because of the low vapor pressures of semi-volatile organic compounds (SVOCs), these compounds may exist in the particle-phase, vapor-phase, or both. To effectively assess the overall exposure, it is recommended that aerosolized pesticides and other chemicals be sampled for both phases in a process called dual-phase sampling (Perez & Soderholm, 1991; Kim &

Soderholm, 2013). The ACGIH has established sampling criteria that account for the components of both phases when dual-phase sampling is necessary, known as the inhalable fraction and vapor (IFV) endnote. The IFV endnote is a ratio of two critical values specific to the SVOC: the Saturated Vapor Concentration (SVC) and the Threshold Limit Value (TLV).

SVC is the air vapor concentration of a chemical at saturation. It is classified as "the mass concentration of the vapor in equilibrium with the pure bulk substance at the ambient temperature" (Perez & Soderholm, 1991). The theoretically modeled SVC for pesticides in standard ambient temperature and pressure conditions (25°C and 760 mmHg) is described in Equation 4 where P_v is the chemical vapor pressure in mmHg, MW is the molecular weight in g/mol, P_c is the pressure constant (760) in mmHg, and V_c is the volume constant (24.45) in L/mol according to the ideal gas law (Perez & Soderholm, 1991; EPA, STIRE Version's 1.0 User's Guide for Pesticide Inhalation Risk, 2010).

Equation 4: $\text{SVC} = (P_v \times \text{MW} \times 1{,}000{,}000) / (P_c \times V_c)$

The chemical-specific TLV is typically the maximum accepted worker exposure level averaging over 8 hours as recommended by ACGIH. When determining if an IFV endnote is necessary, the TLV represents the total chemical airborne concentration. An IFV endnote is given if a chemical's SVC/TLV is between 0.1 and 10. However, four situations in which the validity of an IFV endnote recommendation must be evaluated separately. Those situations include when 1) "sampling liquids with TLV reported in ppm with SVC/TLV ratios > 10," 2) "sampling liquids with TLV reported in ppm with SVC/TLV ratios < 10," 3) "sampling solids with TLV reported in mg/m^3 with SVC/TLV > 10," and 4) "when temperatures [and other composition variables (i.e. chemical purity)] may influence the state of matter" (ACGIH, 2020). Table 1.1 displays several pesticides that have IFV endnotes in the 2017 ACGIH TLV Handbook.

The TLV can also be compared to the SVC and used to gauge whether a pesticide's particle or vapor-phases are more prevalent in an environment. When SVC>TLV, the aerosolized pesticide with a concentration near the TLV is more often present in the vapor-phase. Conversely, when SVC<TLV, the aerosolized pesticide with a concentration near the TLV is more often found in the particle-phase.

1.7. Ambient Pesticide Exposure Monitoring

Occupational exposure limits (OELs) are established by organizations to protect workers as they perform tasks involving potentially toxic chemicals. TLVs created by ACGIH represent the maximum average airborne concentration that adult workers may be exposed to during an 8-hour workday and 40-hour work week. Under the conditions of the TLV, it is believed that workers may be repeatedly exposed to that concentration over a working lifetime, without experiencing adverse health effects (ACGIH, 2023). Although nonregulated, abidance to TLVs is considered the best industry practice. OSHA establishes permissible exposure limits (PELs) which are often less conservative than TLVs. Per federal (and sometimes state) laws, worker exposures are required to be below the OSHA PEL.

Personal exposure monitoring assists in quantifying the chemical exposure of a worker. Two types of personal exposure monitoring methods are considered: passive and active sampling. Passive exposure monitoring, otherwise known as diffusive sampling, involves the diffusion of an analyte (limited to gases and vapors) onto a sorbent medium at a scientifically determined fixed rate (SKC Limited, 2022). Diffusive sampling is intuitive and inexpensive. It does not require the use of a sampling pump, making it ideal for sampling in remote areas. Active exposure monitoring, also known as active sampling, requires drawing air through collection media using an air pump. A wide range of analytes can be collected with this method including gases, vapors, droplets, and particles; however, active sampling is less intuitive and often more expensive.

Dual-phase samplers implement the particle-capturing properties of inhalable samplers and the adsorbing properties of vapor samplers. The OSHA Versatile Sampler (OVS) is a dual-phase sampler and is commonly used for quantifying occupational pesticide exposure. The SKC Inhalable Fraction and Vapor (IFV) Pro Sampler is also a dual-phase sampler, but unlike the OVS, the IFV Pro was designed with size-selective sampling properties.

1.7.1. OSHA Versatile Sampler (OVS)

The OVS is a glass tube (13-mm O.D. 11-mm I.D. x 50-mm) that comprises of a 13-mm filter and a two-layer sorbent bed, held in place by a polytetrafluoroethylene (PTFE) holding ring and foam plugs (see Figure 1.2). The sorbent media, consisting of AMBERLITE® XAD-2 resin for pesticides, is located downstream of the filter to control evaporative loss that takes place during sampling. The filter is either glass fiber (OSHA method) or quartz fiber (NIOSH method). The outlet of the glass tube is joined to a smaller tube (6-mm O.D. x 4-mm I.D. x 25-mm). A plastic, protective sheath is placed around the OVS to prevent damage during sampling. A spring-loaded metal clip on the sheath attaches the OVS, with the inlet facing downward, within the worker’s breathing zone. The OVS may be operated between 0.2 to 1.0 L/min, contingent on the expected SVOC concentration.

Solvents are used to extract samples from the media. Gas chromatography, UV detection, or high-performance liquid chromatography with detector is used for analysis, depending on the analyte (OSHA, 2022; NIOSH, 2016; NIOSH, 1994). Several analytical methods for pesticides have been developed that utilize the OVS including NIOSH 5600, 5601, 5602, and OSHA Analytical Methods 62 and 63.

1.7.2. Inhalable Fraction & Vapor (IFV) Pro Sampler

Designed by SKC Limited, the IFV Pro consists of an aerosol sampling head and a sorbent tube (8-mm O.D. x 110-mm) (see Figure 1.3). The aerosol sampling head was scaled to that of the Institute of Occupational Medicine (IOM) sampler, which closely abides by the inhalable sampling criterion (Alex, Sovers, & O'Shaughnessy, 2021). The IFV Pro has a narrower inlet (10.6 mm) than the IOM (15 mm) to maintain the same face velocity at a lower sampling rate (1.0 L/min versus 2.0 L/min).

The sorbent tube, located downstream from the sampling head, compensates for evaporative loss during sampling by collecting evaporated chemicals on the resin. For pesticides, it typically contains two layers of AMBERLITE® XAD-2 resin, held in place by polytetrafluoroethylene (PTFE) rings or foam plugs. The primary resin layer adsorbs vapors, and the secondary layer is analyzed to determine if the primary layer was overloaded. An overloaded primary layer indicates sample breakthrough. A plastic, protective sheath is placed around the sorbent tube to prevent damage during sampling. A spring-loaded metal clip on the sampler attaches the IFV Pro, with the sampling head and inlet facing forward, within the worker's breathing zone. Solvents are used to extract the samples, and gas chromatography or high-performance liquid chromatography with detector is used for analysis.

1.8. Research Objectives

Many pesticides have been assigned an IFV endnote, indicating a need to sample for both its particle and vapor phases. Current NIOSH and OSHA methods recommend the OVS for performing personal air monitoring (NIOSH Methods 5600, 5601, 5602, and OSHA Analytical Methods 62, 63). However, the OVS was not designed as an inhalable sampler. The IFV Pro, which more closely follows the inhalable sampling criterion than the OVS, may be more accurate in measuring pesticide exposure. Only one study has compared the two samplers, in which the IFV Pro was identified as having a higher collection efficiency in a laboratory setting (Alex et al., 2021). There is a need, therefore, to understand the collection characteristics of the two samplers under environmental conditions that better represent that of a pesticide spraying operation.

Research Aims:

1) Assess the aerosol and vapor sampling characteristics of the OVS and IFV Pro
2) Evaluate the risk of pesticide exposure among Iowa pesticide applicators

Research Objectives:

1) Assess the particle and dual-phase sampling efficiencies of the two samplers in a simulated and real-world setting
2) Perform an exposure assessment of pesticide applicators at three Iowa landscaping companies

Table 1.1. Common Pesticides Having an IFV Endnote in 2017

Chemical Name	**Vapor Pressure (mmHg)**	**TLV (mg/m^3)**	**PEL (mg/m^3)**
Alachlor	2.2×10^{-5} at 25°C	1	-
Aldrin	6.5×10^{-5} at 20°C	0.5	0.25
Chlorpyrifos	1.9×10^{-5} at 25°C	0.1	-
Diazinon	7.3×10^{-5} at 20°C	0.01	-
Dieldrin	3.0×10^{-6} at 20°C	0.1	0.25
Malathion	4.0×10^{-5} at 30°C	1	15
Parathion	3.8×10^{-5} at 20°C	0.05	0.1

Adapted from Kim and Raynor (2013)

Figure 1.1. An OVS Sampler and Its Protective Sheath

Figure 1.2. An Assembled IFV Pro (Filter & Sorbent Tube) and Its Protective Sheath

CHAPTER 2: EVALUATION OF TWO PESTICIDE SAMPLERS & EXPOSURE ASSESSMENT OF IOWA PESTICIDE APPLICATORS

2.1. Introduction

Pesticides have revolutionized how pest and weed populations are controlled. When used properly, pesticides can increase crop yield, kill noxious pests, and improve the quality of life. Herbicides, a pesticide that disrupts plant metabolic processes, are the most common type of pesticide. Typically, herbicides are used in agriculture and gardening. Insecticides, which control insect populations, are often used in private homes and buildings. In 2001, organophosphates were banned from residential use citing public health concerns; however, many organophosphates are still used in agriculture.

Exposure to pesticides has been associated with numerous adverse health effects. Acute exposure can cause dermal irritation, nausea, and dizziness while chronic exposure has been associated with cancer, cognitive impairment, and endocrine system disruption (Fishel & Andre, 2002; Sterling & Arundel, 1986; Stradtman & Freeman, 2021; Peter, et al., 2014). Worldwide, an estimated 385 million cases of unintentional, acute pesticide poisonings occur annually (Boedeker, et al., 2020). The state of Iowa averages approximately 61 cases of occupation-related poisonings each year (Walker, 2013). Because of their occupations, pesticide applicators may be at higher risk of illness from pesticide exposure.

Pesticides that are sprayed via pressurized containers create an opportunity for worker exposure through the respiratory system. Because of their evaporative nature, as defined by their low vapor pressures, sprayed pesticides may exist in the particle-phase, vapor-phase, or both. The American Conference of Governmental Industrial Hygienists (ACGIH) and other scientists recognize that both the particle and vapor phases can contribute to the exposure dose, and they recommend that dual-phase sampling be conducted for aerosolized pesticides to effectively assess the inhalation risk of exposure (ACGIH, 2023; Perez & Soderholm, 1991; Kim & Soderholm, 2013). The ACGIH has established sampling criteria that account for the components of both phases when dual-phase sampling is necessary, known as the inhalable fraction and vapor (IFV) endnote. Many of the chemicals given an IFV endnote status are pesticides.

Two samplers designed to perform dual-phase sampling are the OSHA Versatile Sampler (OVS) and the Inhalable Fraction and Vapor Pro sampler (IFV Pro). For decades, the OVS has been a common sampling method to determine pesticide exposure levels among applicators. Methods such as NMAM 5600, 5601, 5602, and OSHA Analytical Methods 62 and 63 use the OVS for quantifying pesticide exposure. The use of the OVS as the standard sampling method is potentially flawed because the OVS was not designed to function as an inhalable aerosol sampler, unlike the IFV Pro.

Only one study by Alex et al. (2021) has evaluated the particle and dual-phase collection efficiencies of the two samplers. The OVS and IFV Pro were sampled in a chamber with a laminar downward draft and finely graded dusts and alcohols with known aerodynamic diameters. The results from their research indicated that under those defined conditions, the IFV Pro was more closely aligned with the ACGIH-established inhalable sampling criterion than the OVS (1.9-fold difference). No other published research has compared the sampling capabilities of the OVS and IFV Pro in the laboratory or real-world setting.

This study aims to: 1) assess the aerosol and vapor sampling characteristics of the OVS and IFV Pro; and 2) evaluate the risk of pesticide exposure among Iowa pesticide applicators. Study objectives include comparing the particle and dual-phase sampling efficiencies of the two samplers in a simulated and real-world setting, as well as performing an exposure assessment of pesticide applicators at three Iowa landscaping companies.

2.2. Methods

2.2.1. Experimental Setup

2.2.1.1. Experimental Setup – Particle & Dual-Phase Sampler Efficiency

A diagram of the experimental setup for the particle and dual-phase sampler efficiency trials is shown in Figure 2.1. A chamber (1.5 m x 1.5 m x 2.1 m) was constructed to simulate the use of a pesticide sprayer by an applicator. The chamber was constructed with 3.8-cm polyvinyl chloride (PVC) pipes and 6-mm polyethylene sheeting (see Figure A.1 in the Appendix). A 7.6-L pesticide sprayer unit (Bayer, Model No: 190254, Leverkusen, Germany), consisting of a hand-held sprayer and pressurized container, was used to generate aerosols inside the chamber. The hand-held sprayer was attached to a stand inside the chamber; the container was pressurized to 207 kPa and placed outside the chamber.

Two chemicals with low levels of toxicity were used in this experiment to substitute the need for pesticides. Mineral oil (Bluewater Chemgroup, Fort Wayne, IN), which has a vapor pressure of 6.5 x 10^{-4} atm, was the analyte used to evaluate the relative particle-phase efficiency of the OVS and IFV Pro samplers. Ethylene glycol (Lab Alley Essential Chemicals, Lot: 0083K00372), which has been used with other alcohols in evaluating the dual-phase efficiencies of other samplers, was used in evaluating the dual-phase efficiencies of other samplers (Breuer, et al., 2015). In addition, the vapor pressure of ethylene glycol (7.89 x 10^{-5} atm) is also similar to that of pesticides (10^{-14}atm to 10^{-4} atm).

The two chemicals were sprayed against the wall of a 68.1-L tub, 38 cm from the base and 4 cm from the rim of the tub to increase chemical aerosolization upon wall impact. High chemical concentrations were generated inside the chamber to allow for a shorter sampling period. The mass median aerodynamic diameter (MMAD) of the two aerosols was determined by an optical particle counter (GRIMM 11-C, Ainring, Bayern, Germany). An oscillating personal table fan was placed next to the tub to produce an upward draft, increasing the aerosol distribution throughout the chamber. No mechanical ventilation into or out of the chamber took place.

A foam cutout, scaled to the height of an average American male (175 cm), was placed next to the spraying operation. Samplers were directly attached to the cutout using cable ties, 18 cm from the top of the cutout to represent being placed within the breathing zone of an average American male (see Figure A.2). Each sampler was connected to a personal air sampling pump (AirChek 200, SKC Inc., Eighty Four, PA), which remained consistent throughout the study. Pumps were located outside the chamber for quick access.

2.2.1.2. Experimental Setup: Pesticide Applicator Exposure Assessment

Three organizations that perform their own herbicide spraying operations within Johnson and Linn counties were selected by convenience sampling to participate in the applicator exposure assessments. Researchers first recruited organizations by email and then followed up with managers via email, phone calls, teleconferences, and in-person meetings to establish organizational support. Prior to contacting employees, approval by the University of Iowa Institutional Review Board (IRB ID: 202206005) was granted for study recruitment. Workers were screened to determine study eligibility from the companies that agreed to participate. Qualifications for study participation required subjects to be at least 18 years of age, spray herbicides as part of their occupation, and be willing to wear personal air samplers throughout the study. Two subjects from Company A, one subject from Company B, and three subjects from

Company C were recruited for the study. One subject from Company C was sampled twice over a two-day period. Each subject signed a consent waiver prior to study participation.

Subjects wore both the OVS and IFV Pro samplers throughout their entire spraying operation (3-7 hours). A holder, composed of heavy paperboard, electrical tape, and two cable ties, held the OVS and IFV Pro samplers in place (see Figure A.3). Each sampler was randomly assigned a position in the holder. The holder was attached within the subject's breathing zone and on their dominant hand shoulder using two mini-spring clamps. Two personal air sampling pumps, one for each sampler, were carried by the subject using a backpack or clipping the pumps directly onto the subject's belt/pocket (see Figures A.4 and A.5).

An 11-question survey was administered to subjects following their application duties (see Figures A.6 and A.7). Survey questions were grouped into two sections. Questions posed in Section 1 addressed the worker's education and experience in the pesticide industry. Section 2 reflected the subject's thoughts and behaviors while participating in the study. The survey served as a tool for identifying factors that may have influenced pesticide exposure during study participation.

2.2.2. Aerosol Samplers

2.2.2.1. OSHA Versatile Sampler (OVS)

The OVS is commonly used for quantifying aerosolized pesticide exposure because it samples both the particle and vapor phases of a chemical. The device consists of a 13-mm glass fiber filter (GFF) and a sorbent layer. The filter is held steady with a polytetrafluorethylene (PTFE) ring; the primary sorbent layer is separated from the backup layer by polyurethane foam. Unlike other inhalable samplers, the inlet of this device faces vertically downward while in operation (see Figure 1.1).

Because the analyte in question defines the sorbent type, two OVS samplers with different sorbent layers were used. An OVS with an AMBERLITE® XAD-7 resin (Cat. No: 226-57, SKC Inc., Eighty Four, PA) was used in evaluating the relative dual-phase sampling efficiency (ethylene glycol as the analyte). The XAD-7 resin is an acrylic ester and is therefore more efficient in adsorbing organic compounds. An OVS with an AMBERLITE® XAD-2 resin (Cat. No: 226-30-16, SKC Inc., Eighty Four, PA) was used in assessing the pesticide applicator exposure. The XAD-2 resin is a hydrophobic polyaromatic compound, ideal for adsorbing pesticides. All pesticide and ethylene glycol resins were analyzed with their corresponding filters.

To evaluate the relative particle-phase efficiency of the sampler (mineral oil as the analyte), the OVS was modified by removing the contents inside and inserting a single 13-mm PVC filter. By removing the resin, this modified sampler only collected the particle-phase mineral oil. The filter was held in place by a cylindrical plastic piece on the bottom and a PTFE ring on the top (see Figure A.8). All OVS sampling modifications were operated at 1 L/min in accordance with NIOSH and OSHA sampling methods with the inlet of the sampler facing downward. The device sat inside a protective, plastic sheath while in operation.

2.2.2.2. SKC Inhalable Fraction & Vapor (IFV) Pro Sampler

The IFV Pro consists of a 25-mm GFF, cassette, and 8x110-mm sorbent tube. In dual-phase efficiency trials in which ethylene glycol was the analyte, an AMBERLITE® XAD-7 sorbent tube (Cat. No: 226-95, SKC Inc., Eighty Four, PA) was used. An AMBERLITE® XAD-2 sorbent tube (Cat. No: 226-30-06, SKC Inc., Eighty Four, PA) was used for evaluating pesticide applicator exposure. Both tubes have primary and backup sorbent layers, separated by foam. Similarly to other inhalable samplers, the inlet for this sampler faces horizontally away from the user (see Figure 1.2).

In evaluating the relative particle-phase efficiency of the IFV Pro, the sampler was modified so that only the IFV Pro head was used. The sampler's lower half, which holds the sorbent tube, was not used (see Figure A.9). The sampler head consisted of a 25-mm PVC filter, stationed inside a cassette. Filter masses were determined gravimetrically. All IFV Pro sampling modifications operated at 1 L/min per the OSHA and NIOSH sampling methods.

2.2.3. Testing Procedures

Three testing procedures were created. For all procedures, each sampler was paired with a personal air sampling pump, which remained consistent for the duration of the experiment. Pumps were calibrated before and after each series of efficiency trials and exposure assessments to 1 L/min using a primary calibrator (Gilibrator-2® Primary Flow Calibrator Model No:800272, Sensidyne, St. Petersburg, FL) for each experiment with test media in the sampling train. For all the sampling modifications, representative samplers were used in conjunction with their adapters for calibration (see Figure A.10).

The OSHA and NIOSH analytical methods do not account for the analyte residue left inside the OVS tube after sampling. To remain consistent with the methods, only the filters and sorbent layers, when applicable, were analyzed for both the OVS and IFV Pro. No wall deposits were measured for either sampler type.

2.2.3.1. Testing Procedure: Particle & Dual-Phase Efficiency

Each filter was weighed using a six-digit microbalance (Mettler Toledo MT5, Columbus, OH). PVC filters with a 5 µm pore size (SKC Inc., Eighty Four, PA) were applied to the modified OVS and IFV Pro samplers.

Once attached directly to the foam cutout, samplers alternated positions to limit orientation bias. They switched between position 1 (left side) and position 2 (right side), relative to the cutout, after each trial (see Figure A.2). The IFV Pro was in position 1 for all odd-number trials and position 2 for all even-number trials. Conversely, the OVS occupied the opposite position.

Pumps were activated within 2 seconds of each other, and the sprayer was activated immediately after. Using a stopwatch, the sprayer released mineral oil aerosols for 2.5 minutes, after which the sprayer unit was depressurized, and spraying ceased. Approximately 12-15 minutes into sampling, a measurement of the chamber's internal temperature and relative humidity were recorded (Vaisala, Model No: HMP75, Vantaa, Finland).

After 17.5 minutes, the pumps were deactivated, and the chamber was propped open and ventilated for 5 minutes before entering the chamber. The filters were removed from the samplers and gravimetrically analyzed immediately after to calculate a mass. Masses were corrected for temperature and humidity using field blanks. Following the corrections, masses were converted into mass concentrations.

The relative dual-phase efficiency testing procedure was identical to the particle-phase, with a few exceptions. Ethylene glycol replaced mineral oil as the analyte and OVS (GFF & XAD-7 resin) and IFV Pro (GFF & XAD-7 sorbent tube) samplers were assembled to the foam cutout inside the chamber. After each trial, samplers were removed and immediately stored in a freezer (-20°C) until they were shipped on solid CO_2 (dry ice) to an AIHA-certified lab (Wisconsin Occupational Health Laboratory (WOHL)) for ethylene glycol analysis. Four paired ethylene glycol samples were analyzed by gas chromatography, according to NMAM 5523. All filters were analyzed with their corresponding primary sorbent layers.

2.2.3.2. Testing Procedure: Applicator Exposure Assessment

Personal air sampling took place over four days in September and October 2022. Environmental conditions such as wind speed, humidity, and temperature varied during those four days. Temperature and relative humidity were periodically measured on-site (Vaisala HMP75, Vantaa, Finland). Wind speeds were obtained by the National Weather Service.

Herbicide aerosols were generated using various pieces of equipment owned by the three organizations. The spraying needs of each organization determined which equipment was used. Company A used a Z-Spray Stand-On® Sprayer and a Toro Multi-Pro® Turf Sprayer with an enclosed cab on grass fields (see Figure A.12). Company B subjects used a Solo backpack sprayer around trees and a Z-Spray Stand-On® Sprayer on grass fields (see Figure A.13). Company C modified a Gravely Zero Turn Mower into a spraying operation by attaching a 380-L tank and hand-sprayer to the lawnmower. During this operation, one subject walked and sprayed by hand while another subject followed 3-5 meters away on the mower (see Figure A.14). This operation was used to spray around trees, fields, and fencelines.

Subjects were instructed to perform their regular spraying duties while donning the two aerosol samplers (OVS (GFF& XAD-2 resin) and IFV Pro (GFF & XAD-2 sorbent tube). Sampling took place for as long as the subject performed pesticide-related activities (3-7 hours). The types of herbicides used also varied depending on the applicator and the needs of their organization. The three herbicides sampled among the three companies included glyphosate (RoundUp®), dicamba, and MCPA (Horsepower®).

At the completion of the subject's shift or spraying tasks, the samplers were removed and stored for transportation. The post-application survey was then immediately administered to the subjects. Samples were stored 1-2 hours later in a freezer (-20°C) until they were shipped on solid CO_2 to the WOHL for analysis. Six paired glyphosate samples were analyzed according to

OSHA PV2067. One pair of dicamba and MCPA samples were analyzed according to NMAM 5001. All sampler filters were analyzed with their corresponding primary sorbent layers.

2.2.4. Analysis Procedure

2.2.4.1. Data Analysis Procedure: Particle-Phase Efficiency

Twenty paired mineral oil samples were collected; however, one paired sample was a significant outlier and was removed from data analysis. A two-tailed, paired t-test was used to determine whether the mean concentration of one sampler differed from the mean concentration of the other ($\alpha=0.05$). Additionally, a linear regression analysis was used to compare the performance of the two samplers.

2.2.4.2. Data Analysis Procedure: Dual-Phase Efficiency & Applicator Exposure Assessment

Due to the limited sample size, a qualitative assessment was used to examine trends between the concentrations collected by the two samplers and determine if the IFV Pro collected higher concentrations than the OVS for ethylene glycol and field samples. For non-detect field samples, the mass concentrations were presented as the mass LOQ/sample volume.

2.3. Results

2.3.1. Particle-Phase Efficiency

The chamber internal temperature and humidity varied throughout the trials, ranging from 16.0-27.9℃ and 43.5-89.0%, respectively (see Table A.1 for a summary of environmental conditions). The MMAD of mineral oil droplets within the chamber ranged from 3.57-4.36 µm (see Figure A.15).

The mean mineral oil sampling concentrations for the OVS and IFV Pro were 5.80 mg/m^3 (SD=1.77) and 5.56 mg/m^3 (SD=1.55), respectively (see Table A.2 for paired sampling concentrations). A two-tailed t-test identified an insignificant difference in the collected particle mass concentrations between the OVS and IFV Pro using an inert oil aerosol (t=1.48, p=0.11). In examining the positional differences of the samplers, there was no significant trend (t-test p>0.06). Figure 2.2 displays a linear regression plot of the OVS and IFV Pro sampling concentrations. A linear regression analysis generated a significant slope of 0.827 (95% CI: 0.676-0.977) and an insignificant intercept of 0.769 (p=0.09).

2.3.2. Dual-Phase Efficiency

The temperature and relative humidity levels remained consistent inside the chamber, ranging from 30.3-32.0℃ and 17.3-19.9%, respectively (see Table A.3 for a summary of environmental conditions). The MMAD of ethylene glycol droplets within the chamber ranged from 3.18-6.05 µm (see Figure A.16).

The OVS displayed 30% higher ethylene glycol particle and vapor concentrations than the IFV Pro (Figure 2.3). All four paired samples and Blank 2 exhibited sample breakthrough. The IFV Pro exhibited an average of 13% more breakthrough than the OVS (see Table A.4 for paired sample masses).

2.3.3. Applicator Exposure Assessment

A total of six paired glyphosate and one paired dicamba/MCPA sample were analyzed by the laboratory. All sample masses were below the limit of quantification (LOQ), or the ideal mass to determine quantitative results with high certainty. All glyphosate samples had masses below the minimum mass that can be determined to be statistically different from a blank sample, or the limit of detection (LOD). Dicamba levels on the paired dicamba/MCPA samples were below the LOD; however, small amounts of MCPA were found in the paired samples and their corresponding blanks (see Table A.5). These samples did not exhibit any breakthrough.

Six subjects were monitored for aerosolized pesticide exposure, with Subject 2 being monitored twice. Only one field sample was above the laboratory LOQ (Subject 1A – MCPA) (Table 2.1). No subjects were potentially exposed to more than 1.1 mg/m^3 of pesticides. Seventy-one percent of the air monitoring sessions involved subjects spraying less than 3.8 L of pesticide. Subjects reported using long sleeve pants and shirts, closed-toe shoes, chemical-resistant gloves, and safety goggles/glasses 86% of the time. The equipment, task, pesticide name, sampling time, and PPE used associated with each subject's air monitoring session are summarized in Table A.6.

Survey results indicate that 67% of the subjects spray pesticides monthly during the summer and fall months. Most subjects (83%) stated that they had received formal training on proper pesticide application. Other general/occupational information obtained by the subjects is reported in Table A.7. Per the post-application survey, subjects also described how they considered wind direction and speed during their air monitoring session. Those considerations are summarized in Table A.8.

Temperature, relative humidity, and wind speed measurements during the applicator exposure assessment were all recorded (see Table A.9). Workers from Company C sprayed in the coolest average temperatures (13.2℃ on 9/23 and 14.0℃ on 9/28) and the highest average humidity levels (48.7% on 9/28 and 67.6% on 9/23). Company A sprayed in the warmest average temperature (20.6℃) and lowest average humidity level (40.8%). Wind speeds were relatively low for the three companies, never surpassing 16.1 km/hr (10mph), in accordance with RoundUp® label guidelines (Monsanto, 2007). The average wind speed was lowest for Company A (5.6 km/hr) and highest for Company C (11.3 km/hr on 9/28 and 14.5 km/hr on 9/23).

2.4. Discussion

2.4.1. Particle & Dual-Phase Efficiency

In the relative dual-phase efficiency trials, the OVS exhibited an insignificantly (p=0.11) higher particle-phase collection of an inert oil aerosol. Due to budgetary constraints, only four dual-phase trials were performed. All four dual-phase OVS samples displayed 30% higher ethylene glycol concentrations than the IFV Pro; however, the number of samples was too small to perform a statistical analysis and obtain 80% power to detect differences between the samplers.

Only one other study by Alex et. al. (2020) involves the evaluation of the particle and dual-phase collection efficiencies of the OVS and IFV Pro samplers. Contrary to the results of this study, Alex et. al concluded that the IFV Pro samples more mass than the OVS. Their study, although similar in concept, was notably different in design. One such difference is the aerosol distribution inside the chambers. Alex et al. produced a laminar *downward* draft of aerosol-laden air to pass over the two samplers. In this study, an *upward* draft of aerosols was created using an oscillating fan.

The difference in the aerosol directional flow may indicate one reason why the results from these two studies contradict. Because the OVS sampler inlet faces vertically downward, the upward draft in this study may have assisted the sampler in collecting the analyte. This differentiated from the downward draft in the study by Alex et al., possibly contributing to the underperformance of the OVS. The IFV Pro inlet, which faces parallel to the ground, is less likely to be influenced by vertical changes in directional air flow.

There is no established analysis method for the IFV Pro because it has only recently been made commercially available. Two laboratories were contacted to perform the analysis of the IFV Pro samples; however, both laboratories were unfamiliar with analyzing and reporting the multiple samples (filter, filter cassette, & adsorbent). Given the confusion, the WOHL used methods such as OSHA PV2067 (glyphosate) and NMAM 5523 (glycols) and 5001 (2-4 D, Dicamba, & MCPA) to assist in analyzing the samples. They did not follow the manufacturer's recommendation (SKC Inc.) to analyze the filter cassette and sorbent tube simultaneously.

The filter cassette is an inherent design feature of the IFV Pro and allows for inhalable, size-selective sampling to occur. Like the IOM sampler cassette, the analyte deposits inside the IFV Pro cassette are included in the inhalable fraction. Thus, analyte deposits should be analyzed in conjunction with the filter and sorbent tube. In this study, the laboratory was not familiar with the new sampler and did not follow the manufacturer's guidance to analyze the cassette with the filter and sorbent tube. To be consistent with the WOHL practices, the filter cassette was also not analyzed gravimetrically during the particle-phase mineral oil trials. Consequently, the true IFV Pro mineral oil, ethylene glycol, and pesticide concentrations are likely underestimated in this study. A standardized method should be developed to facilitate the analysis of the IFV Pro filter cassettes and sorbent tubes to prevent further analysis confusion.

2.4.2. Exposure Assessment

The purpose of conducting an exposure assessment with both the OVS and IFV Pro was to compare the concentrations collected by the two samplers. A direct comparison using field samples would have been valuable in determining the sampling characteristics of the OVS and IFV Pro in real-world pesticide application settings. This study design had never been performed previously using the two samplers. Unfortunately, the comparison between samplers was not feasible due to the low exposure concentrations collected from the subjects.

All applicator exposure assessment samples had masses below the laboratory LOQ for dicamba (2 μg), MCPA (6 μg), and glyphosate (160 μg). If the sampling time for the three pesticides were all equal, this would indicate that analysis methods are more sensitive to dicamba and MCPA. The only pesticide that was detected by the laboratory (where mass > LOD) was MCPA on a single paired sample, in which the IFV Pro collected 258% more MCPA than the OVS after blank corrections (see Table A.5 for sample and blank masses). Subject 1 (Company A) sprayed Horsepower® (MCPA and dicamba) for five hours, primarily while operating a Z-Spray Stand-On® Sprayer. Environmental conditions differed slightly from the trial averages. Temperatures were slightly higher (+6.3℃) and the relative humidity and wind speeds were slightly lower (-5.1% and -3.6 mph). No observed differences were recorded regarding the positioning of the two sampler inlets while sampling. There are no obvious indications as to what may have caused the significant difference between the samplers.

Data censoring is often used to perform an analysis when samples are below the laboratory's limit of detection (LOD). Censoring involves arbitrarily allocating masses (often relative to the LOD; e.g., LOD/2 or LOD/√2) to nondetectable samples and used to conduct an analysis (Hewett & Ganser, 2007). However, data censoring was not appropriate in this study due to the high number of nondetectable samples.

The pesticide applicators that participated in this study experienced an overall low exposure to pesticides. The highest calculated potential for exposure was from Subject 6 (<1.1mg/ m^3) because he sprayed glyphosate (high LOQ – 160 µg) for the shortest period of time (146 mins).

Upon observation, Subject 2 was anticipated to experience the highest exposure level. During his second day of participation, Subject 2 sprayed about 300 yards of fenceline. The fence had been overgrown by vegetation, and Subject 2 sprayed the entire fence at various heights, including above the head (see Figure A.17). By spraying closer to his breathing zone, it was anticipated that his exposure would be higher than other subjects who sprayed at lower heights. However, the results of this study do not support this assumption.

Four subjects stated during the exposure assessment that they were concerned about high levels of pesticide exposure. This concern was derived from the subjects' ability to smell the pesticide odor while mixing and spraying chemicals even while wearing respirators. It is assumed that despite smelling the chemical odor, the concentration of vapor was not necessarily large enough to produce a mass dose. Thus, the workers breathed vaporous pesticides but not in a high enough concentration to be detected via personal air monitoring.

When applied in high wind conditions, pesticides can drift away from the intended target and up to 90 km from the source (Harnley, et al., 2005; Van den Berg, et al., 1999). When asked, in this study, if subjects considered wind speed/direction while spraying, 100% of the subjects stated 'Yes.' Strategies implemented by subjects to reduce drift and potential exposure were to lower the sprayer nozzle to the target area, spray downwind, and cease spraying in high wind conditions.

Formal safety trainings are often neglected for temporary and seasonal workers. Fabiano et al. identified that temporary workers are at higher risk of injury/illness than their full-time counterparts due to a lack of experience and training (2007). Five out of the six subjects in this study had previously received formal training on safe pesticide handling and application. Subject 3 stated that he had not received formal training because he is a seasonal employee. This constitutes a higher risk of injury/illness for Subject 3.

Dicamba is the only pesticide in this study that has a recommended exposure limit (PEL: 5 mg/m^3). The lack of occupational exposure limits for these pesticides is unsettling as high exposure can cause significant illness and disease. This absence also complicates the interpretation of exposure monitoring results, as there is no established health reference for comparison.

2.4.3. Limitations

Filter cassettes are an inherent part of an inhalable sampler. The OVS does not have a cassette and the OSHA and NIOSH analytical methods do not provide guidance for analyzing aerosols deposited within the sampler (i.e., in between the sorbent layers). The IFV Pro does have a filter cassette. However, as stated previously, the lack of a standardized method causes confusion in the analysis of the IFV Pro samples. The manufacturer's recommendation (SKC Inc.) is to analyze the filter cassette, filter, and sorbent tube simultaneously to account for wall deposits on the cassette. In addition to accounting for aerosol deposits, analyzing all the IFV Pro components simultaneously can significantly decrease analysis costs. Despite the manufacturer's recommendation, the WOHL only analyzed masses from the filter and adsorbent layers due to unfamiliarity with the device. Thus, aerosol wall deposits were not obtained for the IFV Pro relative efficiency trials and the applicator exposure assessment, contrary to the manufacturer's recommendations. Ignoring wall deposits in the IFV Pro cassette biases toward lower concentrations.

2.5. Conclusion

This study aimed to: 1) assess the aerosol and vapor sampling efficiencies of the OVS and IFV Pro; and 2) evaluate the risk of pesticide exposure among Iowa pesticide applicators. The first study objective involved the comparison of the relative particle and dual-phase sampling efficiencies of the two samplers. Under the conditions of this study, no significant difference was identified between the OVS and IFV Pro particle-phase sampling efficiencies ($p=0.11$). Descriptive statistics of the relative dual-phase sampling efficiencies failed to prove a difference between the two samplers. However, both the OVS and IFV Pro exhibited breakthrough with the IFV Pro averaging 13% more breakthrough per sample. Additional dual-phase trials ought to be performed to 1) assess the relative efficiencies of the OVS and IFV pro without breakthrough and 2) increase the statistical power to detect differences between the two samplers.

The second study objective involved performing an exposure assessment of pesticide applicators at three Iowa landscaping companies. The assessment was used to 1) compare the sampling results of the OVS and IFV Pro and 2) identify whether Iowa pesticide applicators are at risk of high pesticide exposure. The OVS and IFV Pro field samples collected from six participants provided negligible masses of glyphosate and near negligible masses of MCPA and dicamba. As a result, actual subject exposure concentrations could not be determined and a comprehensive comparison between the samplers was not feasible.

Nevertheless, the negligible results do indicate that subjects from the three Iowa-based companies are not exposed to significant levels of pesticides. Exposure reduction strategies currently implemented by the companies (spray under ideal environmental conditions, use chemicals/equipment as directed by the manufacturer, restrict spray time, don proper PPE, etc.) are encouraged to continue limiting their overall exposure.

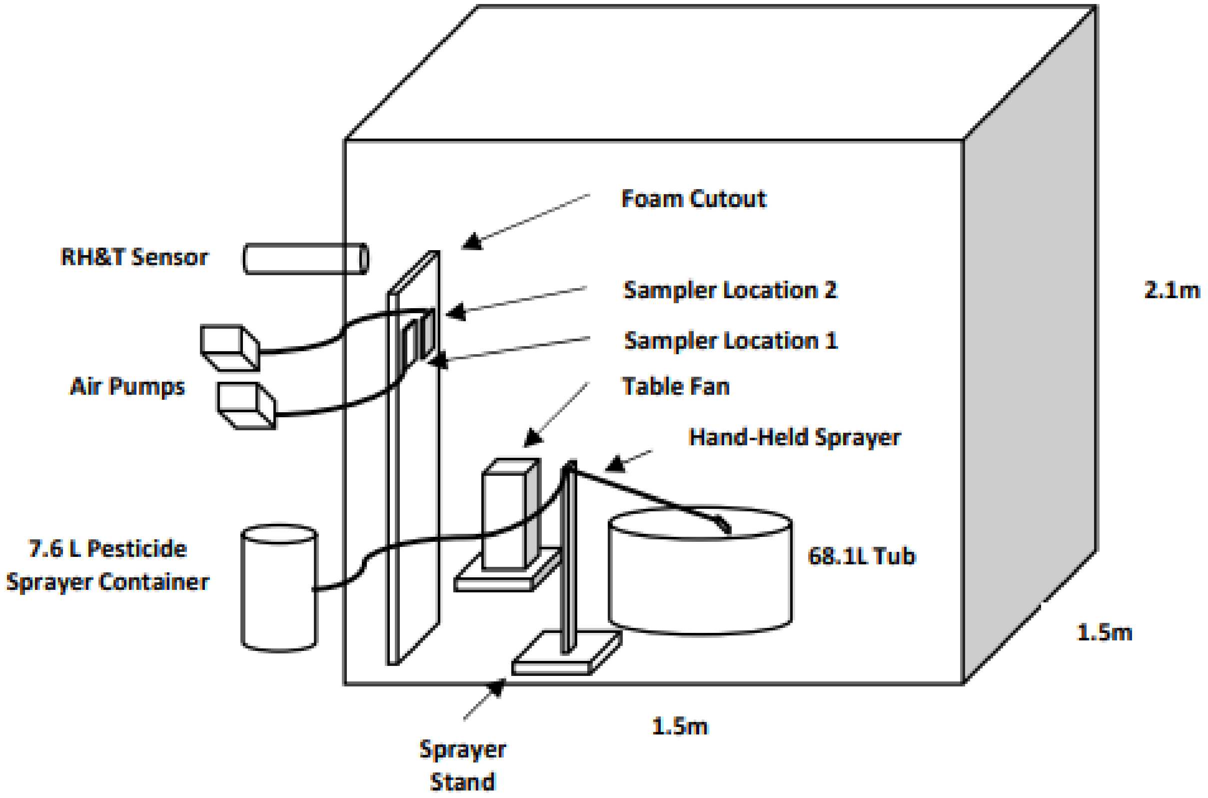

Figure 2.1. Spray Chamber Design

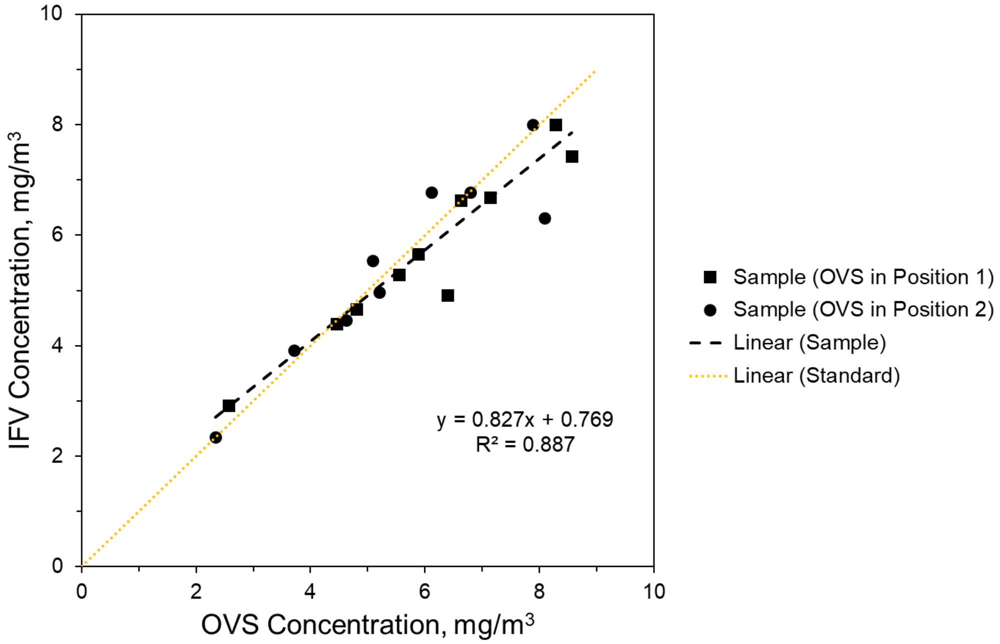

Figure 2.2. Regression Plot of the OVS & IFV Pro Mineral Oil Filter Mass Concentrations in a Chamber (Particle-Phase Trials)

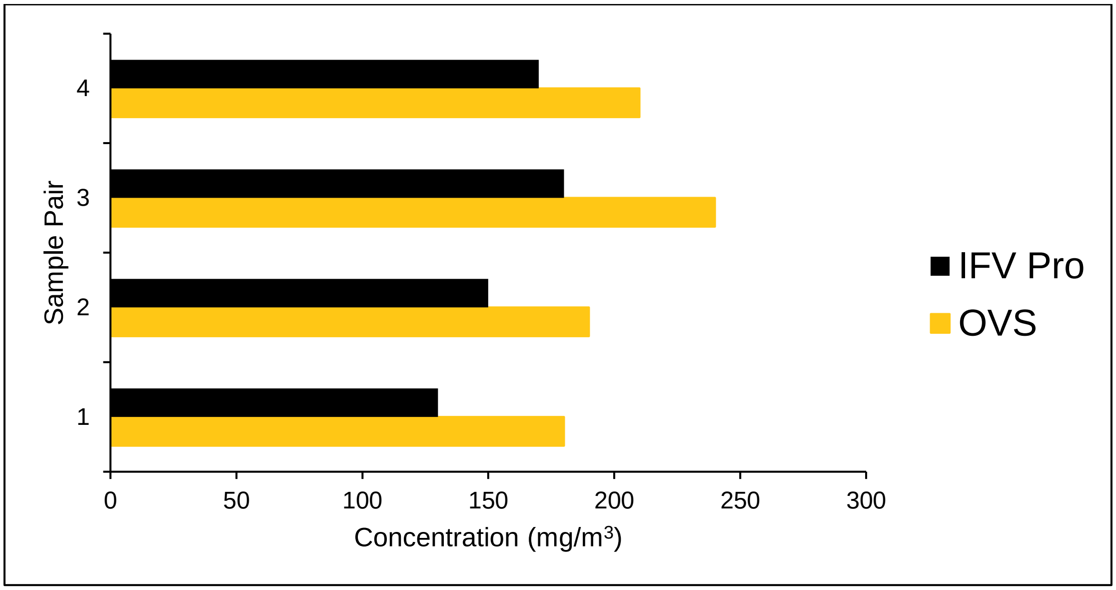

Figure 2.3. Dual-Phase Comparison of the OVS and IFV Pro Ethylene Glycol Particle & Vapor Concentrations in a Chamber (Dual-Phase Trials)

Table 2.1.The Pesticide-Specific Subject Exposure Concentrations Based on the Laboratory Limit of Quantification and the Corresponding Pesticide Exposure Limits

Subject (Company)	**Pesticide**	**Sample Time (min)**	**LOQ (mg)**	**Exposure Concentration Based on Laboratory LOQ (mg/m^3)[1]**	**Recommended Exposure Limit (mg/m^3)**	
					PEL	**TLV**
1 (A)	Dicamba	320	0.002	<0.01	5	-
1 (A)	MCPA	320	0.006	<0.02	-	-
2 (C)	Glyphosate	169	0.160	<0.95	-	-
2 (C)	Glyphosate	375	0.160	<0.43	-	-
3 (C)	Glyphosate	156	0.160	<1.03	-	-
4 (C)	Glyphosate	369	0.160	<0.43	-	-
5 (B)	Glyphosate	284	0.160	<0.56	-	-
6 (B)	Glyphosate	146	0.160	<1.10	-	-

1 - Actual sampling results were below the limit of quantification. As a result, a potential exposure concentration was calculated using the pesticide-specific LOQ and the volume of air sampled per subject.

CHAPTER 3: CONCLUSION

This study aimed to: 1) assess the aerosol and vapor sampling characteristics of the OVS and IFV Pro; and 2) evaluate the risk of pesticide exposure among Iowa pesticide applicators. Study objectives included assessing the relative particle and dual-phase sampling efficiencies of the two samplers in a simulated and real-world setting, as well as performing an exposure assessment of pesticide applicators at three Iowa landscaping companies.

Because the IFV Pro is designed as an inhalable sampler, the IFV Pro was expected to outperform the OVS in both the particle and dual-phase efficiency trials. Contrary to the results of another study (Alex, et al., 2021), this assessment indicates that the samplers are equally efficient when operated under similar conditions as this study. The mean concentration differences between the OVS and IFV Pro in the particle-phase trials were insignificant (p=0.11), and descriptive statistics failed to identify a meaningful difference between the relative dual-phase efficiencies of the two samplers.

A notable condition that may have contributed to the results of this study was an upward draft of aerosols that was created using an oscillating fan. Because the OVS sampler inlet faces vertically downward, the upward draft may have assisted the sampler in collecting the analyte. This differed from the study performed by Alex et al. in which a laminar downward draft was created, and the OVS collected less analyte mass than the IFV Pro (2021). The IFV Pro inlet, which faces parallel to the ground, is less likely to be influenced by vertical changes in directional air flow.

A limited number of samples and breakthrough among both samplers during the dual-phase trials complicated the ability to derive conclusions on their relative dual-phase efficiencies. Due to the expensive nature of sample analysis, only four paired samples and two paired blanks were analyzed by the laboratory. Of the four samples analyzed, the IFV Pro averaged approximately 13% more breakthrough per sample. The breakthrough indicates oversampling and that some of the analyte was likely lost during sampling. This breakthrough underestimates the true amount of analyte sampled, especially that of the IFV Pro. Consequently, the study results indicate that the more efficient dual-phase sampler is inconclusive.

In retrospect, several of the dual-phase efficiency trial methods were flawed and resulted in sampler breakthrough. If given the opportunity, I would consider making several changes to optimize the potential of notable results. First, decrease spraying duration. The spray rate of the pesticide sprayer was not determined prior to the efficiency trials, so the amount of aerosolized ethylene glycol was unknown during the study. Unknowingly, too much ethylene glycol was aerosolized within the chamber. If money allowed, additional trials using less ethylene glycol would have been performed.

Second, a change to decrease the sampling duration would take place. In this study, a total of 17.5 L of air was sampled at 1 L/min. The minimum sampling volume for glycols is 5 L (NIOSH 5523). Thus, the sampling duration could have been decreased to 5 min/sample, preventing sampler breakthrough.

A final change is to increase the number of dual-phase trials. Due to budgetary constraints, only four paired samples were feasible at the time. Consequently, the sample number was too small to perform a statistical analysis of the results. A second effort in which conducting more trials (i.e., 20) to increase the statistical power to detect the relative dual-phase efficiency differences between the two samplers would be beneficial.

The filter cassette is an inherent design feature of the IFV Pro and allows for inhalable, size-selective sampling to occur. Like the IOM sampler cassette, the analyte deposits inside the

IFV Pro cassette are included in the inhalable fraction. Thus, analyte deposits should be analyzed in conjunction with the filter and sorbent tube. In this study, the laboratory was not familiar with the new sampler and did not follow the manufacturer's guidance to analyze the cassette with the filter and sorbent tube. To be consistent with the WOHL practices, the filter cassette was also not analyzed gravimetrically during the particle-phase mineral oil trials. Consequently, the true IFV Pro mineral oil, ethylene glycol, and pesticide concentrations are likely underestimated in this study. A standardized method should be developed to facilitate the analysis of the IFV Pro filter cassettes and sorbent tubes to prevent further analysis confusion.

The purpose for performing an exposure assessment was to 1) compare sampling results of the OVS and IFV Pro and 2) identify if Iowa pesticide applicators are at risk of high pesticide exposure. Exposure assessment objectives were to identify if one sampler outperforms the other in the field and to perform an exposure assessment of pesticide applicators at the three Iowa landscaping companies. The OVS and IFV Pro field samples collected from six participants provided low concentrations of glyphosate and near negligible concentrations of MCPA and dicamba. As a result, a comprehensive comparison between the samplers was not feasible. The negligible results do indicate that subjects from the three companies are not exposed to significant levels of pesticides. Exposure reduction strategies currently implemented by the companies (spray under ideal environmental conditions, use chemicals/equipment as directed by the manufacturer, restrict spray time, don proper PPE, etc.) are encouraged to continue limiting their overall exposure.

Future studies should further investigate the role that environmental conditions have in the relative particle and vapor sampling efficiencies of the OVS and IFV Pro. An inquiry into the samplers' functionalities under high/low temperatures and humidities would be beneficial in determining if a sampler is preferred in different climates. Additionally, an investigation of the impact that vertical and horizontal drafts have on the OVS and IFV Pro should take place.

Subjects in this study were from three Iowa landscaping companies and spraying pesticides is not their primary role. Other applicators in industries specializing in pest control and agriculture spray chemicals in different quantities and frequencies, so conducting research to compare exposures across industries would be beneficial. The lack of recommended exposure limits for pesticides makes the interpretation of exposure data difficult. Additional studies focused on establishing recommended exposure limits for pesticides are recommended. Finally, increasing access to IFV endnote and IFV Pro resources would be advantageous given the lack of information and analytical methods associated with the two.

The EPA and several pesticide manuals advise applicators to follow the pesticide product label to “manage the potential risks [to humans and the environment] from pesticides” (EPA, 2023; NASDA & EPA, 2014). The label is a legal document that provides information on how to mix, apply, and store pesticides. Unfortunately, labels are often removed, lost, or disposed of by employees. In addition, they may be damaged by weather conditions or the corrosive properties of pesticides.

Published pesticide applicator manuals recommend replacing pesticide labels once they become illegible or storing labels in a safe place and marking the individual containers with signs and symbols (NSDA, 2014; NASDA & EPA, 2014). I observed in this study that all three companies had pesticide containers with legible, descriptive labels. In addition, all chemicals were stored in secure storage areas.

Organizations such as Companies A, B, and C that diligently follow chemical labeling recommendations are likely to expect a reduction in the potential risks to human and environmental health. However, not all organizations give such an emphasis on chemical labeling. I suggest an improvement to the chemical labeling process take place at the manufacturer's level. One possible solution would be to print/stamp pertinent chemical information (ie. chemical name, active ingredients, health effects, and required PPE) directly onto the container, as opposed to a paper/plastic label taped to the container. This practice would withdraw the ability to remove a label from the container, reducing the number of unlabeled chemical containers at a work site. However, a major disadvantage to this approach is that it would likely increase production costs for manufacturers.

Pesticide applicator manuals also describe methods to reduce the potential drift of pesticides. Several strategies include lowering the spray nozzle/boom closer to the target, implementing buffer zones/no-spray zones, spraying in low wind conditions, using drift-preventing additives, etc. Applicators in this study implemented several of these techniques. For example, Companies B and C requested multiple times to reschedule study participation due to high wind conditions. Despite the inconveniences, I appreciated their dedication to protecting the environment and their workers. As shown by the sampling results, their efforts are assisting in the reduction of worker pesticide exposure.

I decided to perform this thesis project because I knew that it would challenge me professionally, intellectually, and personally. I learned very quickly the importance of having a professional support system. In the beginning, I was naïve to the research process, and over time I encountered more setbacks and difficulties than I had anticipated. Certainly, I could not have succeeded in overcoming those barriers without the help of incredible colleagues, professors, and mentors. I learned to be meticulous in my recordkeeping, to use creativity in problem-solving, and to be proactive and assertive without solicitation. Because of the wide scope of my thesis, I improved my various industrial hygiene skills such as performing air sampling, measuring filters, operating scientific equipment, and interpreting results. In addition, I was able to practice communicating scientific concepts both orally and written.

The most memorable aspects of this project were designing a project of my own and working with such amazing people. It was evident during the design stages that my aspirations were high and that this study would take an abundance of time and planning. It was difficult at times to complete the many project-related tasks while simultaneously juggling other student, family, and volunteer obligations. However, it has been rewarding to see what I can build and accomplish when I put in the effort. I particularly enjoyed working with the applicators in this study. It was a great opportunity to use my skills in the field and a privilege to befriend those individuals.

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APPENDIX A: SUPPLEMENTAL INFORMATION FOR CHAPTER II

Figure A.1. Chamber Used in the Particle and Dual-Phase Efficiency Trials

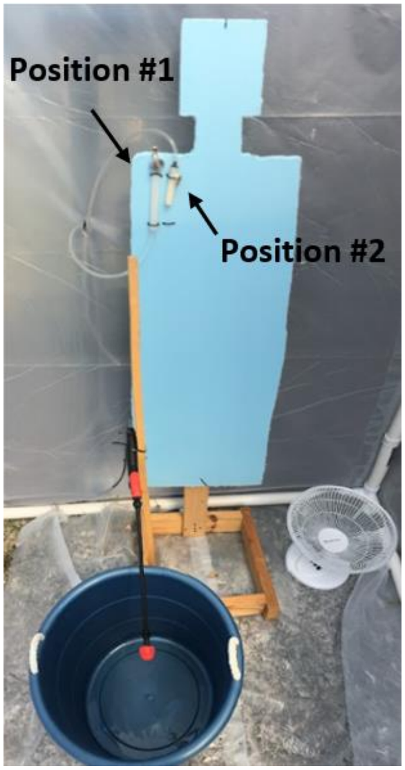


Figure A.2. Equipment Setup & Sampler Positions Inside the Chamber

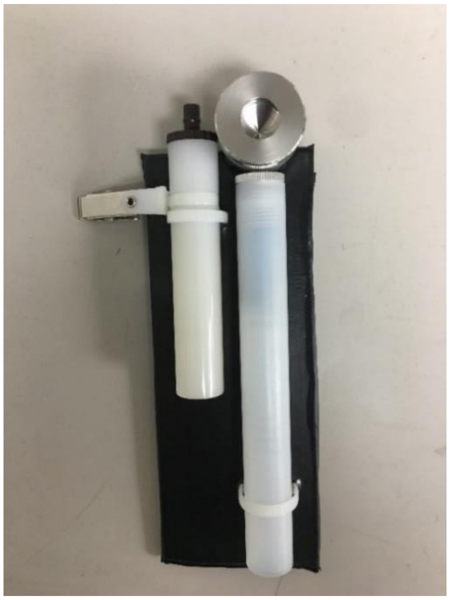
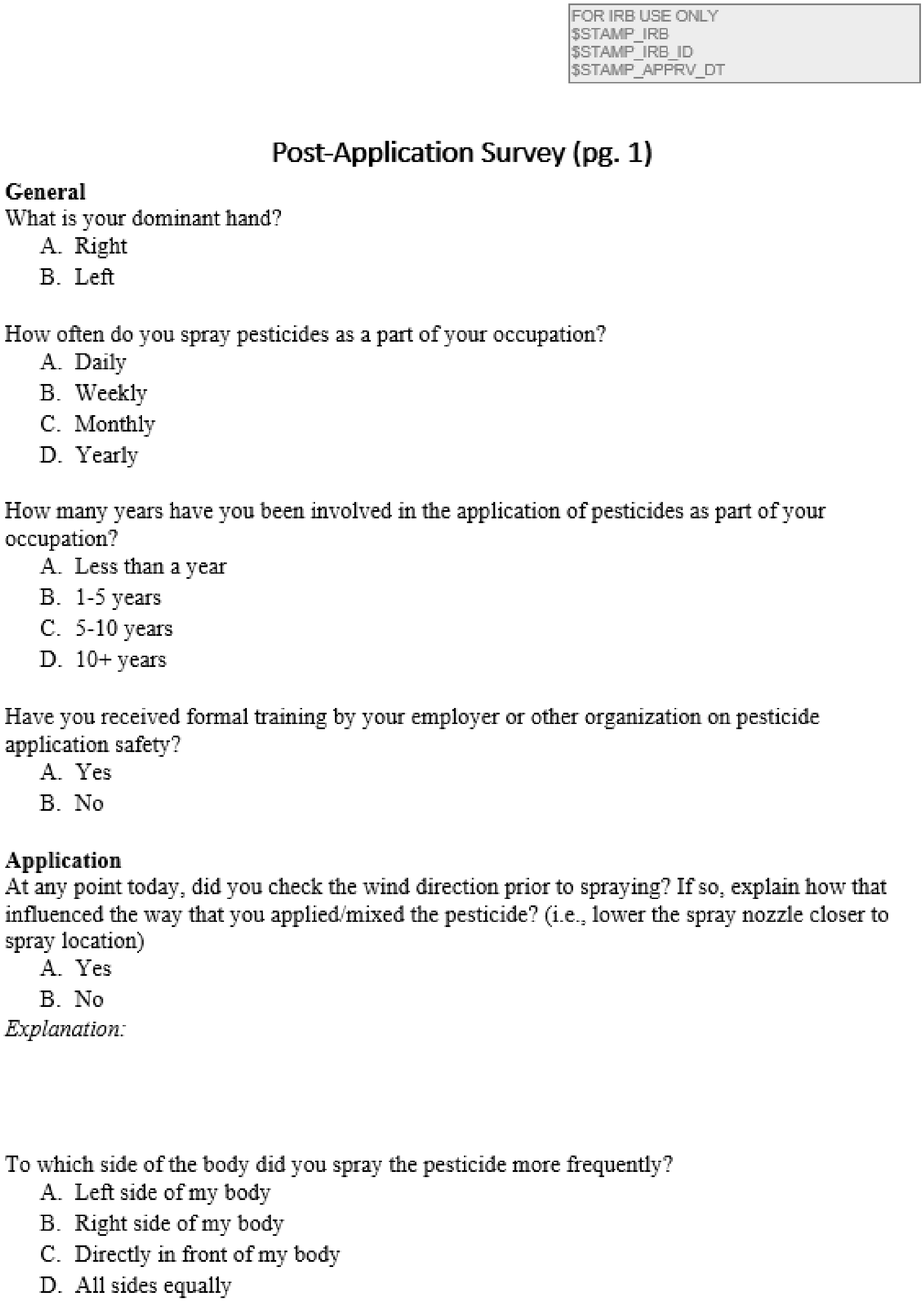


Figure A.3. Sampler Holder for Exposure Assessment

Figure A.4. Samplers & Pumps Attached to Worker Via Backpack

Figure A.5. Samplers & Pumps Attached to worker Via Clips



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Post-Application Survey (pg. 1)

General

What is your dominant hand?

A. Right
B. Left

How often do you spray pesticides as a part of your occupation?

A. Daily
B. Weekly
C. Monthly
D. Yearly

How many years have you been involved in the application of pesticides as part of your occupation?

A. Less than a year
B. 1-5 years
C. 5-10 years
D. 10+ years

Have you received formal training by your employer or other organization on pesticide application safety?

A. Yes
B. No

Application

At any point today, did you check the wind direction prior to spraying? If so, explain how that influenced the way that you applied/mixed the pesticide? (i.e., lower the spray nozzle closer to spray location)

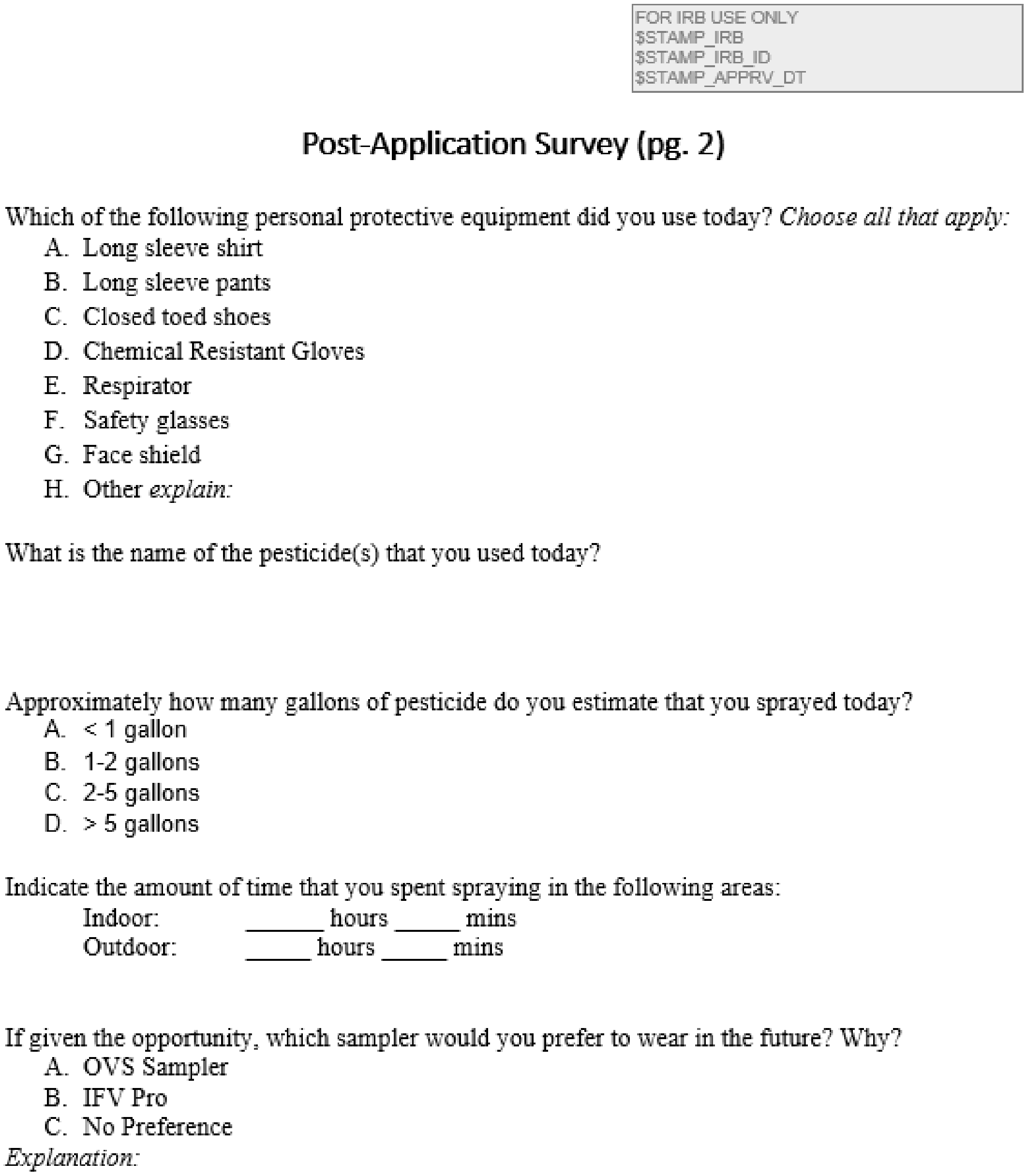
A. Yes
B. No

Explanation:

To which side of the body did you spray the pesticide more frequently?

A. Left side of my body
B. Right side of my body
C. Directly in front of my body
D. All sides equally

Figure A.6. Post-Application Survey Administered to Participants (page 1)



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Post-Application Survey (pg. 2)

Which of the following personal protective equipment did you use today? *Choose all that apply:*

A. Long sleeve shirt
B. Long sleeve pants
C. Closed toed shoes
D. Chemical Resistant Gloves
E. Respirator
F. Safety glasses
G. Face shield
H. Other *explain:*

What is the name of the pesticide(s) that you used today?

Approximately how many gallons of pesticide do you estimate that you sprayed today?

A. < 1 gallon
B. 1-2 gallons
C. 2-5 gallons
D. > 5 gallons

Indicate the amount of time that you spent spraying in the following areas:

Indoor: ______ hours _____ mins
Outdoor: _____ hours _____ mins

If given the opportunity, which sampler would you prefer to wear in the future? Why?

A. OVS Sampler
B. IFV Pro
C. No Preference

Explanation:

Figure A.7. Post-Application Survey Administered to Participants (page 2)

Figure A.8. Modified OVS Tube with Resin Removed for the Particle-Phase Efficiency Trials

Figure A.9. Modified IFV Pro (IFV Pro Head Without Sorbent Tube) for the Particle-Phase Efficiency Trials

Figure A.10. Modified OVS & IFV Pro Calibration Trains for Particle-Phase Trials

Figure A.11. OVS & IFV Pro Sampling Trains

Figure A.12. Subject 1 (Company A) Applying Dicamba and MCPA to Fields Using a Toro Multi-Pro® Turf Sprayer and a Z-Spray Stand-On® Sprayer

Figure A.13. Subjects 5 and 6 (Company B) Operating a Z-Spray Stand-On® Sprayer and a Solo Backpack Sprayer

Figure A.14. Subjects 2 and 4 (Company C) Using a Modified Gravely Zero Turn Mower for Spraying Pesticides

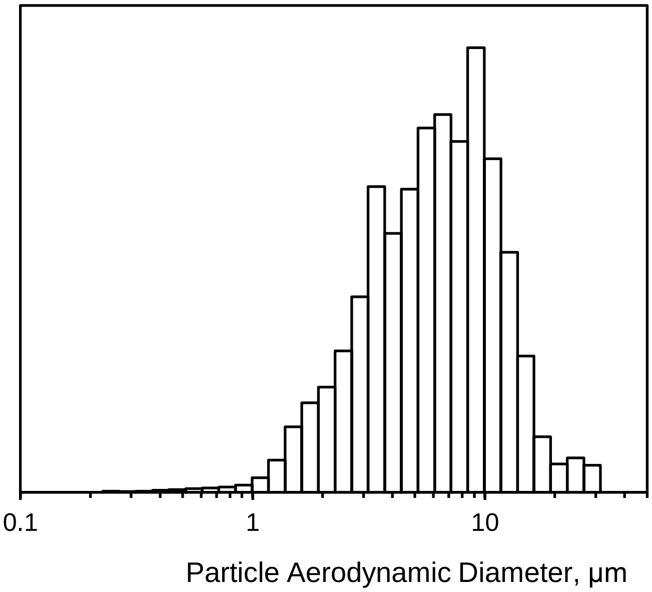


Figure A.15. Particle Size Distribution of the Particle-Phase Trials (Mineral Oil)

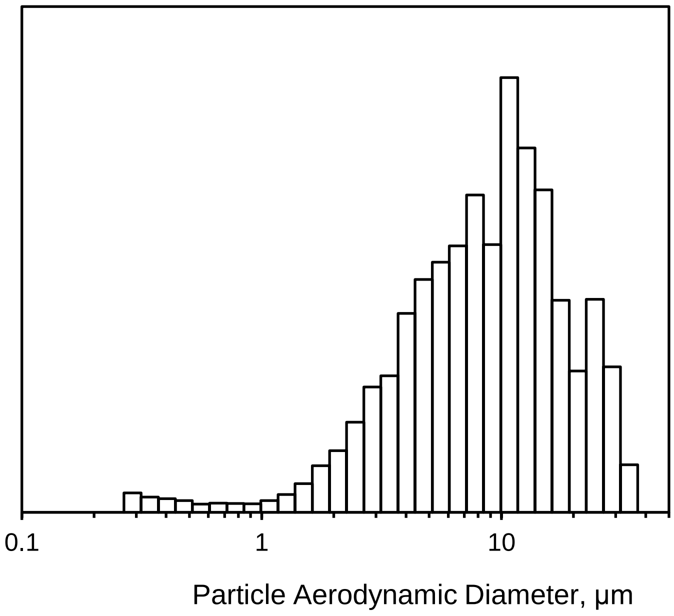


Figure A.16. Particle Size Distribution of the Dual-Phase Trials (Ethylene Glycol)

Figure A.17. Subject 2 (Company C) Spraying a Fence Above His Head

Table A.1. Environmental Sampling Conditions (Particle-Phase Trials)

Trial (Date)	**Temperature (°C)**	**Relative Humidity (%)**
1	20.5	78.9
2	21.7	72.9
3	23.5	67.0
4	24.6	65.4
5	24.6	65.4
6	23.4	89.0
7	23.9	88.1
8	24.5	84.2
9	23.4	67.1
10	23.9	64.2
11	24.5	58.2
12	23.4	52.2
13	23.8	68.6
14	25.9	72.1
15	27.9	64.6
16	16.0	64.6
17	16.0	58.0
18	16.3	52.0
19	16.6	43.5
Mean (SD)	22.3 (3.6)	67.2 (12.0)

Table A.2. Mineral Oil Sampling Concentrations of the OVS and IFV Pro (Particle-Phase Trials)

Sample Pair	OVS Concentration (mg/m^3)	IFV Pro Concentration (mg/m^3)
1	5.20	4.97
2	4.80	4.66
3	6.80	6.77
4	7.14	6.69
5	6.40	4.91
6	4.63	4.46
7	6.63	6.63
8	6.11	6.77
9	5.89	5.66
10	8.09	6.31
11	8.29	8.00
12	2.34	2.34
13	2.57	2.91
14	3.71	3.91
15	4.46	4.40
16	5.09	5.54
17	5.54	5.29
18	7.89	8.00
19	8.57	7.43
Mean (SD)	5.80 (1.77)	5.56 (1.55)

Table A.3. Environmental Sampling Conditions (Dual-Phase Trials)

Trial	Temperature (°C)	Relative Humidity (%)
1	30.3	19.2
2	31.0	19.9
3	31.4	18.8
4	32.0	17.3
Mean (SD)	31.2 (0.7)	19 (1.1)

Table A.4. Ethylene Glycol Sampling Masses of the OVS and IFV Pro (Dual-Phase Trials)

Pair	OVS		IFV Pro	
	Primary[1]	Breakthrough[2]	Primary[1]	Breakthrough[2]
1	3.11	0.09	2.13	0.11
2	3.29	0.03	2.47	0.11
3	3.91	0.25	2.96	0.23
4	3.41	0.20	2.83	0.20
Blank 1	0.00	0.00	0.00	0.00
Blank 2	1.32	0.64	0.01	0.00
Sample Mean (SD)	3.43 (0.34)	0.14 (0.10)	2.60 (0.37)	0.16 (0.06)

1 - Total mass (mg) collected on the sampler filter and primary resin layer
2 - Total mass (mg) collected on the sampler secondary resin layer (breakthrough)

Table A.5. Raw Masses of MCPA Collected at Company A

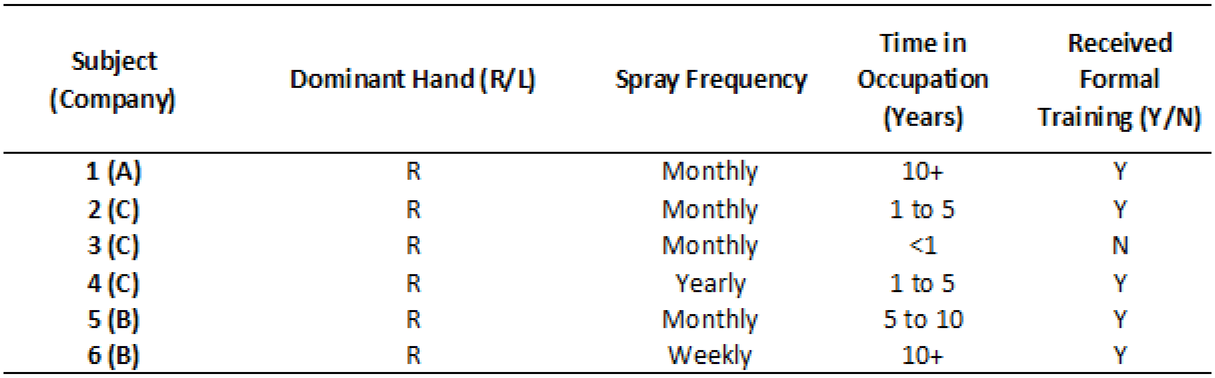
Subject	OVS[1]	IFV Pro[1]
1	0.58	2.1
Blank	0.1	0.86

1 - Total mass (μg) collected on the sampler filter and primary resin layer

Table A.6. Characteristics of Spraying Tasks by Subject

Subject (Company)	Equipment (Task)	Pesticide	Pesticide Sprayed (L)	Time (min)	PPE Used
1 (A)	Sprayer (Mini Boom and Z-Sprayer)	MCPA/Dicamba	3.8 to 7.6	320	Long Sleeve Shirt, Closed Toe Shoes, Chemical Resistant Gloves, & Safety Glasses
2 (C)	Sprayer (Adapted Lawnmower)	Glyphosate	<3.8	169	Long Sleeve Shirt, Long Sleeve Pants, Closed Toe Shoes, Chemical Resistant Gloves, & Safety Glasses
2 (C)	Sprayer (Adapted Lawnmower)	Glyphosate	<3.8	375	Long Sleeve Shirt, Long Sleeve Pants, Closed Toe Shoes, Chemical Resistant Gloves, Safety Glasses, & Respirator
3 (C)	Driver (Adapted Lawnmower)	Glyphosate	<3.8	156	Long Sleeve Shirt, Long Sleeve Pants, Closed Toe Shoes, & Safety Glasses
4 (C)	Driver (Adapted Lawnmower)	Glyphosate	<3.8	369	Long Sleeve Shirt, Long Sleeve Pants, Closed Toe Shoes, Chemical Resistant Gloves, & Safety Glasses
5 (B)	Sprayer (Z-Sprayer)	Glyphosate	3.8 - 7.6	284	Long Sleeve Shirt, Long Sleeve Pants, Closed Toe Shoes, Chemical Resistant Gloves, & Safety Glasses
6 (B)	Sprayer (Backpack)	Glyphosate	<3.8	146	Long Sleeve Shirt, Long Sleeve Pants, Closed Toe Shoes, Chemical Resistant Gloves, & Safety Glasses

Table A.7. General Subject & Occupational Information



Subject (Company)	Dominant Hand (R/L)	Spray Frequency	Time in Occupation (Years)	Received Formal Training (Y/N)
1 (A)	R	Monthly	10+	Y
2 (C)	R	Monthly	1 to 5	Y
3 (C)	R	Monthly	<1	N
4 (C)	R	Yearly	1 to 5	Y
5 (B)	R	Monthly	5 to 10	Y
6 (B)	R	Weekly	10+	Y

Table A.8. Subject Thoughts on Spraying Pesticides During Windy Conditions

Subject (Worker)	Considered Wind While Spraying (Y/N)	Comments
1 (A)	Y	"I don't spray if wind speed is over 12 mph [19.3 km/hr]"
2 (C)	Y	"[When windy], I spray low, close to the target area and adjust the pressure on the tank and nozzle to prevent drift"
3 (C)	Y	"[The wind] helped me decide which side of the sprayer I drove on"
4 (C)	Y	"[When windy], I lower the nozzle and don't face into the wind."
5 (B)	Y	"I used flags on campus or my posted flags' [to see the wind's direction]"
6 (B)	Y	"[When windy], I lower the nozzle tip or find less wind affected areas to spray"

Table A.9. Environmental Conditions While Field Sampling (Exposure Assessment)

Company (Date)	Temperature (°C)		Relative Humidity (%)		Wind Speed (km/hr)	
	Low	High	Low	High	Low	High
A (10/10)	13.6	27.5	21.9	59.7	1.6	9.7
B (10/4)	12.1	22.2	32.9	62.5	6.4	12.9
C (9/23)	12.6	13.7	65.9	69.3	12.9	16.1
C (9/28)	6.4	21.5	29.7	67.7	8.0	14.5
Mean (SD)	11.2 (3.2)	21.2 (5.7)	37.6 (19.4)	64.8 (4.5)	9.1 (3.4)	13.3 (2.7)

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