PPE Effectiveness in Agricultural Settings

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Abstract

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Personal Protective Equipment (PPE) is usually required for pesticide applications, but how effective it actually is against exposure to chlorpyrifos, solvents and oils is unknown. Therefore, a pilot study has been created to get a more accurate estimate of whether or not there is pesticide breakthrough while wearing a half mask respirator and 15 mil nitrile gloves and if so, when that breakthrough occurs. An ambient sampling train and a sampling train behind a cartridge were created to compare the air concentrations in respirators, and positioned near the applicator during pesticide application. Passive media patches were placed underneath gloves to measure dermal exposure. Charcoal media was used to sample for horticultural oil, and PUF media was used to sample for chlorpyrifos. Two sites were sampled; chlorpyrifos and horticultural oil was sprayed at Site A and only horticultural oil was sprayed at site B. Media was changed out once a day. The sampling media was tested for hydrocarbons, alkanes, aromatics, chlorpyrifos, chlorpyrifos oxon, pentadecane, siloxanes and trimethyl benzene. The concentrations of the compounds were measured, and the frequency of breakthrough was calculated for each kind of media. A mass-to-mass ratio, comparing the ambient concentrations from the cartridge concentrations, was also calculated. The results show that the PPE that is worn is not providing adequate protection from the pesticides that are being sprayed, but more study is needed to elaborate on these results.

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Chapter 2: Introduction

For decades pesticides have been acknowledged as harmful not only to pests, but to humans who come in contact with them as well. It was not until years after Rachel Carson's book, Silent Spring, that many people began to take notice of the harm that pesticides can do. Many studies have been done to test the hazards of various pesticides and the best ways to be protected from them. With the new trend of eating organic foods, many people are aware of pesticides on the food they eat, but fewer think about the hazards that the pesticide applicators themselves face daily as part of their jobs.

Since there are many varieties of pesticides that are used in America's agricultural production, there are many different levels of hazards. These products harm living organisms (pests), and so therefore they can do great harm to people as well. Storage of chemicals, preparing the sprayer, handling and mixing of chemicals and field applications are all parts of the pesticide process that can be hazardous to humans, both through inhalation, ingestion and absorption through skin (Baker , 1997).

Apple orchard workers in places such as Yakima Valley in Washington, like millions of other farmers around the country, use pesticides as a way of maximizing the profit for the apples that they sell. The pesticide that these particular farmers use are Lorsban-4E, which is largely made up of chlorpyrifos, an organophosphate. Coupled with Lorsban-4E is Supreme Oil, which contains hydrocarbons and other solvents that also may be harmful to humans. Although these pesticides are still widely used, they present many hazards. The workers wear complete Personal Protective Equipment (PPE) while working on the farms spraying pesticides, but it is uncertain if

enough protective measures are being taken. These farmers wear 15 mil reusable nitrile gloves, Tyvec Chem resistant suits, chemical resistant goggles, chemical resistant boots, hats, and an organic vapor (OV) respirator cartridge with an R-95 pre-filter. The respirator cartridges are changed out once a day, or after an 8 hour shift; whichever is longer. Questions have been raised about whether the 8 hour a day single change out schedule for the organic vapor and pre-filter combination used with half mask air purifying respirators is adequate or not. There have been some studies where breakthrough times for cartridges and chemicals have been determined in controlled atmospheres and in laboratories, but these tests do not simulate the situations that are encountered in the agricultural setting and therefore cannot provide accurate data to help answer the question of change out time. To determine breakthrough time for the specific combination of an organic vapor cartridge and an R95 pre-filter that is typically worn for the pesticide application, sampling media will be used to test the airborne concentrations of solvents and oils and chlorpyrifos that are generated by the application of the pesticides with the air-blast sprayers.

Another form of PPE, the reusable gloves, is also not replaced very frequently, and it is uncertain if there is dermal exposure due to breakthrough from the gloves. Therefore, the airborne concentrations of the chlorpyrifos and some solvents and oils will be measured by placing patches on the inside of the gloves. The same compounds that were tested for inside the respirators will be tested for inside of the gloves.

Both of the types of PPE that is being evaluated will be tested for breakthrough twice a day, or have a change-out of sampling media during the workers' lunch break. If there is breakthrough after only half a day, or if the amount of solvents detected in the afternoon sampling media is greater than the solvents detected in the morning media, then this will show

that the workers should be changing out their PPE more frequently than the once a day change out that they currently do, and will provide a rough time schedule of when change-out should occur.

Samples will be taken to evaluate the effectiveness of the respirator cartridges by taking matched pairs of ambient samples and samples behind a respirator cartridge to see the difference in air concentrations, and then to determine a workplace protection factor. Samples will be taken to evaluate the effectiveness of the 15 mil nitrile gloves on the front and back of the hand to determine if there is breakthrough through the gloves and where the breakthrough is the most prevalent (Introduction and project proposal adapted from grant proposal written by Galvin, et. al.)

Chapter 3: Background Information

This background section will discuss in more detail the pesticides that are used, the hazards that are faced by farmers as they apply the pesticide, and the current practices of application and awareness of hazards.

3.1: Chlorpyrifos

Lorsban-4E, which is the insecticide that the apple orchard workers will be using, is generally used for the control of certain insects that infest field, fruit, nut, and vegetable crops. It should not be applied directly to water, as drift and runoff may be hazardous, and is combustible. It should not be applied in a way that will contact other workers or other people in the vicinity, particularly in the case of insecticide drift. Lorsban is considered an emulsifiable agent for use in certain listed crops. In addition, it resists wash-off once it is dry (Dow AgriSciences 2007). The active ingredient is chlorpyrifos: O, O-diethyl-O- (3,5,6 –trichloro-2-pyridinyl) phosphorothioate, which accounts for 44.9% of Lorsban. Also, the mixers and loaders using the mechanical transfer loading system must wear chemical-resistant gloves, a chemical resistant apron, a NIOSH- approved dust mist filtering respirator with MSHA/NIOSH approval number prefix TC-21C or a NIOSH-approved respirator with any R,P, or HE filter. There are certain engineering controls that are also in place, such as the requirement to wear the personal protective equipment, protective eyewear, and be aware of what to do in an emergency(DowAgriSciences, 2006).

Chlorpyrifos is classified as an organophosphate, which is an ester with phosphoric acid.

Organophosphates are in many common pesticides and present a serious health hazard to millions of pesticide applicators. The organophosphate group affects the functioning of the nervous system, and is among EPA's highest priority for review under the Food Quality Protection Act (Environmental Protection Agency, 2002). Chlorpyrifos can cause cholinesterase inhibition in humans, and is classified as a neurotoxin. The most common exposure pathway is inhalation (US EPA). The symptoms of Chlorpyrifos poisoning can appear within minutes or hours after exposure. These symptoms can last for days or weeks as the body works on replacing the depleted enzymes in the nervous system so that it can function properly again. Exposure to small amounts of chlorpyrifos can cause runny nose, tears, increase saliva, sweating, headaches, nausea, and dizziness. Greater exposures can cause vomiting, abdominal muscle cramps, muscle twitching, tremors and weakness, and loss of coordination. Severe poisoning can lead to unconsciousness, loss of bladder and bowel control, convulsions, difficulty in breathing, and paralysis (Environmental Protection Agency, 2002). In addition to affecting the nervous system, chlorpyrifos can also affect the cardiovascular and the respiratory system, as well as being a skin and eye irritant (National Pesticide Information Center, 2010). People who have certain respiratory ailments, cholinesterase impairment, or liver malfunctions can be at greater risk from exposure to chlorpyrifos (Dow, 2012). Chronic effects of chlorpyrifos can include many of the same symptoms as that from acute exposure, but can also include impaired memory and concentration, disorientation, confusion, irritability, depression, speech difficulties, and insomnia (Environmental Protection Agency, 2002). Once there is exposure, chlorpyrifos quickly spreads all over the body. chlorpyrifos is not toxic in its pure form, but it creates a toxic form called chlorpyrifos oxon when the body attempts to break it down. chlorpyrifos oxon binds permanently to enzymes in the body that control the messages that travel between neurons, leading to nerves and muscles not functioning correctly. However, generally the body can break

down chlorpyrifos oxon in small amounts and it will be excreted in the urine or feces within a few days (National Pesticide Information Center, 2010) The NIOSH Recommended Exposure Limit for chlorpyrifos is 0.2 mg/m3 (Organophosphorous Pesticides, 1994).

3.2: Horticultural Oil

Supreme Oil is also an insecticide that will be used by the workers that are being monitored. The active ingredient is mineral oil. Long sleeved shirts and long pants are required when using this insecticide, shoes plus socks, as well as chemical resistant gloves. Only protected handlers may be in the area during the application of this product, and PPE is required for entry into an area within four hours of application. It cannot be applied when winds are greater than 15 mph, due to wind drift. It must be released at a height of no more than four feet, or if an aerial application a height no more than 10 feet (Loveland 2010). In order to measure for contamination of supreme oil, according to the NIOSH standards for aromatic hydrocarbons, a solid sorbent tube (100mg/50mg) must be used, with gas chromatography for measurement. The reagents of hydrocarbons can include carbon disulfide, low benzene, and chromatographic quality (Aromatic Hydrocarbon 2012).

Any horticultural oil that is being used contains amounts of hydrocarbons. Most of the dangerous hydrocarbons are derived from petroleum distillates and include aliphatic (straightchain) hydrocarbons and aromatic (benzene-containing) hydrocarbons. Respiratory symptoms can begin in the first few hours after exposure to hydrocarbons. Most of these symptoms are resolved after 2-8 days, but there can be complications that may include hypoxia, barotrauma due to mechanical ventilation, and acute respiratory distress syndrome. Prolonged exposure to aromatics and aliphatics may result in encephalopathy, seizures, and death (Goldstein et al.2011).

The NIOSH approved REL for aromatic hydrocarbons is 3.5 mg/m^3 (Aromatic Hydrocarbon 2012).

Trimethyl benzene is also something that can be harmful in the pesticides that are being applied. Any direct contact with 1,2,4-trimethyl benzene is irritating to the skin and breathing the vapor is irritating to the respiratory tract, which can pneumonitis. Breathing high concentrations of the chemical vapor causes headache, fatigue, and drowsiness (EPA, Office of Pollution Prevention and Toxics, 1994). The NIOSH REL is 125 mg/m^3 (CDC NIOSH, 2010).

3.3: Current Practices

The farmers in Yakima Valley undergo training through cooperation with Washington State University Cooperative Extension and other members of the farming community. Hands on handler training was implemented in the late 1990s. There is a daylong training session, which provides pesticide safety training by use of interactive techniques. According to the training website, some of the goals for undergoing this training are to: "Provide high-quality, relevant training to pesticide handlers, increase the training potential within the Hispanic community, and increase training opportunities by partnering with the agricultural community to sponsor handson training events" (Washington State Department of Agriculture). It is thought that this type of training is very effective because both the trainers and the trainees are valued for the experience and knowledge that they bring to the table (Washington State Department of Agriculture).

Chapter 4: Literature Review

According to an article about the Bureau of Mines, It is well known that respirators are the last resort for protection from harmful solvents. If at all possible, according to the hierarchy of controls, administrative or engineering controls should be used first to protect the individual worker without resorting to Personal Protective Equipment. However, quite frequently industrial hygienists view respiratory protection as the be all end all for inhalation exposure, but there are not really schedules that are in place for certain types of exposure. These are just some of the problems that the Bureau of Mines has with certain types of respirators (Jordan, 149).

However, there have been previous studies on the effectiveness of respirators in the workforce. Sampling inside of a respirator cartridge has always been a problem, as there is not a good way to put sampling media on the internal side of a cartridge. However, many creative ways have been developed to sample the amount of breakthrough through the cartridges.

A study was done in that looked at the effectiveness of respirators in a paint plant in Iran. The respirator cartridges were previously only changed out every 48 to 72 hours, but it was established that they should be changed out every four hours. Direct reading instruments were used to measure for breakthrough of the respirators, and tested for benzene, toluene and xylene. A sampling train was created that went from the respirator to a direct reading instrument that was attached to a pump. The set up was set up in the vicinity of the workers in order to get an accurate assessment of their exposure. All of the pumps were calibrated using a calibrated

rotameter. The results of the study were that ultimately established that ventilation and other engineering controls would be useful for countering the effects of the respirators. (Karimi, et al, 2013). Another study was done at a Japanese plastics factory, and the effectiveness of the respiratory protective equipment that was worn was evaluated. However, in this study, there were three types of respirators that were evaluated, but one was a half mask OV respirator. The methodology for doing this study was comparing the amounts of styrene that was extracted from passive samplers that were placed on the collars of the workers and urinary samples collected from the workers, which showed the amount of styrene that the workers had in their body. The results of this study showed that the amounts of styrene that the workers were exposed to, which was measured in ppm, exceeded the exposure limit for safe work. (Nakayama et al, 2013)

In another study, Styrene was measured in the breathing zone and inside the face piece of air-purifying half mask respirators worn by workers while they were making fiberglassreinforced bathtubs and shower stalls. The participants were fit tested for half mask respirators according to protocol, and probes were inserted into the cartridges. These were the same probes that were used for fit testing of respirators. Charcoal solvent tubes were attached to the probe, which was attached outside of the mask. The sampling train apparatus was worn by the workers for an hour shift, which is the same amount of time that they would normally wear the respirators to do their work. Styrene concentrations were measured outside of the breathing zone. Air samples were collected inside and outside the respirators simultaneously. This study was primarily done to measure the fit of the respirators, and it established that with different people, who obviously have different face shapes, there are different fits (Galvin et al, 1990).

Generally, in the agriculture world, employers are not willing to spend a great deal of money on the protection of their employees. Therefore, it can be difficult to persuade people to buy new respirator cartridges, when it may be the preference to just reuse the cartridges.

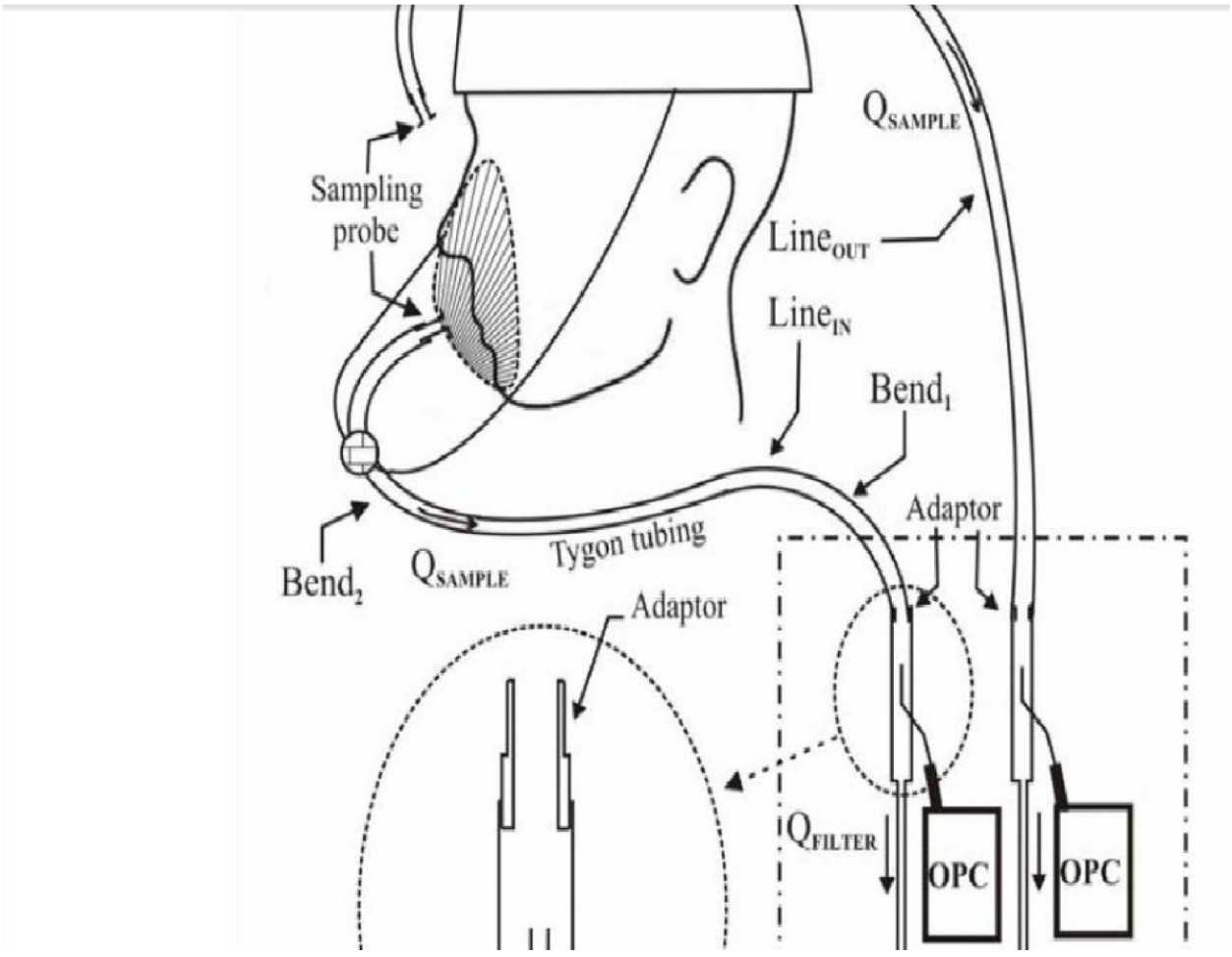
Therefore, in a study on reusability of respirator cartridges- an equation was developed. (Wood et al., 2011).

This project clearly will be a bit different than the previous projects because it deals with personal protective equipment for agriculture use. In one study, respiratory health hazards from organic dust in grain handling and poultry and swine livestock productions was analyzed. Qualitative evaluations were conducted on which respirator the workers most preferred. Personal samples were attached to the workers, with closed faced cassettes attached to personal air sampling pumps. In mask samples were collected using an aluminum probe to the front of the respirator. However, the effectiveness of this method and the probe are yet to be evaluated. There was a large amount of variability of performance within the kind of mask, which indicates that some workers do not experience very much protection. Generally the half mask was preferred by various workers, but did not have as great of a WPF as a powered air purifying helmet. (Popendorf et al.,2011). There has also been a study that was done to evaluate the effectiveness of tractor cabs to prevent exposure to pesticides that was done (Heitbrink et al., 2003).

A new system was used to determine the workplace protection factors (WPF) for dust and bio-aerosols in agricultural environments. In short, the sampling system consisted of two sampling lines (in-face-piece and ambient sampling lines) that were used to collect particle samples inside and outside the respirator. Airborne dust and microorganisms were sampled

through the sampling probes at a flow rate of 10 L/min and drawn through Tygon tubing to a metal sampling chamber at the end of each sampling line. A portion of each aerosol flow (2.8 L/min) was sampled from the chamber into an optical particle counter for dust measurement. The rest of the aerosol flow (7.2 L/min) passed through a filter sampler that collected the airborne microorganisms. Thus, the APF of 10 for N95 filtering facepiece respirators seems inadequate against microorganisms **[Figure 1]** (Lee, et al 2005).

Figure 1: Method for Sampling Inside Respirators



In another study, the quantitative fit tests were evaluated. Currently, all Quantitative Fit Tests performed by aerosol detection are conducted with a sampling probe imbedded in the respirator body in the breathing region between nose and mouth or at the mouth. This idea has been used to attempt to determine a methodology for how to sample the inside of the respirator. Disposable sampling probes were designed to be compatible with different filtering face-piece respirators so that the wearers would be able to choose different brands of respirators for the fit test. Therefore, based on the principle of the fit test setup, a portable personal sampling setup has been designed in this study for measuring the concentrations of dust and microorganisms inside and outside a respirator. This study therefore adapted conventional quantitative fit testing that would be performed in a laboratory setting, for field use in workplace environments (Lee 2004).

Chapter 5: Significance and Necessity

This project has a connection to the DEOHS MA/AF mission, with the focus on specific measures to reduce pesticide exposure for Washington State workers. The study results will target larger audiences than just the agricultural community; the results will be disseminated to the individual participants, the agricultural community, and other planned PNASH dissemination activities.

There is a great necessity for this project. The overall project covers the testing of three different kinds of PPE: respirators, gloves, and testing for personal protective hats, which is not covered in this study. The need for the evaluation of these types of PPE have been identified but not yet addressed by the Intervention project's Expert Working Group. This project is important because it will have an evaluation of breakthrough for chemical mixtures at air concentrations during the work activity. In addition, conducting this study in the field will provide data that is directly relevant to workers in Washington State, or to many other workers in the occupation of applying pesticides. Also, the methodology that was created will be able to provide the basis for further development of this methodology for sampling in this manner for many other industrial hygiene applications. This is a pilot study, so this may provide a baseline for further use of these methods and the realization that more study is needed on this topic in the future.

There have been some breakthrough times that have been determined for single chemicals, including carbon tetrachloride and liquid particulates, but these studies have been done in the lab, and limited studies have actually taken place concurrent with workplace conditions. The laboratory testing does not reflect all of the conditions that would be

encountered in the agricultural workplace, and therefore cannot provide adequate data to satisfactorily answer the change out schedule question (NIOSH 2006, 2007).

Chapter 6: Specific Aims

For this project, the current PPE used during the application of pesticides where agricultural workers are concerned will be evaluated. The specific aims are as follows:

1. **To create a sampling train that can be used to simulate respirator use**

   The sampling train will consist of a respirator cartridge (identical to the ones that the workers wear), sampling media, various tubing, and two pumps to create a sampling train that can be used to simulate a worker breathing. There will be a sampling train to measure the ambient air concentrations compared to a sampling train that will measure the air concentrations when filtered through a respirator cartridge.

2. **To evaluate a respirator cartridge and filter combination to determine its' effectiveness**.

   The matched sampling train set with the sampling media will be attached to a tractor close to an applicator's breathing zone and should collect the chlorpyrifos and oils and solvents that are present in the pesticides and the pump will be representative of the employees' breathing rate.

3. **To determine whether nitrile gloves provide adequate protection against dermal exposure to agricultural oil**

Dermal patch testing will be used to test for solvents and oil breakthrough that would result in dermal exposure. Patches will be placed on the palm and the back of the hand to determine where the breakthrough is most likely if breakthrough occurs.

4. **To share the results of this study** with each participant and agricultural worker, as well as the agricultural community and anyone else that the data would apply to.

Chapter 7: Design and Methods

All of these designs and methods that are described below are based on an evaluation of the PPE that is actually worn under field conditions while the handlers apply pesticides, and will include a functionality or efficacy component. This study will determine if the respirators and gloves are capable of providing adequate protection under typical field use conditions. A comprehensive list of materials including serial numbers that were used in the respirator and glove project can be found in **Appendix A**.

7.1: Design

The Primary Question: Is the current practice of respirator change out and glove change out adequate? Sampling of media will determine the time and the magnitude of breakthrough due to chlorpyrifos, oils and solvents.

> **H_0: $\beta_{\text{difference in breakthrough}} = 0$:** The null hypothesis is that there is no difference between the air concentrations of chlorpyrifos, solvents that are found in the cartridge sampling train and the ambient sampling train.
>
> **H_a: $\beta_{\text{difference in breakthrough}} \neq 0$:** The alternative hypothesis is that there is a difference between the air concentrations of chlorpyrifos, solvents and oils that are found in the cartridge sampling train and the ambient sampling train, or that the cartridge has a protective effect.

For the respirator portion of the project, it was necessary to determine how much chlorpyrifos, oils and solvents would breakthrough while the respirator was being used in an occupational setting. Since the breakthrough would be very difficult to measure while someone is wearing a respirator cartridge, a sampling train was to be created that would be exposed to the same amount of pesticides that the applicator is exposed to without the necessity of actually measuring a respirator while it is being worn by an applicator. Side by side air samples, or a matched set, were to be collected to test the ambient air concentration and for the amount, if any, that breaks through the cartridge/filter combination. Matched sets were created for sampling both the solvents and oils and for sampling the chlorpyrifos, so there were two matched sets, or four total sampling trains (ambient solvents, cartridge solvents, ambient chlorpyrifos, and cartridge chlorpyrifos). Charcoal media was used to sample for solvents, and PUF media was used to sample for chlorpyrifos.The approximate time that it takes for the breakthrough (if any is evident) to occur was also to be measured. The sampling train for the ambient sample was to consist of a charcoal tube or a PUF tube, an SKC personal pump, and tubing to connect it. The sampling train for the sample behind the cartridge (hereafter referred to as cartridge sample) was to consist of a R95 respirator cartridge with pre-filter attached to either a charcoal tube or a PUF tube, a Leland Legacy Pump, and tubing for connection. The sampling trains were to be positioned close together and attached to a tractor close to the workers breathing zone, since it is easier to attach to a tractor than to an actual person, and this can also help minimize interference from the worker and can side step the challenge of inside respirator sampling for multiple chemicals. The pumps from the sampling train were to be placed in a clear polycarbonate case with holes drilled in the top for the tubing of the sampling train to come out of. The sampling media and the respirator cartridge were to be on the outside of the sampling train.

There were to be three entire sets (or two matched pairs) of sampling trains in boxes simultaneously; each on an individual tractor that is used for applying pesticides. Each box (which contains two ambient samples and two cartridge samples, or one matched pair for each kind of media) is classified as a "set". There was to be one change-out per set during the day; when the tractor drivers take a break for lunch. The respirator cartridge was to be kept on, so that breakthrough can be determined, and the pumps were to be left on, but the sampling media was to be changed. The respirator cartridges were to be reused for the entirety of the study at one site, in order to determine how long they could be functional without respirator change out. The sampling trains were to run throughout the entire work day; at least eight hours. If break-through of the filters does occur, then a workplace protection factor would be able to be therefore be determined. Sampling was to be carried out for six total days, spanning two sites (or three days at each site). The sample size for each set (ambient air sample with a charcoal tube and sampling train sample with a charcoal tube) is eight (two ambient samples and two cartridge samples of both kind of media), when combining the front and back section on the charcoal tubes and the PUF tubes. This accounts for the once a day change out of the sampling media. There are six days that will be sampled with three sets each day, which amounts to 18 sets. [**Table 1**].

Table 1: Amount of Field Samples for Respirators

	Air Samples		**Cartridge/filter assembly**		
Compound	**Solvents/Oils**	**Chlorpyrifos**	**Solvents/Oils**	**Chlorpyrifos**	
Media	**Charcoal**	**PUF Tubes**	**Charcoal**	**PUF Tubes**	
Sample Periods	2	2	2	2	
Sets	3	3	3	3	
Subtotal	6	6	6	6	
Days	6	6	6	6	
Total # field Samples	36	36	36	36	
Total field samples					144

The workers also wear a thick reusable nitrile glove, but this may not provide adequate protection. The main issue with these gloves is that they are not the recommended material for Lorsban 4E, since solvents are part of the formation of the glove (Dow Agrisciences 2007). In the US EPA Chemical Resistance Category Chart, Vitron and barrier laminate are recommended for materials for gloves (US EPA 2012). However, these gloves are not entirely compatible with pesticide application tasks and can be very expensive, nor have they been adopted with the industry. A dermal patch is to be attached to the skin under the glove in order to determine whether there is dermal exposure to solvents under the gloves. Initial bench studies by the Department EH lab will be conducted to determine the most suitable media for the chlorpyrifos and horticultural oil dermal patch.

For gloves, the design was approached in a different way. It was necessary to test the gloves that the applicators usually wear to see if they are effective enough for the job that they are being used for. A PermaTech charcoal patch and a foam circlewas attached to the inside of the glove on both the palm of the hand and the back of the hand to test for solvents and oils and chlorpyrifos, respectively. The charcoal cloth circle was adhered with aluminum foil tape to ensure that it stays in the correct placement on either the palm or the back of the hand, and the foam patch was attached with medical tape covered by aluminum foil tape.

Three applicators at each site, who are classified as “subjects”, are to wear a set of two patches on their dominant hand each morning and afternoon that they apply oils and solvents with pesticides for three days. There will be one change out at their lunch break. One of the patches was to be on the palm side, and one was to be on the back side of the hand. The solvent patches will be attached in the same location on both the palm of the hand and on the back of the hand each time that they are changed out, and the gloves will be reused by the same workers for

the entirety of the study, in order to test for dermal breakthrough over time. The amount of pesticide applied by the applicator, the number of tanks, the duration of application, and the timing and duration of the spray and the break periods will be recorded [**Table 2**].

Table 2: Amount of Field Samples for Gloves

	Patches on Palm of Hand		Patches on Back of Hand		
Compound	**Solvents/Oils**	**Chlorpyrifos**	**Solvents/Oils**	**Chlorpyrifos**	
Media	**Charcoal**	**Foam**	**Charcoal**	**Foam**	
Sample Periods	2	2	2	2	
Subjects	3	3	3	3	
Subtotal	6	6	6	6	
Days	6	6	6	6	
Total # field Samples	36	36	36	36	
Total field samples					144

Each of the samples were to be taken back to the EHS lab and analyzed for various compounds. Then, a breakthrough time was to be determined, as well as a workplace protection factor.

7.2 Methods in Lab and Field

This section illustrates how the design was carried out and changed; both the preparation in the lab and the carry out of the design in the field work, as well as with the methods of the analysis of the results. Initially, this project was meant to measure the amount of chlorpyrifos, as well as oils and solvents that the tractor drivers were exposed to. However, due to weather conditions and other factors, only one day of chlorpyrifos sampling happened. Therefore, the research project was focused on the oils and solvents, of which there is more data. The results

were still reported for the chlorpyrifos data, but the majority focused on the solvent data. The methods used for sampling chlorpyrifos can be found in **Appendix B.**

7.2.1: Pump Flow Rates

A pump was used on the sampling train to simulate the lungs of the applicators. Many factors are involved with inhalation exposures, since the oxygen exchange with carbon dioxide takes place in the distal portion of the lung, and so therefore, lung volume is also dependent on many factors. In regards to the activity level of the apple orchard farmers, as they were driving tractors all day, their activity can be defined as sedentary, since driving the tractors does not require a great deal of movement. Assuming that the workers are in the age range of approximately 21 to 60, an average inhalation range of 8.2 L/min will be used. It should be noted that these amounts are regarding short term exposure values (Salem and Katz 28).

Therefore, the Leland Legacy pumps that were attached to the cartridge sampling train were calibrated to run at 8 L/min (8 L/min was used instead of 8.2 L/min in order to make calibration of the pumps easier) to simulate this breathing rate as closely as possible. However, the ambient sample was not attached to a respirator, and therefore did not have the interference that a respirator cartridge could bring. The face velocities at the entrance of both the ambient sample and the respirator cartridge had to be matched so the sampling media would have an equal amount of solvents drawn into it, so therefore the ambient sample had to be set to run at a much lower flow rate.

The face velocity was calculated by using the formula of flow rate divided by area. The diameter of a charcoal tube (the media for the ambient sample) was measured. Using the flow rate of 8 L/min, the face velocity of the respirator cartridge was calculated, which was set equal

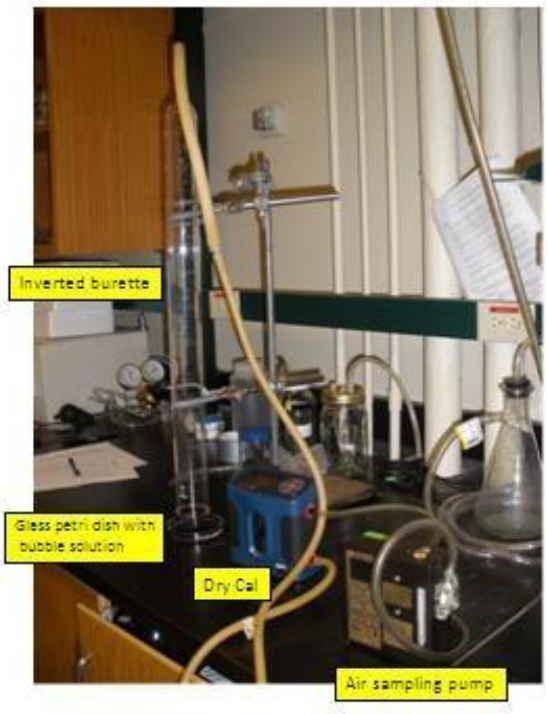
to the face velocity of the charcoal tube. Using this face velocity, the flow rate of the charcoal tube for the ambient sample could be calculated [**Appendix C**]. The flow rates for the ambient samples for charcoal were 1.037 L/min, and the flow rates for the cartridge samples were 8 L/min.(The flow rates for the ambient samples for PUF tubes were 4.62 L/min, and the flow rate for the cartridge samples was again 8 L/min).

The Leland Legacy Pumps would flow fault when they were attached to a charcoal tube, used as the sampling media for the solvents and oils. Therefore, since charcoal or carbon was required for the cartridge sampling train to match to the ambient sampling train, charcoal cloth inside cassettes was used as sampling media instead.

7.2.2: Lab Preparation

There are several preparations that were made in the lab prior to work in the field.

Figure 6: Set-up of the DryCal with the Bubble burette



7.2.2.1: DryCal Calibration

The first standard operating procedure that was performed was the calibration of the calibrator with a bubble burette in the lab. In order to do this, a small amount of child's bubble solution was poured into the burette, and the bubble solution was swirled to coat the inside of the burette. The burette was inverted and attached to the lab stand using the glassware clamps. ¼" Inner Diameter (ID) rubber latex tubing was attached to the

inverted burette and the other end of the rubber latex tubing was attached to the bottom inlet of the DryCal. Another extension of ¼" ID Latex tubing was attached to the top inlet of the DryCal, with the other end of the tubing connected to the Leland Legacy Pump [**Figure 2**]. The glass petri dish was partially filled with bubble solution and placed below the inlet of the burette, without letting the top layer of the bubble solution touch the burette inlet. Once the burette and calibration train has been set up, the pump and DryCal was turned on and the pump was set to 8 L/min, since that is the highest flow rate that will be run in the field. The bowl was briefly lifted to the burette rim so that the top layer of the bubble solution in the bowl touches the rim of the burette and a thin bubble is formed that traveled up the length of the tube. This process was repeated several times to re-coat the inside of the burette with bubble solution; timed trials were not started until bubbles were able to travel the entire length of the burette without popping. For timed trials, the DryCal was reset by re-starting it and briefly touching the top layer of the bubble solution in the bowl to the burette rim so that a thin bubble is formed. When the bubble reached the 1,000 mL mark on the inverted burette, the stopwatch was started, and when the bubble reaches the 0 mL mark on the inverted burette, the stopwatch was stopped, and then the DryCal was stopped. The travel volume (which should be 1,000 mL), the travel time, and the flow rate displayed on the DryCal were all recorded on the calibration sheet. Each of the timed trials was repeated three times with the Leland Legacy Pump. Then, the entire procedure was repeated with the SKC personal sampler pump (when connecting the DryCal to the SKC pump, the ¼" Tygon tubing was still used), with the flow rate at 1.038 L/min instead of 8 L/min.

The DryCal average per pump speed setting was recorded. Then, the pump had time to equilibrate (approximately 2-3 minutes) before repeating the burette coating and the timed trials at other flow rates.

The bubble meter flow rate (in L/min) was calculated by dividing the bubble travel volume (1,000 mL) by the bubble travel time. This was repeated for each trial.

$$\text{Flow rate (L/min)} = \frac{\text{travel volume (L)}}{\text{travel time (min)}}$$

Then, the DryCal flow rate versus the bubble meter flow rate was plotted and a linear model was fit to the data. The slope equation was calculated from the data (the calibration curve) $y = mx + b$

- y = rotameter reading in L/min
- m = slope
- x = DryCal reading I L/min
- b = y- intercept

The equation of the best-fitting line was used to adjust the DryCal flow-rates to be equivalent to the desired "true" flow-rate. The line of best fit for the DryCal verses the bubble burette flow rate is y= .9997x +.0003, and the r^2 value is 1. See **Appendix C** for the data and graph on the DryCal flow rates as compared to the bubble burette.

7.2.2.2: Media Preparation

In order to calibrate and successfully set up the media, (the charcoal tubes and the charcoal cloth circles) to be sampled, there were several preparations that had to take place in the lab prior to going out into the field. The ideal total number of media needed was calculated, and is shown in **Appendix E.** For the respirator project, 50 samples of each different kind of media were to be prepared (since each sample has two charcoal cloth circles on it, the number was

doubled for that). Therefore, 50 charcoal tubes were prepared, and 100 charcoal cloth circles were prepared. For the glove project, 70 samples of PermaTech charcoal patches were needed.

7.2.2.2.1: Preparation of Charcoal Tubes

The 1800/200 mg charcoal tubes that were used in the ambient sampling train to measure solvents and oils had to be cut in the lab prior to going out into the field. The glass charcoal tubes were to be cut with a clean break at the top of the tube, where there is no charcoal present. It was important to have an even face all around the break, so that this would not affect the flow of the particles into the charcoal tube. Safety glasses and glass proof gloves were required for cutting the charcoal tubes, as well as a broken glass container. Once the safety equipment has been put on, a small amount of dish soap was rubbed around where the desired cut will be. Then, the charcoal tube was positioned onto the grove in the glass cutter at the desired place for the cut. After the glass cutter and the tube were placed on a low surface, the glass cutter was closed and a large amount of force was used to push on the glass cutter with the charcoal tube inside it while rotating the tube once around (360 degrees) so that an even score is created. Then, the tube was positioned on a pencil with the score at the top of the pencil, and a heavy clamp was used to hit the top of the tube in order to break the scored section off. Once the charcoal tube glass had been cut, all the broken glass was placed in a glass disposal area and the dish soap was carefully wiped off the charcoal tube. Pliers were used, on a flat surface for safety, to attach plastic red caps to the broken end to create a firm seal. Fifty 1800/200 mg charcoal tubes were cut in this manner. Once the charcoal tubes were cut, they were stored in a plastic bag in a freezer.

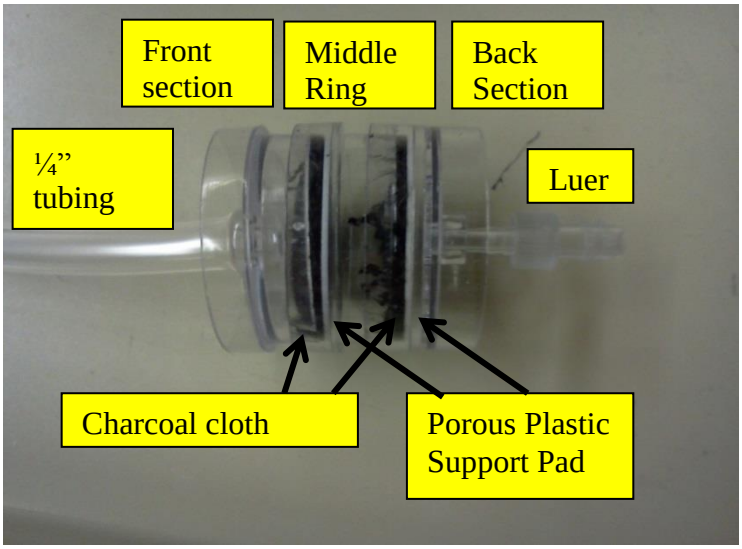
7.4.2.2: Preparation of Charcoal Cloth Circles

For the sampling train with the respirator cartridge, charcoal cloth circles were used instead of charcoal tubes, because the Leland Legacy pumps could not handle the back flow from the charcoal tubes, and thusly would flow fault on a regular basis. In order to use the charcoal cloth circles as sampling media, charcoal cloth was cut in circles that would fit a 37 mm cassette. There were two charcoal cloth circles that were used for each sampling train; a front section and a back section. To cut and prepare the charcoal cloth circles, a craft di-cut was used. Gloves were used as protection from the charcoal cloth and to protect it from any human impurities it may have gotten on it, and then the di-cut and a pair of scissors was rinsed with acetone in a fume hood. The di-cut was used to cut 100 1.5 inch charcoal cloth circles, which were placed in a plastic bag. Between the cutting of each charcoal cloth circle with the di-cut, a .75 mm crochet hook, that had also been washed with acetone, was used to clean the charcoal cloth fibers out of the di-cut so that it did not get jammed. Then, once all the charcoal cloth circles were cut, they were cleaned in a Thermolyne oven with nitrogen. Using acetone-washed forceps, about 50 charcoal cloth circles were placed in the metal tube that attaches to a line of nitrogen in the Thermolyne oven. A stirring rod was used to push all the charcoal cloth circles down into the metal tube. The charcoal cloth circles were placed stacked on top of each and extended fully, so that they would all get an even amount of nitrogen as much as possible. Wrenches were used to tighten the metal tube, which was then attached to the nitrogen valve inside the Thermolyne oven. The charcoal cloth circles were heated in the oven at 260 degrees Celsius for two hours.

Then, the oven door was opened so that the charcoal cloth circles could cool for another hour. Once again with nitrile gloves, the charcoal cloth circles were unloaded using forceps and the

stirring rod onto a lab diaper. Each charcoal cloth circle was placed in a 4 mL vial using two pairs of forceps and capped with the lid, with great care to not puncture the charcoal cloth circles with the sharp forceps. As charcoal cloth is highly absorptive, the charcoal cloth circles were not exposed to air again until they were ready to be used as sampling media.

Figure 8: Cassette Set Up



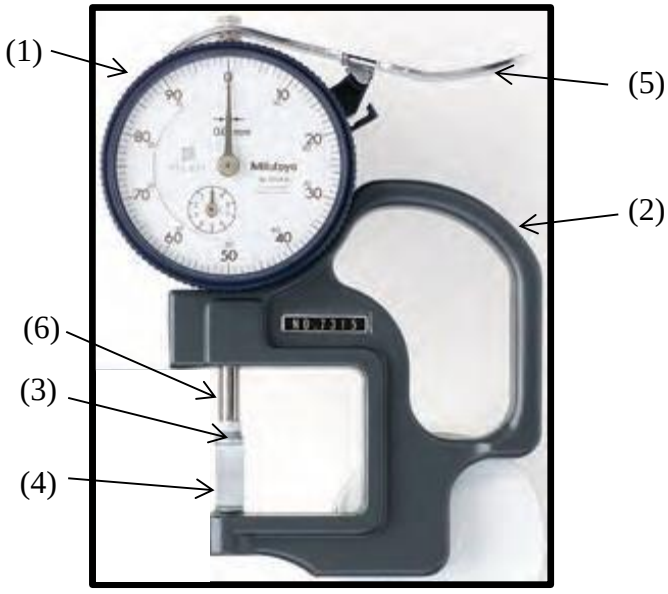
Each cassette had a front and back section, with separate charcoal cloth for each section; separated by a middle ring. A porous plastic support pad was used behind the charcoal cloth as a backing so that the charcoal cloth would stay flush and would not get sucked into the cassette or puckered by the suction of the pump. In order to set up the 37 mm cassettes, acetone washed forceps were used to insert two porous plastic pads into the plastic cassette rings; one was flush with the gridded end of the cassette set, and the other was resting on the middle ring, above it. Using forceps that have been acetone washed, a nitrogen cleaned charcoal cloth circle was taken out of a 4 mL vial and placed on top of each porous plastic pad. See **Figure 8** for clarification on the cassette set-up.

7.2.2.3: Measuring Glove Thickness

There was also preparatory work that had to be done for the glove portion of the project in the lab before going out into the field. In order to measure the amount of oils and other solvents that were getting through the gloves that the pesticide applicators were wearing, the

thickness of the gloves had to first be determined. 5 mil nitrile gloves were donned, which would protect the test glove from any contaminants that could have been introduced by human handling. A Mitutoyo dial thickness gage [**Figure 9]** was used to measure the thickness of the gloves.

Figure 9: A Mitutoyo dial thickness gage.



1) Bezel
2) Handle
3) Contact Point
4) Anvil
5) Lifting Lever
6) Spindle

The gage was held at the handle so that the dial arrow rests at the zero marking. Once the bezel was properly zero-set, the lifting lever was pushed down, with care that the spindle did not move too quickly. The spindle moves up and the contact point moves away from the anvil. A small

space is created which allows the test glove piece to be inserted between the contact point and the anvil. A 15 mil glove, such as the pesticide applicators wear, was inserted so that the palm side was between the contact point and the anvil. See Figure 10 to determine the parts of the glove.

Once the glove was inserted, the spindle was slowly moved down to take a reading. The location of the reading was selected on the palm side where the patch on the glove was expected to be placed. The reading was recorded, and the procedure was repeated two additional times on the palm side for a total of three thickness readings, and then the entire procedure was repeated three times for the back side of the glove. See **Appendix F** for the glove thickness measurements.

7.2.3: Calibration

In the field, pre-calibration and post-calibration for the pumps for the respirator project was done every day. The methods are different for the calibration of the ambient as compared to the cartridge sampling train, since each has different media and a different pump.

7.2.3.1: Calibration of SKC Pump for Ambient Sampling Media

One of the cut charcoal tubes that had already been prepared was labeled as “Calibration only” with lab tape and a Sharpie

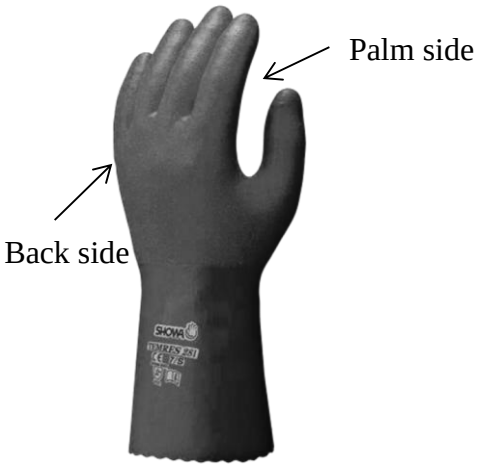
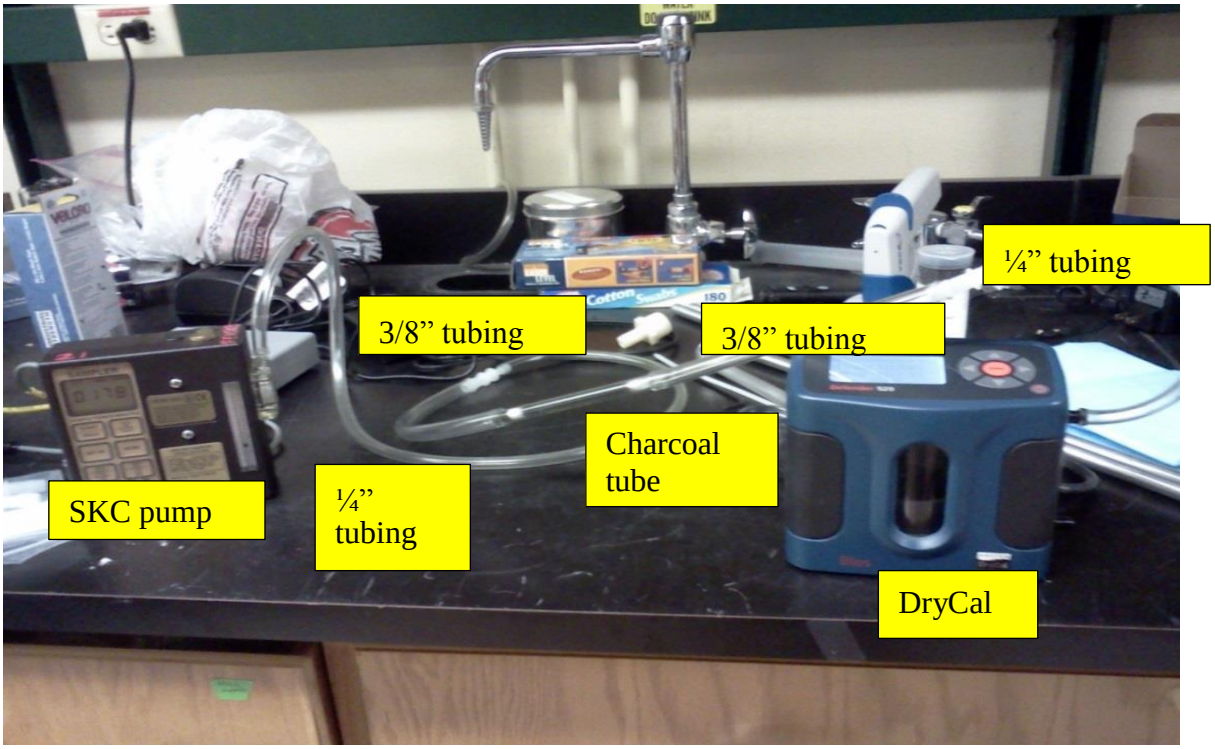


Figure 10: Parts of the Glove

marker. Then, the unbroken tip of the charcoal tube was broken. After putting on safety glasses, the unbroken tip of the charcoal tube was inserted into the smallest hole in the black glass cutter and, over a broken glass container, the end was snapped. This one tube, labeled “Calibration only”, was used as the only Calibration tube for the entirety of the project. An arrow was put on the label that indicated which direction the air should be flowing, so the calibration charcoal tube would never be inadvertently attached backwards. When it was time to calibrate, 3/8” ID Tygon tubing was attached to each end of the charcoal tube. A ¼” to 3/8” reducing connector was attached to the other end of each extension of 3/8” ID tubing, and then the other end of each ¼” to 3/8” reducing connector was connected to the ¼” ID Tygon tubing. The ¼” Tygon tubing was connected to the SKC personal pump. The arrow on the label for the Calibration Tube was always pointing towards the pump. The ¼” Tygon tubing attached to the other end of the Calibration charcoal tube wasattached to the DryCal [**Figure 11**].

Figure 11: Calibration Set-Up for Ambient Sample with Charcoal Tube



Once the Calibration sampling train was set up, calibration for the SKC personal pump to be used for the ambient sampling train was possible. The pump was turned on and allowed to run for one minute in order to stabilize the flow rate. A small 5/62" flat head screwdriver was used to adjust the pump to as close 1.038 L/min as possible. The Defender DryCal was then turned on.

The "Measure" icon was selected by pushing the "Enter" button. The Defender was set to take continuous measurements by clicking the left arrow to select "Continuous". If the flow rate was not in the 1.038 L/min range (with a .01 margin of error either way), then the screwdriver was used clockwise to increase the flow rate or counterclockwise to decrease the flow rate until the flow rate was at the desired amount, or 1.038 L/min. Once the flow rate is in the desired range, the arrow keys were used to select "Reset", and then "Burst" was selected, which gives an average of ten measurements. This average was recorded as the calibration level. The DryCal

Defender was then turned off, and for post calibration, the pump was also turned off, but for precalibration, the pump was left on for its' sampling period. See **Appendix G** for the calibration

data from all of the sampling days for the SKC personal pump for the ambient air samples.

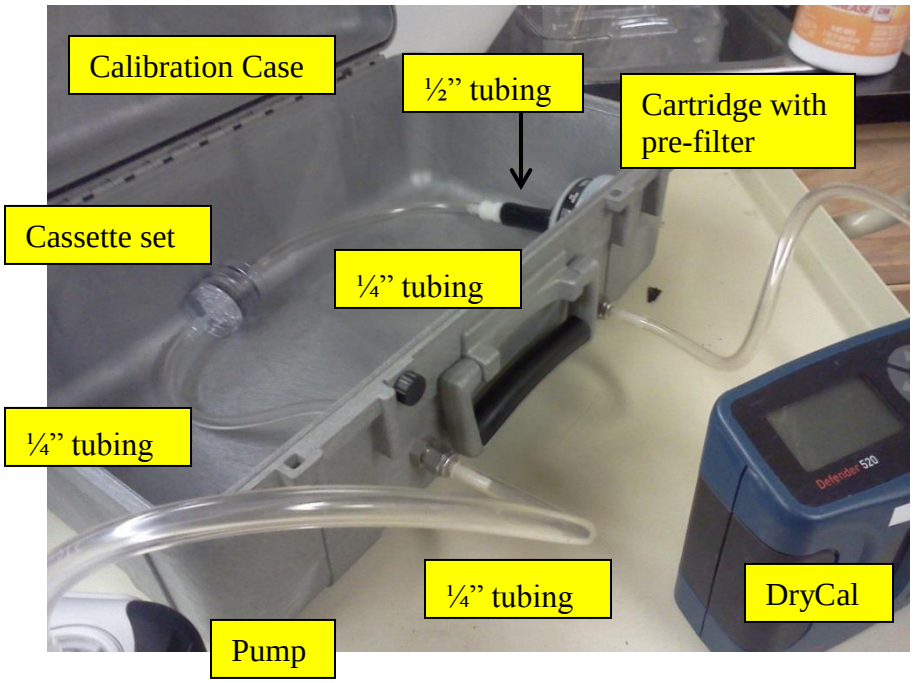
7.2.3.2: Calibration of Leland Legacy Pumps for Cartridge Samples

Since the cartridge sampling train could not be securely fitted from the DryCal to the pump due to the respirator cartridge as part of the sampling train, a gray calibration case was used. The case gave an airtight seal, which ensured that there was a steady flow from the DryCal to the Leland Legacy pump, while still allowing the respirator cartridge to be part of the sampling train. 37 mm Cassettes were used in the Cartridge Sampling Train with the Leland Legacy Pump instead of charcoal tubes to prevent flow faulting. After the cassette was set up in the way that has already been shown in the media preparation section, a cassette was put together with the charcoal cloth circles inside and labeled as "Calibration". This cassette set up was used for every calibration for Leland Legacy Pumps and Cartridge sampling trains. A label with an arrow pointing toward the gridded end of the cassette set-up was used; the label (and the gridded end)goes towards the pump. Luers were securely attached to each end of the cassette set-up. In order to set up the rest of the sampling train, nitrile 5 mil gloves were donned. The R-95 prefilter and cap was detached from the plastic backing, which was discarded. The R-95 pre-filter and cap were attached securely to the North OV cartridge. This same cartridge and pre-filter was used for all future calibrations for the Leland Legacy Pump and the cartridge sampling train. Teflon Tape was then wrapped around the threaded side of a ½" to ¾" hose barb the side of thehose barb that is threaded and was screwed into the matching threaded opening of the cartridge. The hose barb

was not screwed in completely, since the end of the hose barb was too long for the opening that was in the cartridge, and would otherwise be pushing on the internal filter of the cartridge, which could influence the air flow. Then, the ½" ID Tygon Tubing was attached to the extended end of the Hose Barb. A ¼" to ½" reducing connector was attached to the ½" ID Tygon tubing. At the other end of the ¼" to ½" reducing connector, ¼" Tygon tubing was attached. Then, the Calibration cassette set-up was attached to the ¼" Tygon tubing, with the arrow facing away from the cartridge. Another extension of ¼" Tygon tubing was attached to the other end of the cassette set-up. The entire sampling train was then placed inside the grey calibration case, and the extended ¼" Tygon tubing was attached to the left inlet on the inside of the case labeled "to pump". The grey calibration case was then shut and latched. ¼" Tygon tubing was attached to the outlet on the left side of the grey calibration case that is labeled to pump. (This is the other side of the inlet that the sampling train is attached to). The ¼" Tygon tubing was then attached to the Leland Legacy pump. Since the tubing is slightly too small for the pump inlet, a Q-tip dipped in Isopropyl alcohol was used to temporarily melt the inside of the ¼" Tygon tubing in order to

get a secure fit on the Leland Legacy Pump. Finally, another extension of ¼" Tygon tubing was attached to the right side of the outlet on the outside of the grey calibration case that is labeled 'To DryCal'. The DryCal Defender was then attached to the extended end of the ¼" Tygon tubing, thus completing an air-tight seal for calibration [**Figure 12**].

Figure 12: Calibration Set Up for Leland Pump



Once the Calibration sampling train was completed, the Leland Legacy Pump could be calibrated. The Leland Legacy Pump can be turned on by pressing any button to get it out of Sleep mode. Pressing the up and down arrow buttons simultaneously started the Leland Legacy Pump to run. Once it was running, pressing star, up arrow, down arrow, star will cause the pump to go into the "Set-up" mode. The words "flow rate" will appear and the word "set" should be flashing. The up and down arrows can be used to set the flow rate to 8 L/min. The pump was then allowed to run for one minute in order for the flow rate to stabilize; meanwhile the Defender DryCal was turned on. The "Measure" icon was selected by pushing the "Enter"

button. The Defender was set to take continuous measurements by clicking the left arrow to select “Continuous”. The up and down arrows were used to increase and decrease the flow rate on the pump until the DryCal is measuring 8 L/min. Once the flow rate was in the desired range, the arrow keys were used to select “Reset”, and then “Burst” was selected, which gave an average of ten measurements. This average was recorded as the calibration level. In order to set this flow rate on the pump, the star button was pushed until the “End” key appeared, and then pushing up and down arrow simultaneously selects the “end” key, which saves the flow rate. The DryCal Defender was then turned off, and for post calibration, the pump was also turned off, but for pre-calibration, the pump was left on for its’ sampling period. See **Appendix G** for the calibration data from all of the sampling days for the Leland Legacy pump for the cartridge samples.

7.2.4: Set up of Polycarbonate Cases

Polycarbonate boxes were used to contain the sampling trains, attach them to the tractors, and keep the pumps as safe as possible from the vibrations, dust, pesticides, and oils that would incur over a full shift of pesticide application. Holes were drilled in the bottom of the polycarbonate cases, and a U-bracket was attached around a bar on the back of the tractor to secure the polycarbonate case onto the tractor. Aluminum poles were secured with a connector to form a cross shape, and two of these was placed at either end of the polycarbonate case as a place for the sampling media to rest. These aluminum pole crosses were secured to the polycarbonate cases with zip ties. Two holes were drilled in the lid of the polycarbonate cases of the size of

3/8”, which is the size of the outer diameter of the ¼” Tygon tubing. An SKC pump and a

Leland Legacy pump were placed in one polycarbonate case, with the ¼" tubing attached to both pumps. This tubing was threaded out through the holes in the top of the lid, which were secured with rubber stoppers to make sure that no air was getting in or out of the case except through the

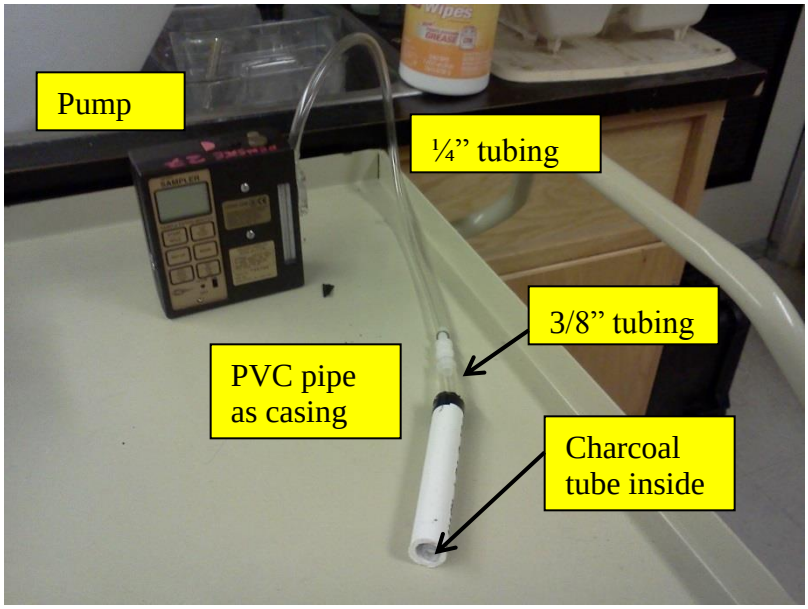
Figure 13: Empty Polycarbonate Case to Contain Sampling Train

tubing. Lubricant was necessary to slide the Tygon tubing into the holes in the lid of the polycarbonate case. Velcro strips were measured and cut to hold the pumps to the polycarbonate case. The hooked end of the Velcro was placed on the bottom of the polycarbonate case and matching fuzzy ends of the Velcro was placed on the bottom of both the SKC pumps and the Leland Legacy pumps. Once the polycarbonate case was secured to the tractor, it was left on the tractor for each of the subsequent days. See **Figure 13** for the empty Polycarbonate Case that was created.

7.2.5: Sampling Train Set-Up

The set-up for both the ambient and the cartridge sampling trains is fairly similar to the calibration set-up. For the ambient sample, the 1800/200 mg charcoal tube was prepared as was discussed earlier in the media preparation section and the tip was broken off over the broken glass container. Then, 3/8" inner diameter Tygon Tubing was attached to the end of the Charcoal tube with the small break, so that the straight cut end of the charcoal tube was facing out. ½" ID PVC pipe was used as a cover for the charcoal tube, since the tube is clear, and the PVC pipe would protect the tube from the sun, getting hot and possible contamination. ½" ID PVC pipe was cut with a hacksaw in the lab prior to going out into the field into the length required by the charcoal tube, and the tube attached to the 3/8" Tygon Tubing was inserted into the cut PVC pipe so the wide cut end was as close to the end of the pipe as possible. The PVC pipe was secured to the 3/8" ID Tygon tubing with electrical tape. Then, the end of the 3/8" ID Tygon Tubing was attached to the ¼" to 3/8" reducing connector, and the ¼" inner diameter Tygon tubing was attached to the open end of the ¼" to 3/8" reducing connector. The other end of the ¼" inner diameter Tygon Tubing was attached to the SKC pump [**Figure 14**].

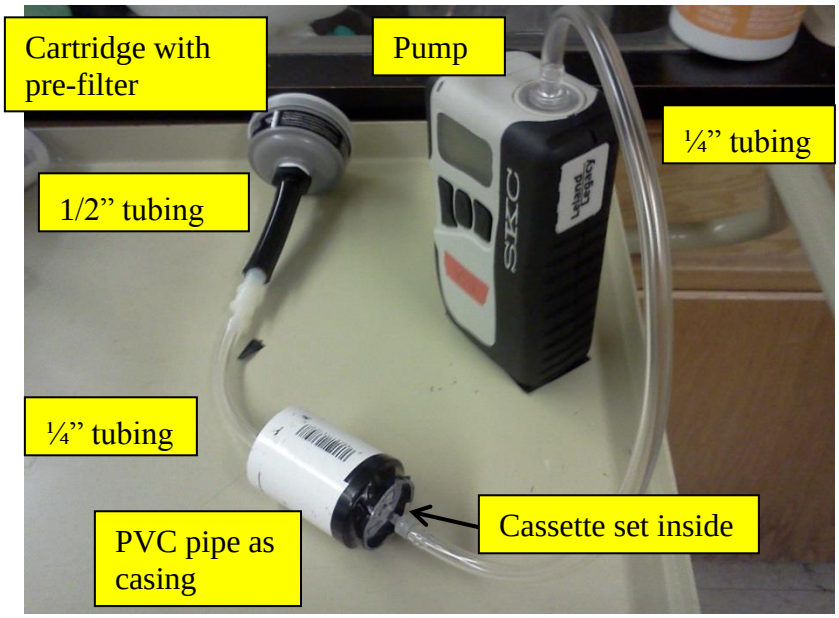
Figure 14: Ambient Sampling Train



The cartridge sampling train used the Leland Legacy pump with 37 mm cassettes and charcoal cloth. After the pump had been calibrated, nitrile gloves were put on and the R95 pre-

filter and cap was removed from the plastic backing and attached securely to the North OV cartridge. Then, Teflon Tape was wrapped around the threaded end of a ½" to ¾" hose barb. The hose barb was screwed into the threaded opening. The ½" inner diameter Tygon tubing was attached to the extended end of the hose barb, and then the ¼" to ½" reducing connector was attached to the ½" inner diameter Tygon tubing. ¼" ID Tygon Tubing was attached to the extended end of the ¼" to ½" Reducing Connector. The cassette set-up was done in the same way as was shown in **Figure 4**. The ¼" Inner diameter Tygon tubing was attached the other side of the cassette set; to the gridded end (this side goes towards the pump). The ¼" Tygon tubing was attached to the Leland Legacy pump. Since the tubing is slightly too small for the pump inlet, a Q-tip dipped in Isopropyl alcohol was used to temporarily melt the inside of the ¼" Tygon tubing in order to get a secure fit on the Leland Legacy pump [**Figure 15**].

Figure 15: Cartridge Sampling Train



7.2.6: Change-out plan

The exact place where the morning media would be disconnected from the sampling train and the exact replacement for the afternoon change-out time was determined. For the ambient sampling train, the ¼" Tygon tubing was cut just below the 3/8" to ¼" reducing connector. The replacement media consisted of a 3/8" to ¼" reducing connector, and a small extension of 3/8"

tubing that was attached to a charcoal tube covered in a PVC pipe. See **Figure 16** for clarification on how the media was replaced.

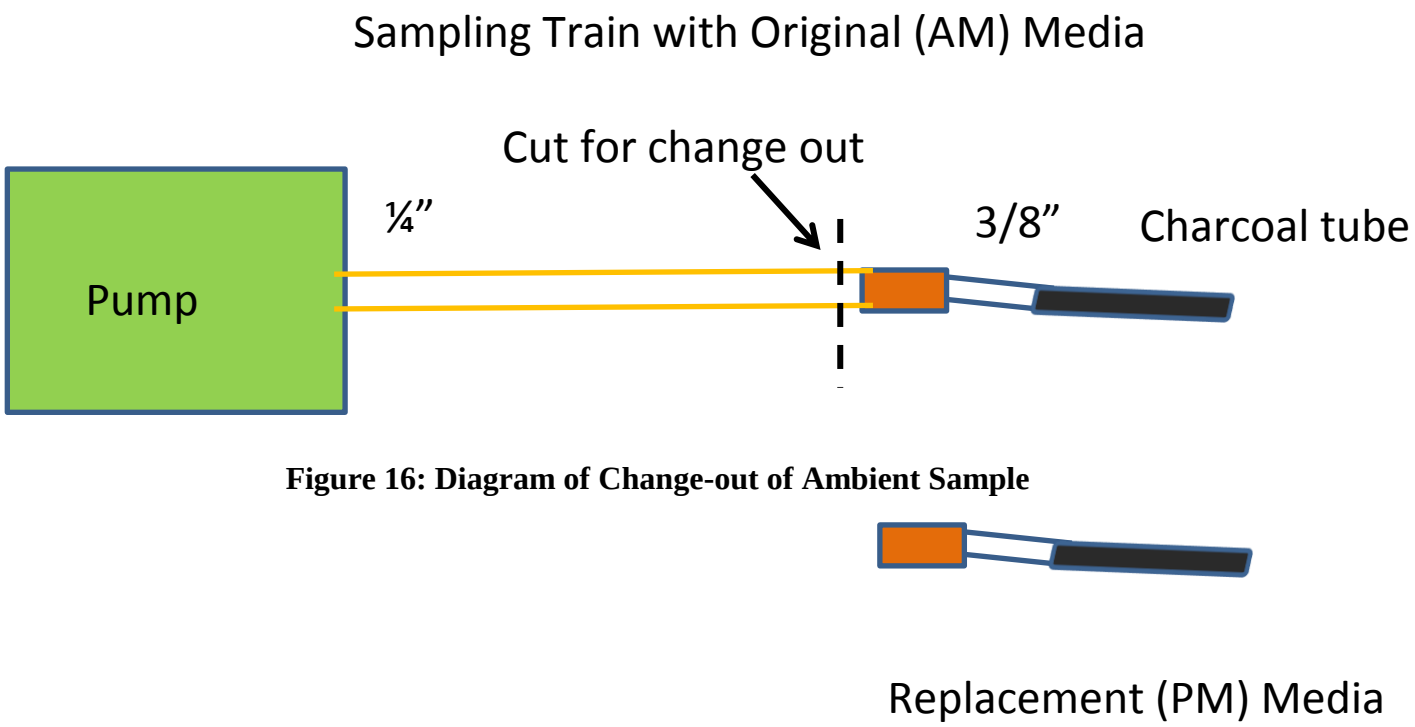
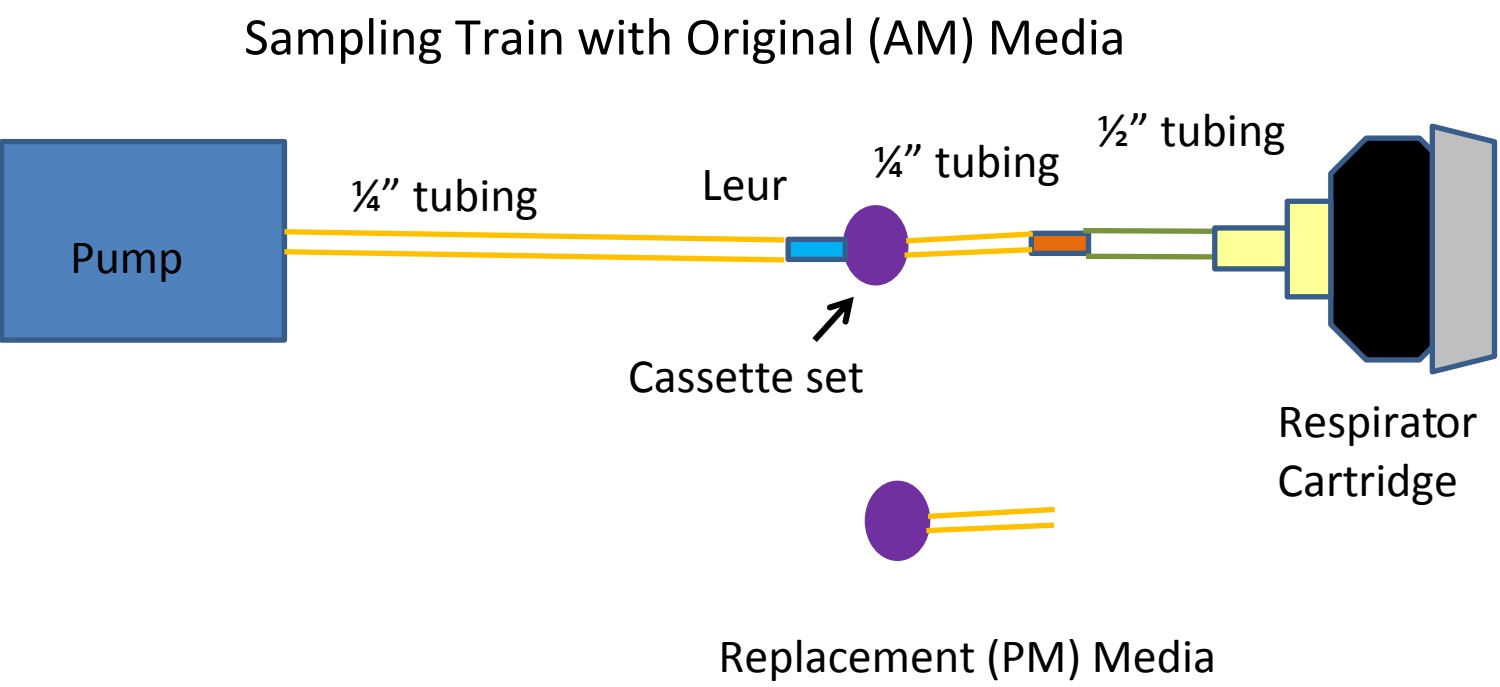


Figure 16: Diagram of Change-out of Ambient Sample

For the cartridge sampling train, the ¼” Tygon tubing that attached to the ¼” to ½” reducing connector between the cassette set and the respirator cartridge was cut, and an X-Acto knife was used to remove the excess tubing from the ¼” to ½” reducing connector. The luer was then disconnected from the cassette set, and the media was placed in the “dirty” box to be taken back and packaged. The replacement media was then easily inserted. See **Figure 17** for clarification on how the media was replaced. It should be noted that because the Tygon tubing was cut on both the ambient and the cartridge sample, the flow distance will be slightly less on the afternoon samples than the morning samples. This was done because there was not

enough time to change out all of the tractors that were coming in during the twenty minutes that the workers had for lunch if exact measurements of the Tygon tubing was take place. However, there are so many other confounding factors, that this should not pose a large variation in data.

Figure 17: Diagram of Change-out of Cartridge Sample



7.2.7: Set-Up of Plastic Bags

The necessary media and supplies for each of the sets was packaged together by set and change out time to make the process of setting up the sampling trains in a limited time setting easier. For each set, there were four plastic bag packages: an AM ambient bag, an AM cartridge bag, a PM ambient bag, and a PM cartridge bag. Packaged in the AM plastic bags for the ambient sample was the PVC pipe for containing the charcoal tube and a small extension of 3/8"

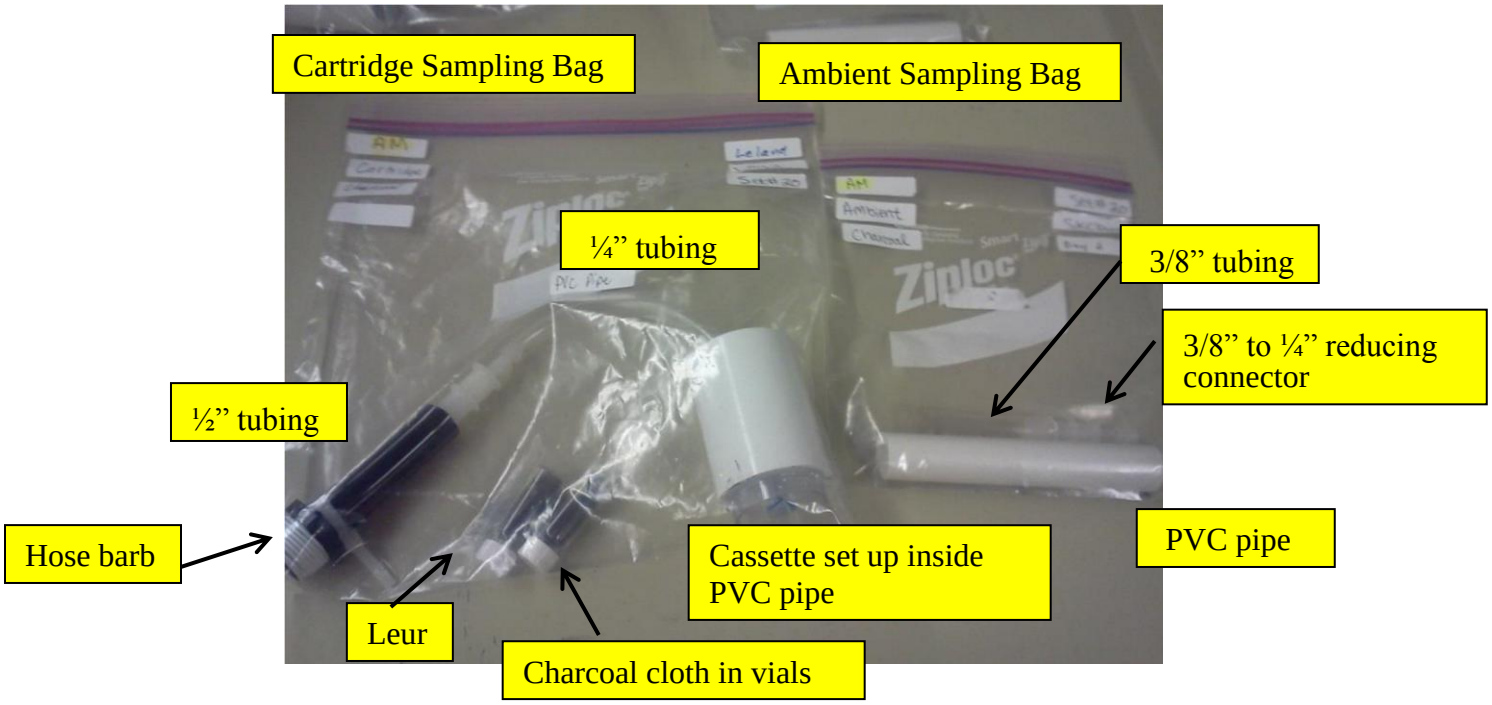
Tygon tubing for the charcoal tube to go into connected to a ¼" to 3/8" reducing connector. Therefore, once in the field, the only necessary preparation was to retrieve the pre-cut charcoal tube from the dry ice in the cooler, break the charcoal tube as was illustrated previously, insert the charcoal tube into the 3/8" tubing, and use electrical tape to secure the PVC pipe around the charcoal tube.

In the plastic bag for the AM cartridge sample there was the cassette set up without the charcoal cloths inserted yet, two 4 mL vials that contained the charcoal cloths, a ½" to ¾" hose barb wrapped with Teflon tape inserted into an extension of ½" ID tubing, which was connected to a ½" to ¼" reducing connector connected to an extension of ¼" Tygon tubing. The Tygon tubing was connected directly to the cassette set up, without the use of luers. The cassette set up had the plastic porous support pads in it, but did not yet have the charcoal cloths inside. A 2" ID PVC pipe was in the bag to be inserted over the cassette set up once the charcoal cloths were in place. Isopropyl alcohol and a Q-tip were used to melt the inside of the Tygon tubing to make it wide enough to fit over the opening to the cassettes. A luer was attached on the back end of the cassette set however, in order to make the change out in the middle of the day easier. In order to set up the cartridge sampling train, an OV cartridge had to be removed from the package and attached to an R-95 pre-filter with a plastic cap, which was then screwed into the hose barb that was wrapped with Teflon tape. The hose barb was then connected to ½" ID Tygon Tubing. The connection between the hose barb and ½" Tygon tubing had to be secure so that there was no air flow leakage, so a zip tie was used around the junction to ensure that no air flow was lost.

Connected to the other end of the ½" ID hose barb was a ½" to ¼" reducing connector, which was connected to a stretch of ¼" ID Tygon tubing. This was connected to the cassette set. Using two acetone washed forceps, the charcoal cloth circles were removed from the 4 mL vials and

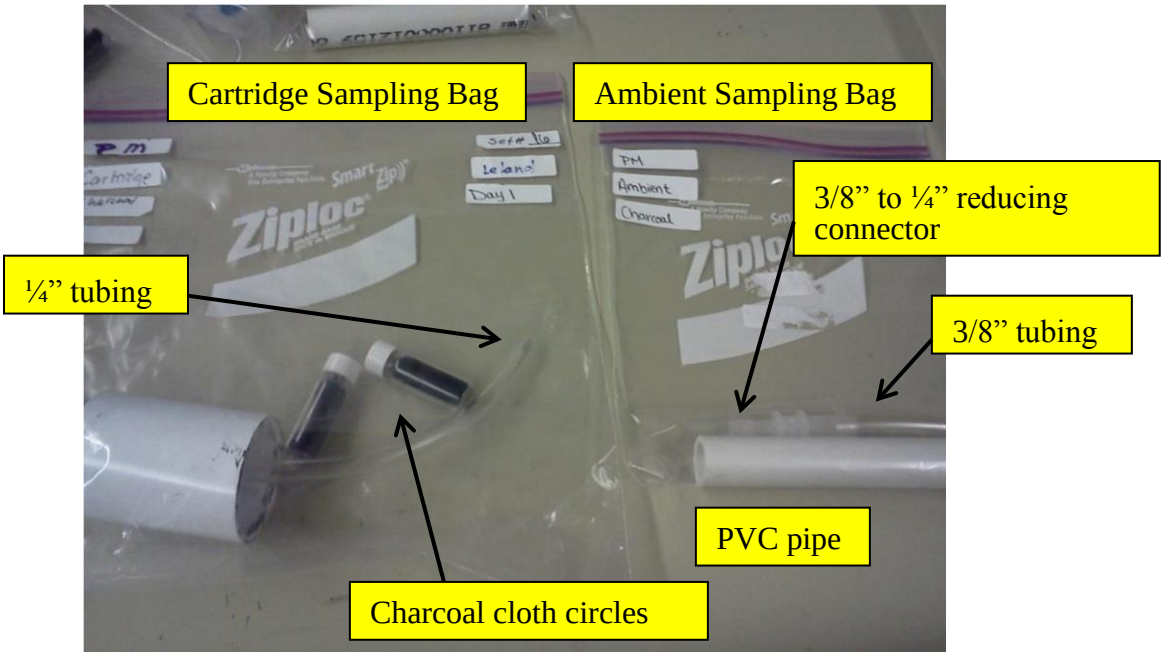
placed carefully inside the cassette set-up so that they were flush on top of the porous plastic support pads. The cassette set was reassembled and placed inside of the 2 inch PVC pipe, which was then wrapped with electrical tape for security and then connected to the rest of the sampling train [**Figure 18**] .

Figure 18: AM Sampling Bags



There were two more plastic bags that were set up for the afternoon media sampling train. The PM bag for the ambient sample with the charcoal tube was exactly the same as the set-up at the beginning of the day; it contained a ½" diameter PVC pipe and a small extension of a 3/8" tubing connected to a ¼" to 3/8" reducing connector. The PM bag for the cartridge sample consisted of ¼" tubing which was attached to the cassette setup, a 2" ID PVC pipe, an extra leur, and two 4 mL vials containing charcoal cloth circles [**Figure 19**].

Figure 19: PM Sampling Bags



7.2.8: In the field for Respirators

The night before going out into the field, all the pumps were calibrated. All five Leland Legacy pumps and all five SKC personal pumps were calibrated, even though three would be used at a time (as there would be three sets a day). Calibrating all of the pumps ensured that should something go wrong with any of the pumps there would be back-ups. All of the calibration data was recorded on the calibration data sheets. Also, the gloves were marked for where the PermaTech patches would go the next day.

A field manual was prepared for both the respirator project and the glove project. The field manuals contained all pertinent information about the projects including the Standard operating procedures (SOPs), materials, personal contact information, safety guidelines, and operation manuals for the instruments. See **Appendix H** for Table of Contents from both field manuals. There was also a data box that contained unused data sheets, completed data sheets, and labels. See **Appendix I** for sample data sheets for both respirators and gloves.

Once in the field, the entire team had to don certain personal protective equipment (PPE) to be around the tractors and collect the samples. Respirators with Organic Vapor combination cartridges with P100 pre-filter were used, a disposable Tyvec Chem suit, chemical protective gloves (5 mil nitrile gloves), chemical protective boots, and chemical protective goggles. Thick coveralls were worn under the disposable Tyvec Chem suit as an added layer of protection. A first aid kit, a fire extinguisher, and personal eye washes were also brought along for emergencies. After the sampling was done for each day, dish soap and toilet brushes were used for decontamination of the PPE, particularly boots.

7.2.8.1: Data Collection

Once in the field, all the materials should have been set up. See **Appendix J** for a comprehensive list of supplies. In the morning before the tractor drivers arrived, the pumps were flow checked with the calibrators to ensure that the pre-calibration that had been done the night before was still accurate, and then the media was set up using the AM bags and the way to set up the sampling trains that have been previously discussed. Once out in the field, the sampling train was set up inside the polycarbonate box. There were two sampling trains in each set that went on a tractor; an ambient sample and a cartridge sample. An extension of ¼" Tygon tubing was attached to the Leland Legacy pump and to the SKC personal pump. Since the tubing is slightly too small for the pump inlet, a Q-tip dipped in isopropyl alcohol was used to slightly melt the plastic on the inside of the Tygon tubing in order to get a secure fit on the Leland Legacy pump. Both the Leland pump and the SKC pump were attached with an extension of ¼" Tygon tubing about a foot long. For each set, a Leland pump with tubing, an SKC pump with tubing, a set-up ambient sampling train and a set-up cartridge sampling train were carried in a kitty litter box out to the

Figure 20a: Sampling Trains in Polycarbonate Case

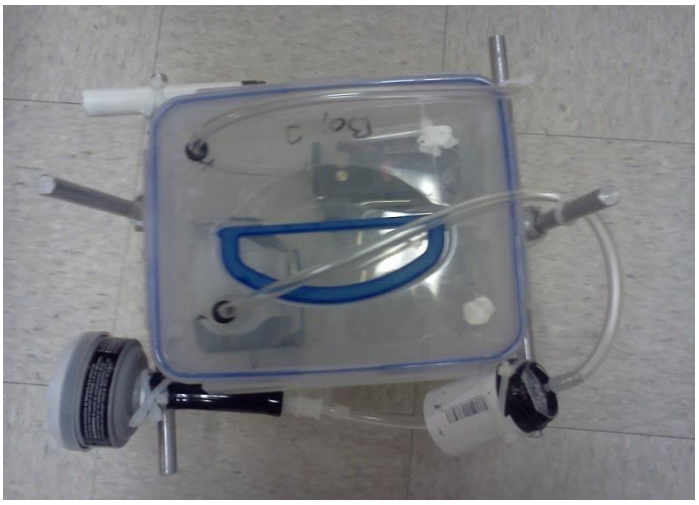
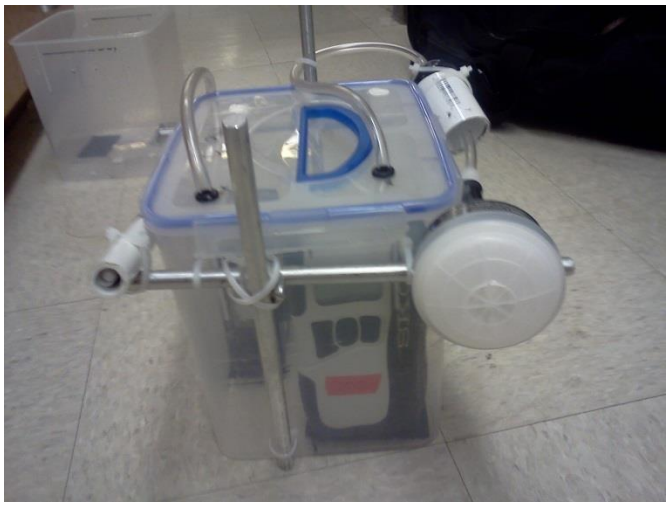


Figure 20b: Sampling Trains in Polycarbonate Case



polycarbonate box on the back of the tractor. The Leland and the SKC pumps were attached to the Velcro on the inside of the polycarbonate case, and the ¼" Tygon tubing that was attached to them was subsequently threaded out of the holes in the lid. The pumps were situated so that they were facing outward, with the total elapsed time running on display. The pumps were not turned off during the changeout in the middle of the day; just the time running was recorded for the pumps.

Once the lid of the polycarbonate case was secure, the ¼" tubing protruding from the case was attached to the ¼" to 3/8" and to the luer on the ambient sampling train and the cartridge sampling train, respectively. The time when the media was attached to the pump (when the sampling train was completed) was recorded. The face of the charcoal tube inside the PVC pipe for the ambient sample and the face of the respirator cartridge for the cartridge sample were positioned on the cross made from the tin poles that was attached to the side of the polycarbonate case. The faces of both sampling trains were positioned in the same way, so that theoretically they would be exposed to a similar amount of pesticides. The portion of the sampling train that

was on the outside of the polycarbonate case was secured with zip ties, although not around the Tygon tubing to avoid creating kinks. See **Figure 20** for a picture of the sampling trains inside.

Once the sampling train was set up inside the polycarbonate case, the entire sampling train was wrapped in aluminum foil to prevent the sun from going through the transparent polycarbonate aluminum case and heating the pumps up too much, as well as protecting the polycarbonate case and sampling train from excess dirt and grime that may have gotten on it during the duration of the sampling period. Blue masking tape was used to secure the aluminum foil. Finally, once the tractors took off for the day, the time that they left was recorded. See **Figures 21a, b** and **c** for a picture of the polycarbonate box wrapped in aluminum foil on the back of the tractor.

Figure 21a: Sampling Train in Box on Tractor

Figure 21b: Sampling Train in Box on Tractor

7.2.8.2: Change-out of Media

The pesticide applicators took an approximately twenty minute lunch break during the day. This was the only opportunity for change out, since there was not another time that they were off their tractors for long enough to be able to change the media out. The media was

Figure 21c: Sampling Train in Box on Tractor

prepared in the same way that it was in the morning, but the PM sampling bags were used, as there was fewer supplies and equipment that was needed. Once the tractors came in for lunch, the prepared change out media was taken out to the tractor in a "clean" box, along with a "dirty" box that would be for the removal of the media off the tractor, that contained scissors, wire cutters to snip the zip ties, and an X-Acto knife to cut the tubing off the reducing connectors. On the tractor set-up, the aluminum foil was removed from the tractor box, but the polycarbonate box with the pumps was not opened or disturbed. The elapsed time was recorded for each of the pumps. The respirator cartridge on the cartridge sample also was not disturbed, as the goal of this project is to determine if breakthrough happens on the respirator cartridge or not.

For the cartridge sampling train, any zip ties tethering the cassettes set to the tractor box were severed with wire cutters. The ¼" Tygon tubing that attached to the ¼" to ½" reducing connector between the cassette set and the respirator cartridge was cut, and an X-Acto knife was used to remove the excess tubing from the ¼" to ½" reducing connector. The luer was then disconnected from the cassette set, and the media was placed in the "dirty" box to be taken back and packaged. The replacement media was easily inserted, and it was re-zip tied.

For the ambient sampling train, the zip ties securing the charcoal tube to the polycarbonate case were cut, and then the ¼" Tygon tubing was cut just below the 3/8" to ¼" reducing connector. The charcoal tube inside the PVC pipe with the tubing still attached was placed in the "dirty" box to be taken down, and the replacement media was easily substituted in. It was then re-zip tied and the entire tractor box was re-wrapped with aluminum foil and re-secured with masking tape. The time that the morning media came off of the tractor and the time that the afternoon media went on the tractor was recorded. **[Figure 22]**.

Figure 22: Change out on Back of Tractor

Once the media was taken off the tractor and taken back to the work station (for both the morning samples and the afternoon samples), the take-down commenced as quickly as possible

so no sampling media would be exposed to any more contaminants once it was no longer on the tractor or around pesticides. The cassette was pried open with a large flat headed screwdriver, and the front and back sections of the charcoal cloth circles were taken out of the cassette with acetone-washed forceps and carefully placed in clean 4 mL vials, which were then labeled and wrapped with Parafilm. The charcoal tubes were disconnected from the Tygon tubing using the X-Acto knife, and were then quickly wrapped with Parafilm or capped with red caps on both ends, and also labeled. All the samples were then placed on dry ice as quickly as possible.

The tubing and the cassettes were discarded after each sample, and the hose barbs, the reducing connector, the PVC pipes and the luers were washed with soap and water for re-use the following day. At the end of the day, the pumps were taken out of the polycarbonate cases, and were wiped down with Clorex disinfecting wipes, and post-calibrated. On the last day of sampling at each site, the polycarbonate boxes were also taken down off of the tractors and cleaned as well.

2.9: In the Field for Gloves

Once the glove thickness has been determined, there was more preparatory work to be done in the lab before going out into the field. Each glove that was to be tested was assigned an identifying number (Glove #) and was written on the glove using a chemical resistant marking pen. The night before sampling, places that the PermaTech patches would be placed were marked using a lab pen on the inside of the glove on both the palm side and the back side of the glove.

7.2.9.1 Data Collection

The dominant hand of each of the subjects was determined, and that glove was used. The dominant hand was used for testing because it was assumed that the subject's dominant hand is

the hand that he or she would use more often, and would therefore be exposed to more oils and solvents. After donning 5 mil nitrile gloves, the PermaTech charcoal cloth circles were placed on the inside of the gloves at the places where they had been previously marked. Then, an aluminum foil tape square was used to cover the PermaTech charcoal cloth circle. This was done for both the palm side and the back side of the glove. The time that patches were placed on the gloves was noted on the data sheets. See **Figure 23** for how the media was put on the gloves in the field.

Figure 23: Putting Media on the Inside of Gloves

7.2.9.2: Change out for Gloves

At the pesticide applicator's lunch break, the patches on the inside of their gloves were changed out. After donning 5 mil nitrile gloves, the gloves of the applicators were turned inside

out, and the aluminum foil tape and the PermaTech patch was removed. Using acetone washed forceps, the PermaTech patch was disconnected from the aluminum foil tape, and carefully placed in a 2 mL vial. The vial was then capped and sealed with ParaFilm and labeled. Then, new PermaTech patches were placed at the same spot on the glove, and covered with aluminum foil tape. The time off of the morning patches and the time on of the afternoon patches were noted on the data sheets. This process was the same for the taking off of the patches at the end of the day, except that no new patches were put on.

The same gloves were used for each consecutive day at a site, in order to determine if, when the pesticide applicators re-use their gloves from day to day, to see if there is a breakthrough if they continue to re-use the same gloves for an extended period of time.

7.2.10: Quality Control

Field blanks and field spikes were used as a control for all of the sampling media, and to ensure that the results from the media are actually the result of field work, rather than other confounding factors. High spikes and low spikes were used. Two high spikes, one low spike, and two blanks were used on the first sampling day at each site, and then just two blanks were used on the second day. The EHS lab performed the blanks and spikes for all of the media. See **Appendix K** for the amount that each media was spiked.

In the field, once the sampling apparatus had been set up, the field blanks and spikes were taken out. For the charcoal tubes, the field blanks were unbroken tubes. Both tips were snapped off using the hole in the glass cutter over the broken glass container (the front end was not cut with the glass cutter as the rest of the media was cut), the charcoal tube was taken outside

to where the pesticides were being applied, and then the ends were capped with either red caps or Parafilm and stored in a freezer. The spikes were cut with a glass cutter, and then broken in the lab and re-capped after the spike was put in. The spikes had their caps taken off, and then were also taken outside to where the pesticides were being applied and then re-capped and stored in a freezer. The time and type of quality control was recorded. The quality control for charcoal cloth circles was very similar. Acetone-washed forceps were used to open a PermaTech patch, which exposed the patch to the air in which the pesticides were being applied. They were then put in 2 mL vials and put in the freezer.

7.2.11: Labeling

Labels were pre-made for every sample. The labeling system for the respirator project displayed the project and year, the site, the set number, the day, the period of sampling, whether the sample was ambient or cartridge set up, the fact that the sample had charcoal tube or cloth, and a unique identification number. The labeling system for the glove project displayed the project and the year, the site, the subject number, the day, the change out time, whether the patch was on the front or the back of the hand, the fact that the sample had PermaTech charcoal cloth, and a unique identification number. The labeling for the quality control had the project and year, the site, the day number, what kind of quality control it was (Blank, High spike, or low spike), media (which was always charcoal), and the unique identification number. See **Appendix L** for an example of a respirator, glove and a QC label.

7.3: Analysis in Lab

For respirators, a total of 13 ambient samples and 13 cartridge samples for horticultural oil were taken, and 4 ambient and 4 cartridge samples were taken for chlorpyrifos. For gloves, 15 back of hand samples and 15 palm samples for gloves were taken for horticultural oil, and 6 back of hand samples and 6 palm samples were taken of chlorpyrifos. A total of 6 blanks of each kind of media (charcoal tube, charcoal cloth, and PUF tubes), 4 high spikes, and 4 low spikes of each kind of media were taken. Once the samples were brought back to the University of Washington, they were stored in the freezer, logged into the computer, and sent to the Environmental Health Lab to be analyzed. The solvents and oils were analyzed by gas chromatography based on

NIOSH 1500 Hydrocarbons, at 216 degrees Celsius. The chlorpyrifos was analyzed by LC-Mass Spectroscopy for PUF disks. All samples were analyzed as separate front and back sections, and then added together for the combined breakthrough.

In the lab, for the analysis of the solvents and oils, all of the unknown peaks were quantified as pentadecane. Aromatics were not distinguished from aliphatics on retention time, as there was no aromatic component. The results were not corrected for spike recovery efficiency, and the results were corrected for both reagent and matrix blank values. Field blanks, when submitted, were analyzed and reported as samples; no correction was made for the field blanks. The samples were analyzed as separate front and back sections. For the charcoal cloth circles, separate front and back section samples were submitted, as each cassette had two charcoal cloth circles. For the charcoal tubes and PUF tubes, the front and back sections were both in the charcoal tubes and were submitted as one sample, and then broken up into front and back sections by the lab. The EHS lab sampled for p-Xylene, o-Xylene, Cumene, 1,2,4

Trimethyl benzene, petadecane, and unknown alkanes. Later, the results were re-processed by the lab and the unknown alkanes was broken up into the categories of non-aromatic hydrocarbons, unknown aromatics (which includes alicyclics and aliphatics), and siloxanes (for respirators) and nonaromatic hydrocarbons, unknown aromatics, and pentadecane (for gloves).

7.4: Statistical Methods

A binary probability analysis was used. Each sample was to be classified as a "hit", or if it was contaminated, or not. In order to do this, it was necessary to determine the mass of the total amount of all of the compounds that came through the respirator cartridge that was not due to pre-existing contamination on the sampling media. Therefore, the amount of mass of solvents that was collected on the blanks (the blank charcoal tubes, the blank charcoal cloth circles, and the blank PUF tubes) was looked at. An average of the mass of solvents that was found on the blanks for each compound for each kind of sampling media was calculated, and then the standard error of the mean was calculated. In order to have a confidence level between 99.0% and 99.5%, 4 standard errors were added to the mean mass, which was established as the upper limit of noncontamination. In other words, any media that had a mass of solvents greater than that of 4 standard errors added to the average mass of the blank media was defined as a "hit", or was judged to be contaminated. This was done for both the media for the respirator cartridges and the media for the gloves, and for the ambient samples, the cartridge samples, and the glove samples. The amounts of each kind of compound on each of the collected sample media was then compared to the value that was calculated. However, for the respirators, the flow rate was not the same for all of the cartridge samples. In order to equalize them, a multiplier was calculated. This multiplier was created by choosing a number close to the average total liters of air that was taken

in at each sample for each type of media. The adjusted mass was calculated by dividing the multiplier by the total liters of air that was taken in in that sample, and then multiplied by the mass of the sample.

Adjusted Mass = Multiplier/Liters air x Reported Mass

Therefore, the adjusted mass was able to be comparable for various flow-rates. Once the adjusted mass was calculated, the adjusted mass for the combined front and back sections of each collected sample media, as well as the mass on the sample media for the gloves, was compared to the upper limit of non-contamination**.** The results are paired by ambient and cartridge samples for the respirators, as well as by AM and PM samples and by set, and by palm and back samples for the gloves, as well as by AM and PM samples. (An adjusted mass was not calculated for the glove sample since there was no concentration).

Once the calculated adjusted mass was compared to the upper limit of noncontamination, then "hits" could be established. The binomial frequencies of hits over total samples for each category of sample was calculated.

A one sided binomial probability p-test was performed on these frequencies that were calculated.

H_0: Frequency of hits in blanks = Frequency of hits in media H_a: Frequency of hits of the media > Frequency of hits of the blanks

An alpha of .05 was used.

A secondary analysis that was done only on the respirators was to calculate an estimated protection factor. Since a standard multiplier was used for the ambient and cartridge samples of the respirator cartridges, a ratio of the standard multipliers was calculated. This ratio could be used to equate the flow rates, by multiplying the ratio by the adjusted mass for the ambient sample. This enabled the ambient samples to be able to be compared to the cartridge samples. Then, a mass to mass ratio, or an estimated workplace protection factor was established by dividing the equated ambient mass by the adjusted cartridge mass. This ratio of expected over observed showed a rough value of what the protection estimate was. If the resulting ratio was equal to 1, then there was no established difference between the mass of alkanes inside and outside of the respirator cartridge, and the cartridge offers no protection. If the resulting ratio was less than 1, then the cartridge absorbs more mass of alkanes wearing no cartridge at all does, and if the resulting ratio was greater than 1, then the cartridge is protective against the absorption of the alkanes. The greater the value is above 1, then the more protective the cartridge is. For the matched sets in which both ambient and cartridge samples were classified as "hits", then a low estimated protection factor is expected. For the matched sets in which neither ambient nor cartridge samples were classified as "hits", a high protection factor was expected, since there did not seem to be evidence of many solvents outside of the cartridge. For the matched sets in which the ambient was classified a "hit" and the cartridge sample was not, there is evidence that the cartridge was in fact protective, since nothing seemed to get through. It was also generally expected that the afternoon samples would have a lower protective factor than the morning samples, since as time goes on it is expected that there will be more absorption and therefore more breakthrough.

See **Appendix M** for pictures from sampling.

Chapter 8: Results

8.1: Lab Analysis

The sampling actually took place for one day in Yakima Valley, and for two days in North Central Washington. Demographic data on the qualitative information about the workers, the tractors, and the farms was taken, and this data can be found in **Appendix N**. The demographic data for the respirator cartridge study focuses on the types and amounts of pesticides, the tractors, and the amount that was sprayed. The demographic data for the glove study focuses on the applicators themselves, and their qualitative demographic data.

On all sites, the amounts of p-Xylene, o-Xylene, cumene, and pentadecane on both the ambient and charcoal sampling media for both the respirators and the gloves was below the limit of detection. Site A had amounts of 1,2,4 Trimethyl benzene for both the ambient and the cartridge samples that were detected, but the amounts on the sampling media for Trimethyl benzene at Site B was below the limit of detection. See **Appendix O** for the limits of detection that were used for each of the solvents that were tested for. However, with regards to the horticultural oil, a great number of unknown alkanes showed up in both Site A and Site B. These alkanes were unexpected as according to the MSDS sheets, and therefore were lumped together as "unknown alkanes". It was attempted to divide up the unknown alkanes category by the peaks that were evident on the spectroscopy that was performed, and then by looking at the peaks on the chromatographs.

8.2: Qualitative Results for Respirator Samples

For the respirators, the mass of the amount of each of the samples was added together for the front and back sections for the ambient and cartridge samples. The total run time for each sample was multiplied by the flow rate in order to get the total liters of air that went through the sample. Then, the mass of the solvents that was detected was divided by the total liters of air in order to get the concentration of each of the solvents. The difference between the matched set of the ambient and the cartridge samples was also calculated. (It should be noted that any amount that was below the limit of detection, see **Appendix O**, was treated as zero). The cells in the table are highlighted in blue if the cartridge concentration exceeded the ambient concentration, or if the difference between the two was a negative number. The two sites that were sampled had very different conditions, and therefore very different results. At Site A, chlorpyrifos and horticultural oil was being sprayed, so both Trimethyl benzene and unknown alkanes were detected. In the second site, only horticultural oil was sprayed, and so only unknown alkanes were detected, and at much smaller quantities.

8.2.1: Unknown Alkanes

The results all show that very small amounts of unknown alkanes were detected [**Table 23, Figure 34 and 35].** There was a high concentration of unknown alkanes behind the cartridge at Site A, but this average was impacted by one very high data point. At Site B, there were greater concentrations of unknown alkanes in the ambient samples than the samples behind the cartridges. However, all of the concentrations found, both ambient and cartridge, were very small.

Table 22: Unknown Alkanes Concentrations

Site	Set	Unknown Alkanes Concentrations		
		Ambient	Cartridge	Difference
A	AM Set 11	1.2	0.37	0.83
	PM Set 11	6.0	11	-5.00
	AM Set 12	0.83	0.30	0.53
	PM Set 12	0.69	0.20	0.49
B	AM Set 13	0.054	0.0021	0.05
	PM Set 13	0.15	0.0039	0.15
	AM Set 14	0.052	0.027	0.03
	PM Set 14	<LOD	<LOD	<LOD
	AM Set 15	0.25	<LOD	0.25
	PM Set 15	0.18	0.0024	0.18
	AM Set 16	0.54	0.006	0.53
	AM Set 17	1.18	0.0065	1.17
	AM Set 18	0.37	0.0064	0.36

Figure 34 Mean Concentrations for Unknown Alkanes at Site A (ug/L)

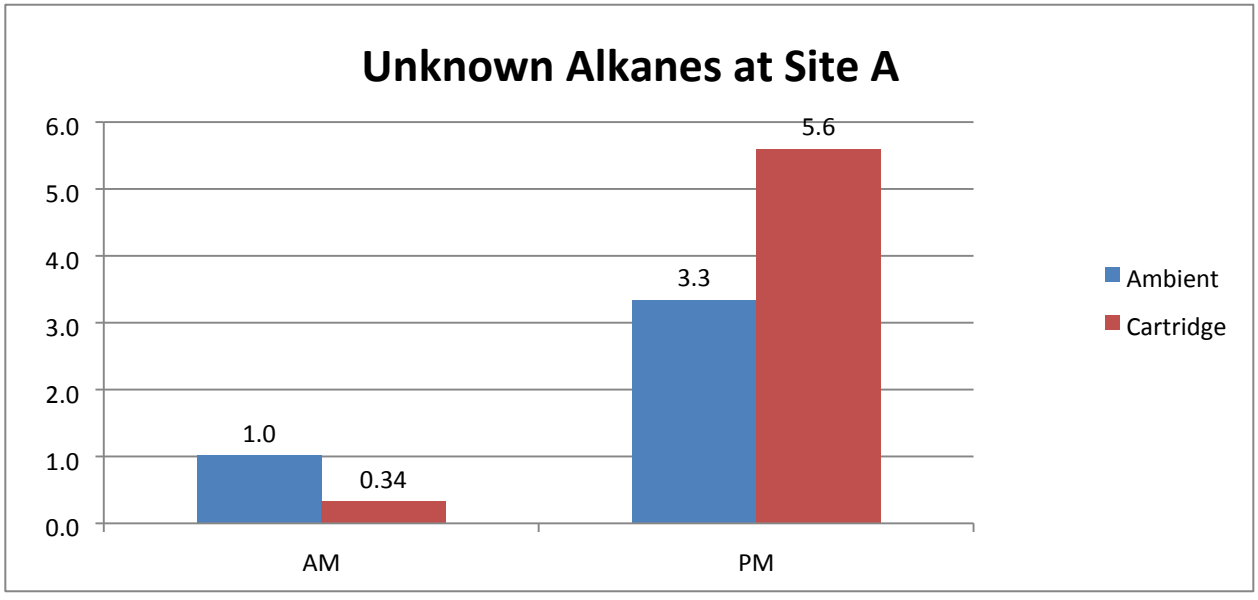
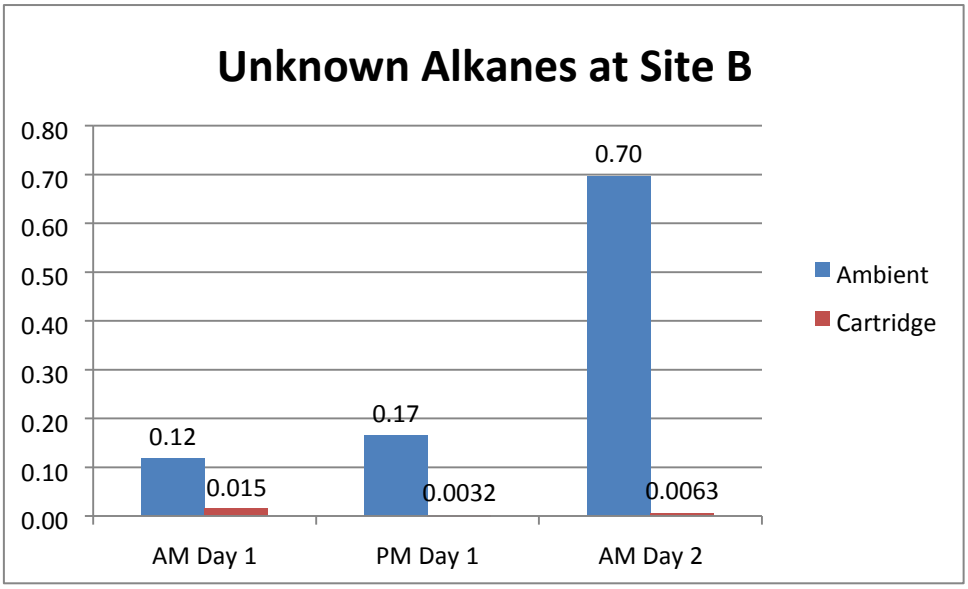


Figure 35: Average Differences in Concentration for Unknown Alkanes at Site B (ug/L)



8.2.2: Non-Aromatic Hydrocarbons

The unknown alkanes were broken up into the three sub categories (non-aromatic hydrocarbons, unknown aromatics, and siloxanes. For non-aromatic hydrocarbons, **[Table 24 and Figure 36 and 37]** there was a much higher concentration that were found in the cartridge than outside it, particularly in the afternoon at Site A. At Site B, there were not many nonaromatic hydrocarbons were found except on the morning of the second day, and very few seemed to get into the respirator.

Table 24: Concentrations of Non-Aromatic Hydrocarbons

Site	Set	Air Concentration of Unknown Alkanes (ug/L)		
		Ambient	Cartridge	Difference
A	AM Set 11	0	436	-436.00
	PM Set 11	1010	19030	-18020.00
	AM Set 12	0	0	0.00
	PM Set 12	0	38	-38.00
B	AM Set 13	0	0	0.00
	PM Set 13	0	0	0.00
	AM Set 14	0	0	0.00
	PM Set 14	0	0	0.00
	AM Set 15	0	0	0.25
	PM Set 15	0	0	0.00
	AM Set 16	150	0	150.00
	AM Set 17	368	0	368.00
	AM Set 18	122	0	122.00

Figure 36: Mean Concentration for Non-aromatic Hydrocarbons at Site A (ug/L)

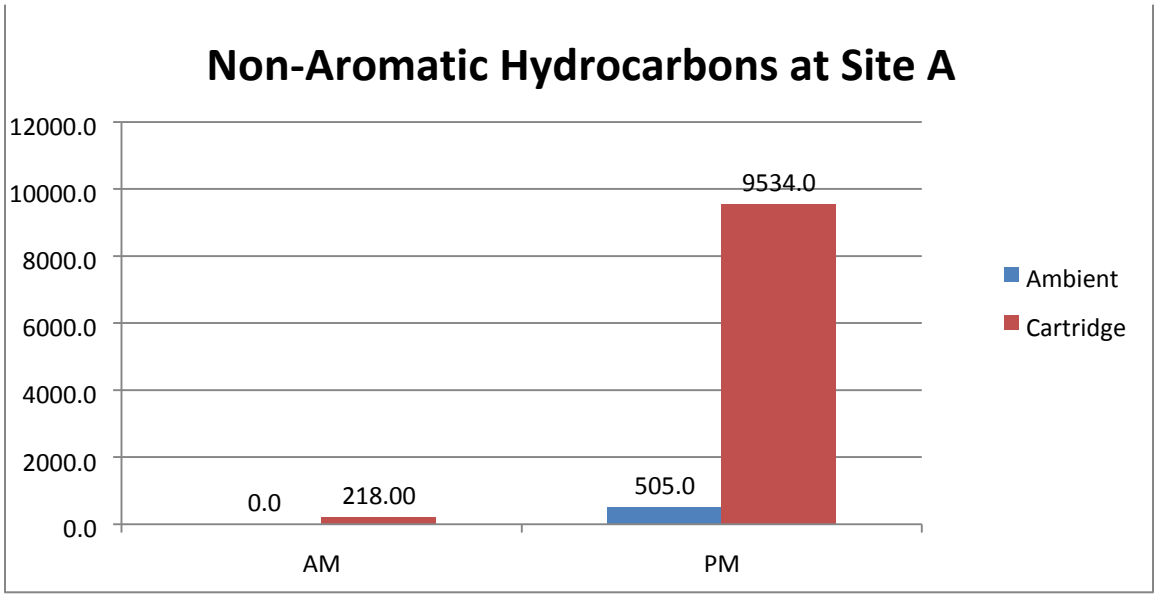
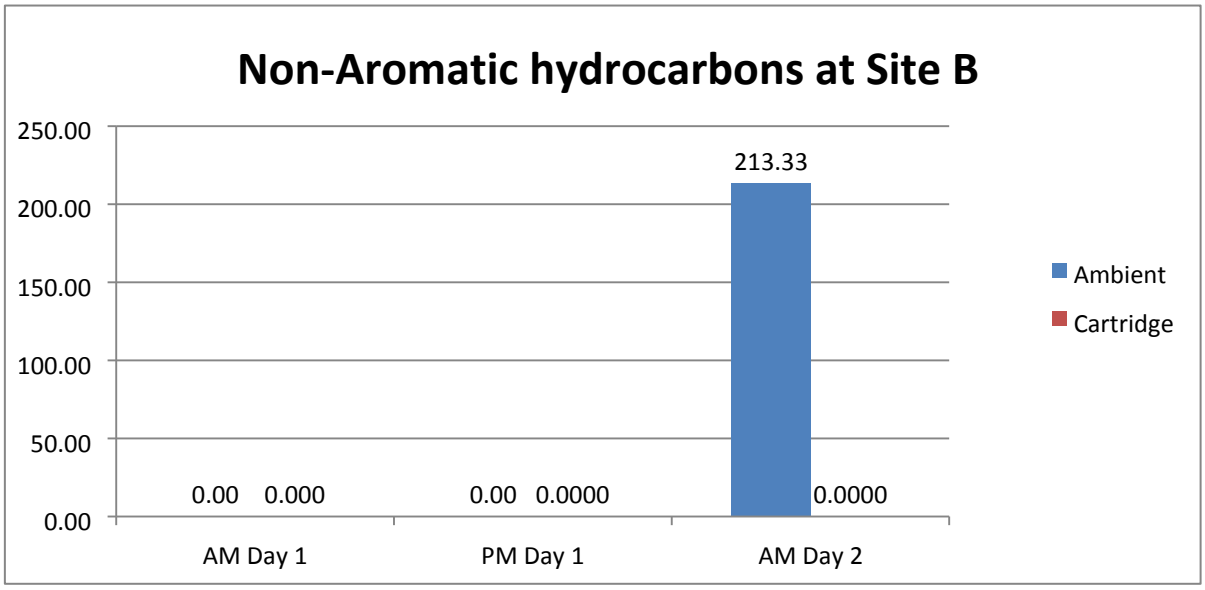


Figure 37: Mean Concentration for Non-aromatic Hydrocarbons at Site B (ug/L)



8.2.3: Unknown Aromatics

For the unknown aromatics **[Table 25 and Figures 38 and 39]** at Site A, there was a high amount that was present both inside the cartridge and outside the cartridge, but there seemed to be a greater amount inside the cartridge. At Site B, generally there also seemed to be a greater amount that was found inside the cartridge as well.

Table 24: Concentrations of Unknown Aromatics

Site	Set	Air Concentration of Unknown Aromatics (ug/L)		
		Ambient	Cartridge	Difference
A	AM Set 11	415	326	89.00
	PM Set 11	535	631	-96.00
	AM Set 12	238	567	-329.00
	PM Set 12	0	288	-288.00
B	AM Set 13	0	11	-11.00
	PM Set 13	0	3	-3.00
	AM Set 14	0	7	-7.00
	PM Set 14	17	4	13.00
	AM Set 15	0	32	0.25
	PM Set 15	0	0	0.00
	AM Set 16	0	15	-15.00
	AM Set 17	0	19	-19.00
	AM Set 18	0	18	-18.00

Figure 38: Mean Concentration for Unknown Alkanes at Site A (ug/L)

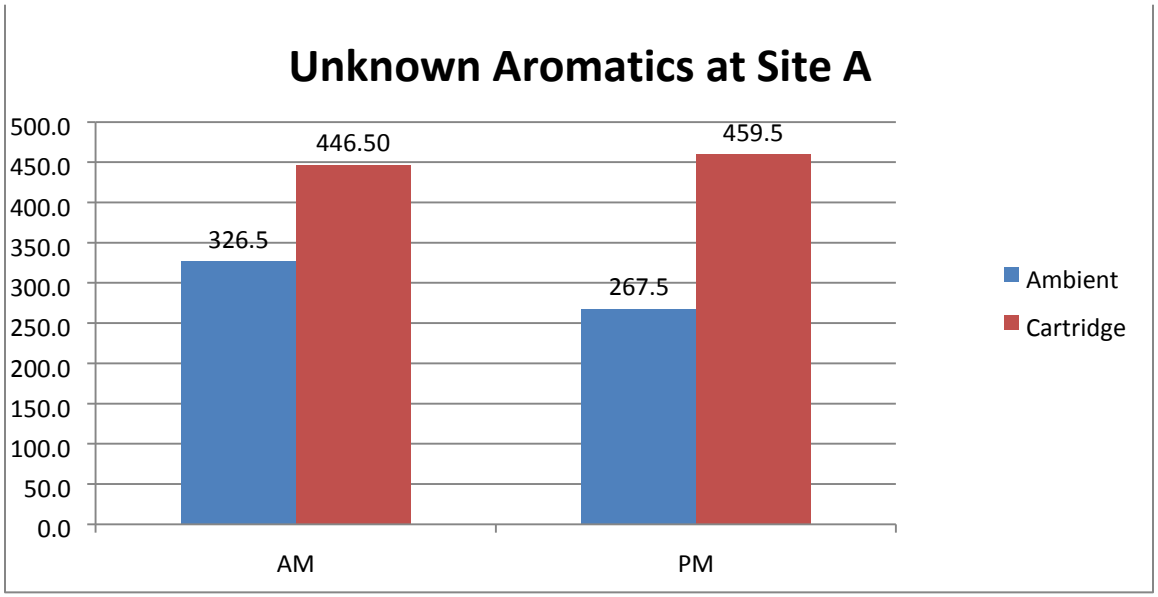
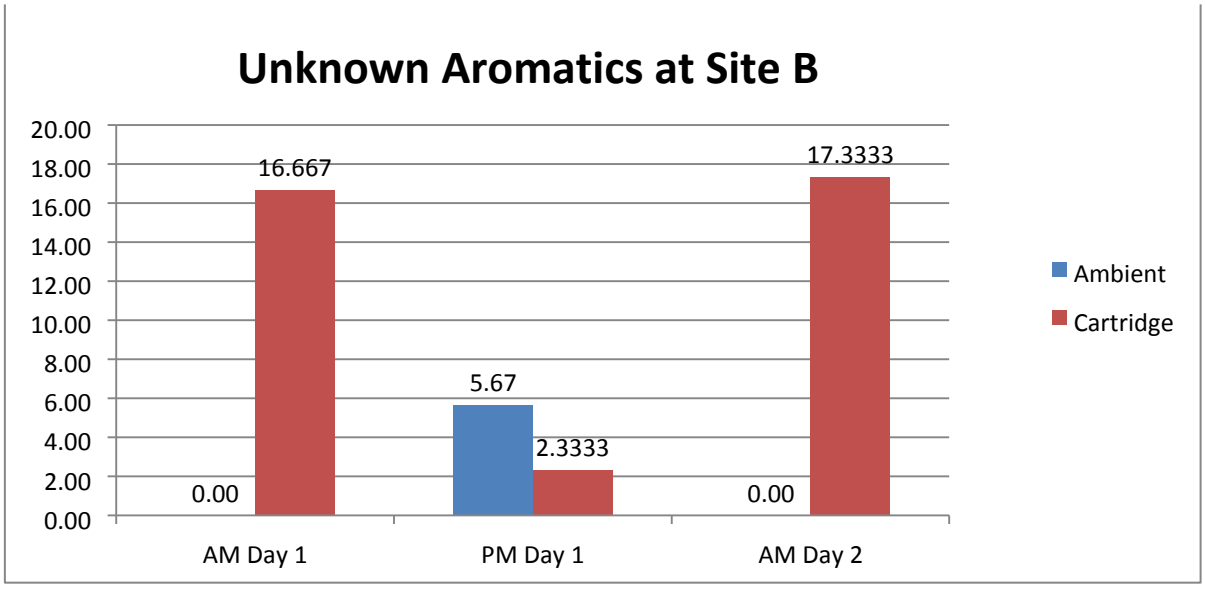


Figure 39: Mean Concentration for Unknown Alkanes at Site B (ug/L)



8.2.4: Siloxanes

There was only one ambient sample that was found that contained siloxanes and one cartridge sample, so it was judged to be a red herring and to be issue with contamination [**Table 26].**

Table 26: Concentrations of Siloxanes

Site	Set	Air Concentration of Siloxanes (ug/L)		
		Ambient	Cartridge	Difference
A	AM Set 11	0	0	0.00
	PM Set 11	90	0	90.00
	AM Set 12	0	0	0.00
	PM Set 12	0	0	0.00
B	AM Set 13	0	0	0.00
	PM Set 13	0	0	0.00
	AM Set 14	0	45	-45.00
	PM Set 14	0	0	0.00
	AM Set 15	0	0	0.25
	PM Set 15	0	0	0.00
	AM Set 16	0	0	0.00
	AM Set 17	0	0	0.00
	AM Set 18	0	0	0.00

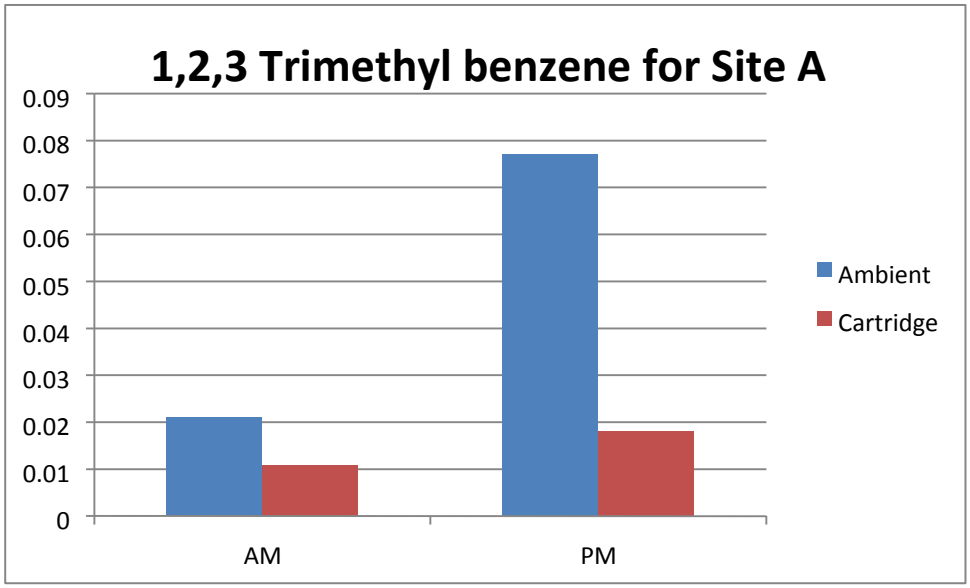
8.2.5: 1,2,4 Trimethyl Benzene

1,2,4 Trimethyl benzene was only detected at Site A in the respirator samples. There was a greater amount of trimethyl benzene in the ambient air than behind the cartridge [**Table 27** and **Figure 40**]

Table 27: Concentrations of Trimethyl benzene

Set	Air Concentration 1,2,4 Triemethyl Benzene (ug/L)		
	Ambient	Cartridge	Difference
AM Set 11	0.032	0.0088	0.0232
PM Set 11	0.077	0.018	0.059
AM Set 12	0.01	0.013	-0.003
PM Set 12	0	0	0

Figure 40: Mean Concentration for Trimethyl benzene (ug/L)



8.2.6:Chlorpyrifos and chlorpyrifos oxon

Chorpyrifos and chlorpyrifos oxon was also detected at Site A, although there was a very small sample size. There seemed to be a much greater concentration behind the cartridge than in the ambient samples at Site A, although there were only four ambient samples and three cartridge samples at Site A, since one of the pumps stopped working. At Site B, there seemed to be a difference in the amount of chlorpyrifos oxon in the ambient and cartridge samples varying with the morning and the afternoon [**Tables 28** and **29**, and **Figures 41** and **42**].Looking at the REL for chlorpyrifos from NIOSH, which is .2 mg/m^3, the amounts found in the ambient air are not close to that. Therefore, the workers theoretically should not be exposed to a great amount of chlorpyrifos at all.

Figure 41: Mean Concentration of Chlorpyrifos

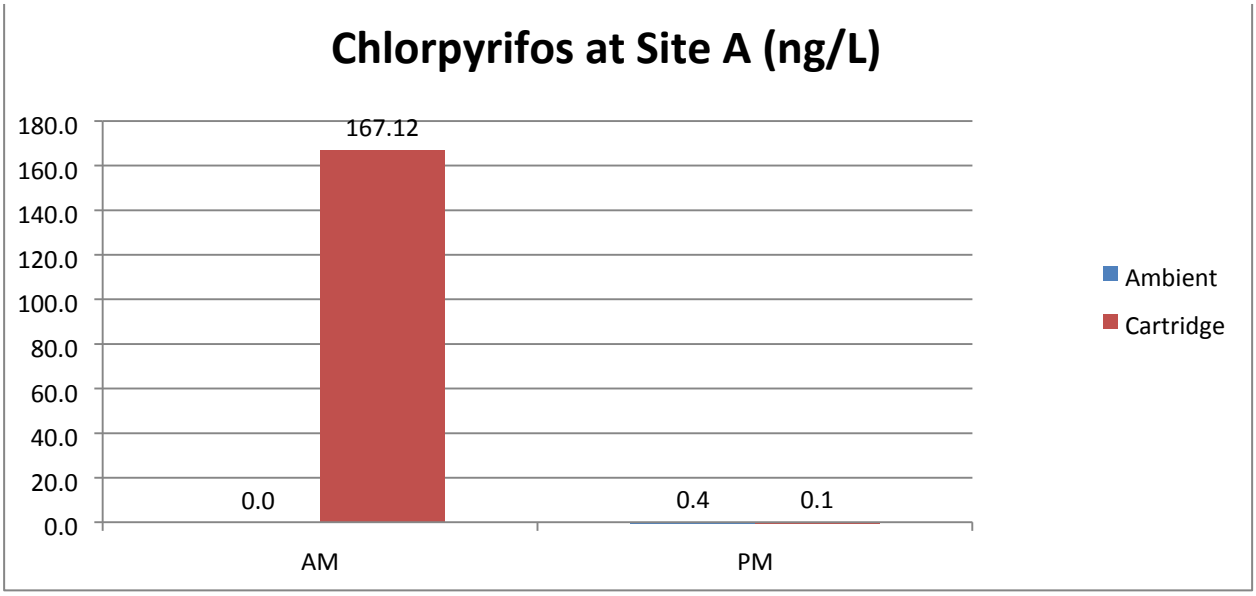


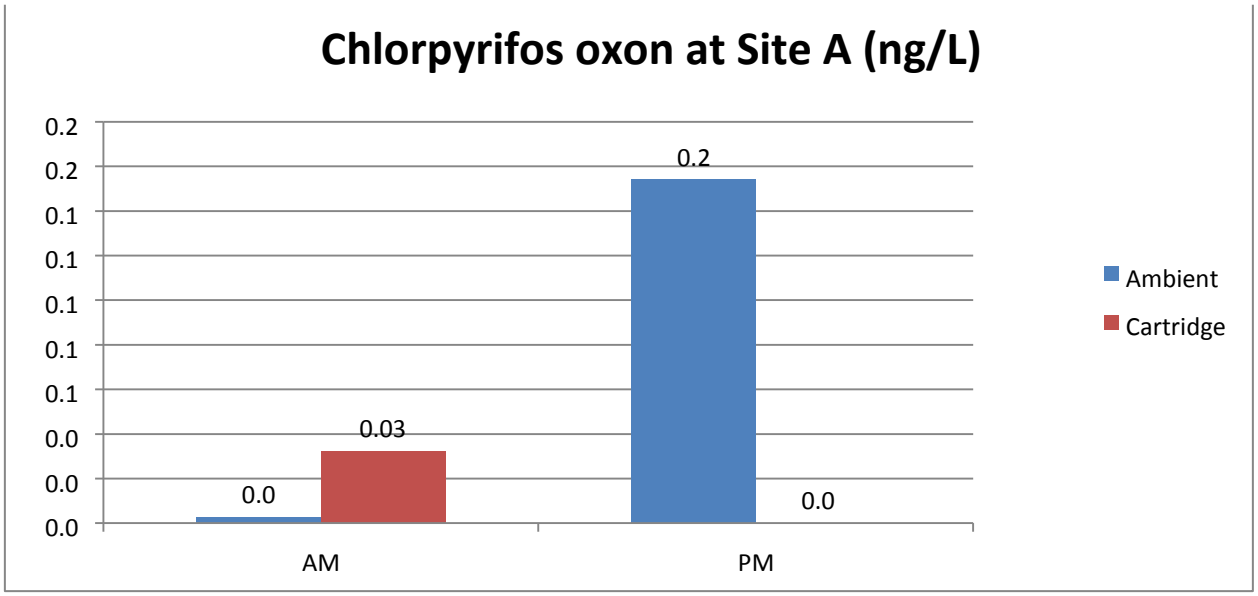
Table 27: Concentrations of chlorpyrifos

Set	Air Concentration chlorpyrifos (ng/L)		
	Ambient	Cartridge	Difference
AM Set 11	**0.00**	**136.48**	**-136.48**
PM Set 11	**0.00**	**-**	**-**
AM Set 12	**0.00**	**197.76**	**-197.76**
PM Set 12	**0.71**	**0.12**	**0.59**

Table 29: Concentration of Chlorpyrifos oxon

Set	Air Concentration chlorpyrifos oxon (ng/L)		
	Ambient	Cartridge	Difference
AM Set 11	0.00	0.03	-0.03
PM Set 11	0.00	-	-
AM Set 12	0.01	0.04	-0.03
PM Set 12	0.31	0.00	0.31

Figure 42: Mean Concentration of chlorpyrifos oxon



8.3: Qualitative Results for Gloves

For the gloves, much higher amounts of compounds were found. There was no concentration recorded for the amount of gloves, since passive samples were placed on the inside of the gloves. Therefore, all of the tables and bar graphs reflect the amount of ug per sample. The amounts of horticultural oil were measured for unknown alkanes, which was then divided up into pentadecane, unknown aromatics and non-aromatic hydrocarbons. There did seem to be exposure on both the back and the palm of the hand. There does not seem to be an increase in the exposure the longer the subject wore the gloves, however. Generally, the back of the hand seemed to have a slightly greater mass of solvents than the palm of the hand did, which makes sense because the back of the hand, in a pronating position, would be more exposed to pesticides that are being sprayed. However, there are exceptions to this statement, such as the Pentadecane at Site B on the first day, or the mean mass of the unknown aromatics on the first day at Site B.

[**Tables 30-33** and **Figures 43-50**].

8.3.1: Unknown Alkanes

Table 30: Mean Mass of Unknown Alkanes

Subject	Time	Mass of Unknown Alkanes		
		Back	Palm	Difference
1	AM	1193	1155	38.00
	PM	1169	1029	140.00
2	AM	1271	1114	157.00
	PM	1387	1427	-40.00
3	AM	1081	947.3	133.70
	PM	1315	-	-
5	AM	1451	1380	71.00
	PM	1630	1280	350.00
	AM	1280	1100	180.00
6	AM	1060	1080	-20.00
	PM	1250	1190	60.00
	AM	1030	1060	-30.00
4	AM	1000	1100	-100.00
	PM	1190	1080	110.00
	AM	1090	1130	-40.00

Figure 43: Mean Mass of Unknown Alkanes at Site A

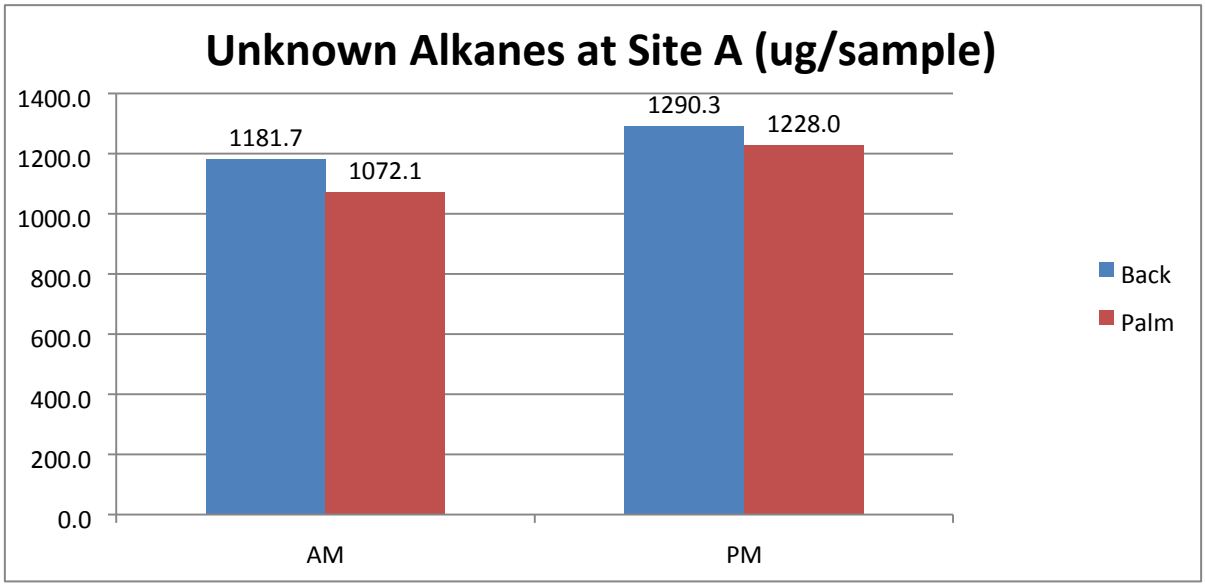
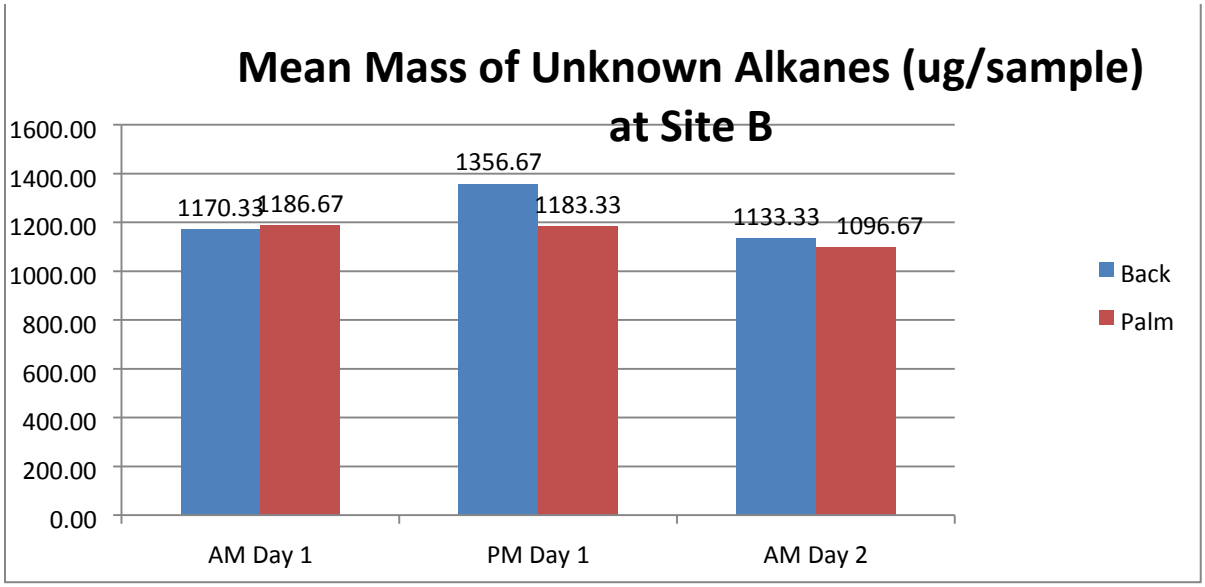


Figure 44: Mean Mass of Unknown Alkanes at Site B



8.3.2: Pentadecane

Table 31: Mean mass of Pentadecane

Subject	Time	Mass of Unknown Alkanes		
		Back	Palm	Difference
1	AM	1	3	-2.00
	PM	1	2	-1.00
2	AM	1	1	0.00
	PM	1	2	-1.00
3	AM	2	1	1.00
	PM	5	-	-
5	AM	2.7	7	-4.30
	PM	6	5	1.00
	AM	4	1	3.00
6	AM	3	1	2.00
	PM	2	1	1.00
	AM	3	1	2.00
4	AM	1	4	-3.00
	PM	1	3	-2.00
	AM	4	6	-2.00

Figure 45: Mean Mass of Pentadecane at Site A

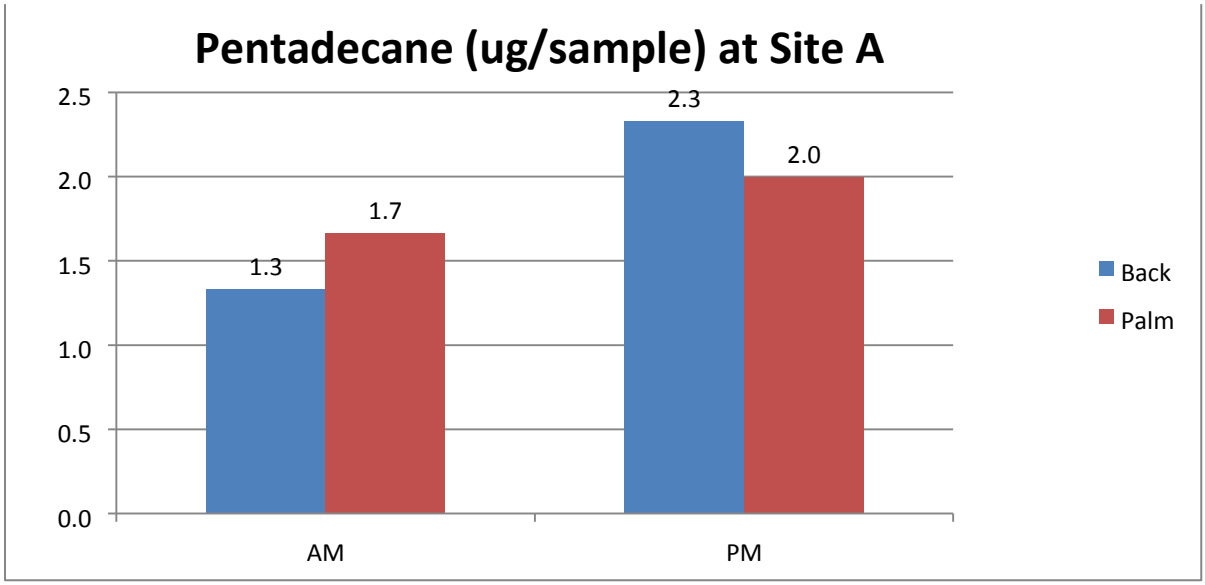
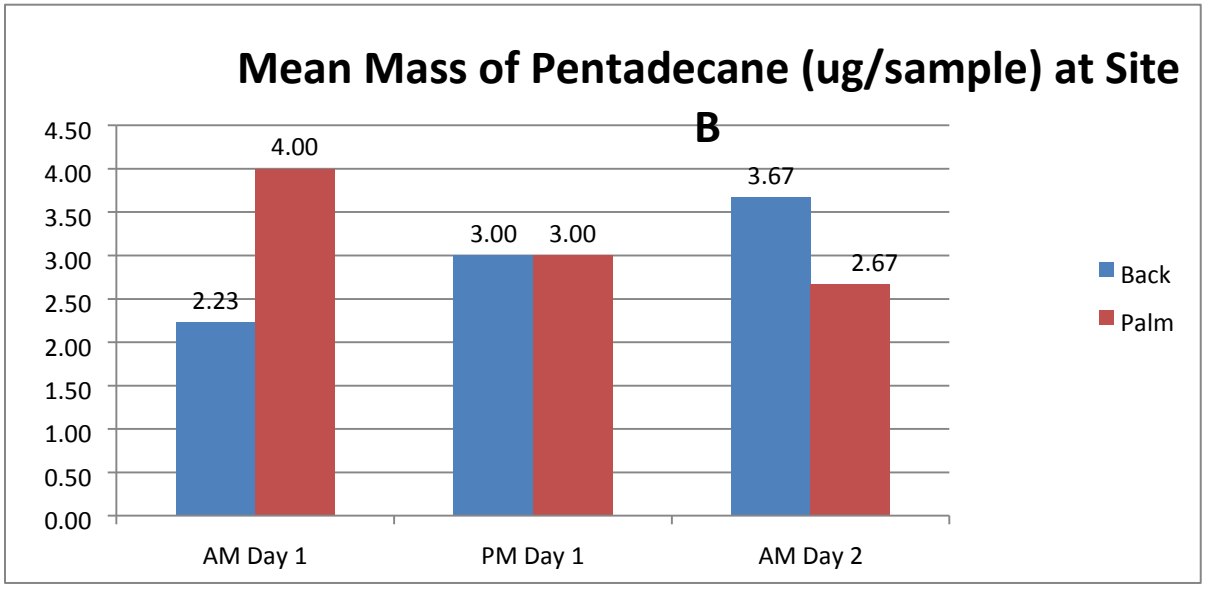


Figure 46: Mean Mass of Pentadecane at Site B



8.3.3: Non-aromatic hydrocarbons

Table 32: Mean mass of Non-aromatic hydrocarbons

	Time	Mass of Non-aromatic hydrocarbons		
		Back	Palm	Difference
1	AM	1130	1060	70.00
	PM	1100	932	168.00
2	AM	1200	1060	140.00
	PM	1400	1420	-20.00
3	AM	1100	962	138.00
	PM	1220	-	-
5	AM	1374	1275	99.00
	PM	1601	1209	392.00
6	AM	1239	1038	201.00
	AM	1022	1032	-10.00
	PM	1181	1114	67.00
	AM	992	1008	-16.00
4	AM	918	1004	-86.00
	PM	1159	1014	145.00
	AM	1082	1077	5.00

Figure 47: Mean Mass of Non-Aromatic Hydrocarbons at Site A

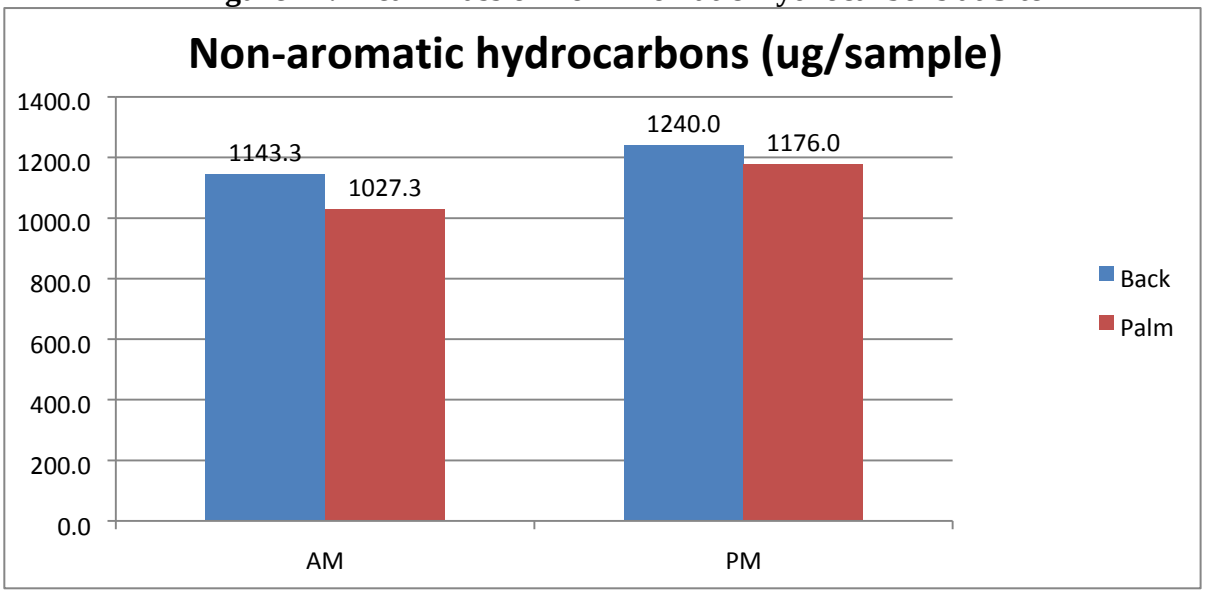
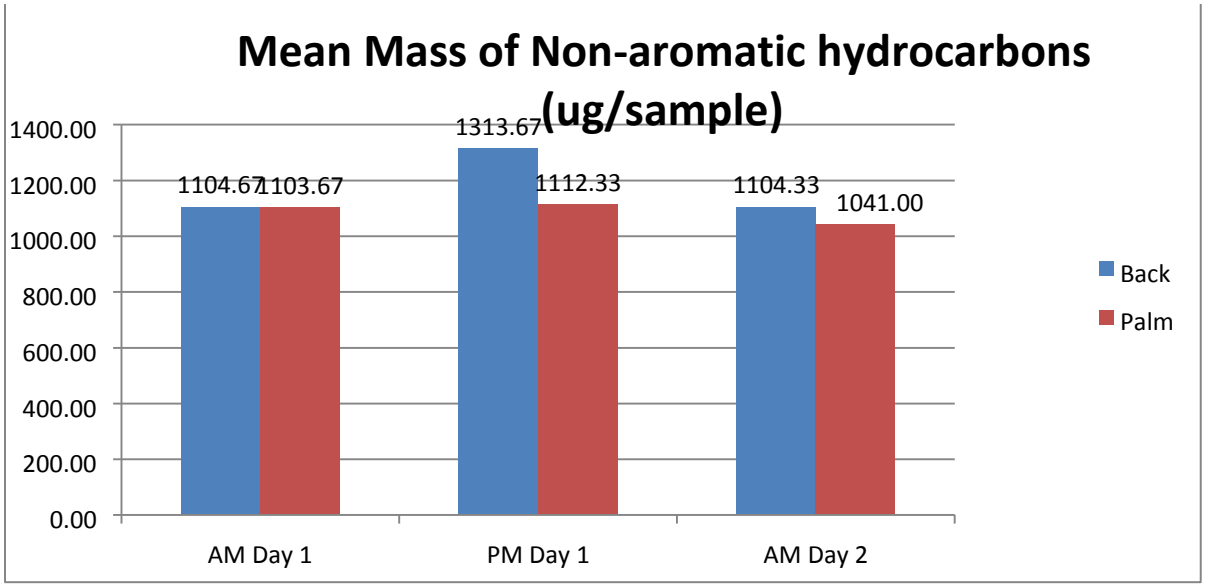


Figure 48: Mean mass of non-aromatic hydrocarbons



8.3.4:Unknown Aromatics

Table 33: Mass of Unknown Aromatics

Subject	Time	Mass of Unknown Alkanes		
		Back	Palm	Difference
1	AM	112	91	21.00
	PM	78	104	-26.00
2	AM	100	52	48.00
	PM	161	92	69.00
3	AM	92	74	18.00
	PM	188	-	-
5	AM	100	125	-25.00
	PM	124	116	8.00
	AM	153	89	64.00
6	AM	103	161	-58.00
	PM	87	96	-9.00
	AM	81	82	-1.00
4	AM	123	127	-4.00
	PM	61	65	-4.00
	AM	68	63	5.00

Figure 49: Mean mass of Unknown Aromatics at Site A

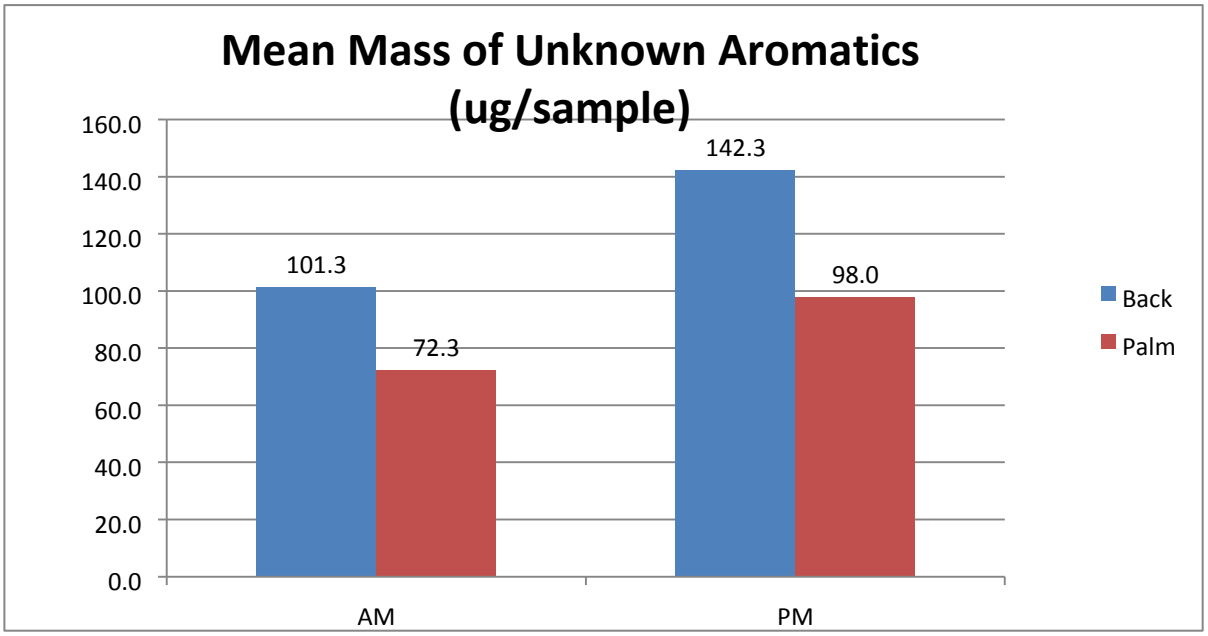
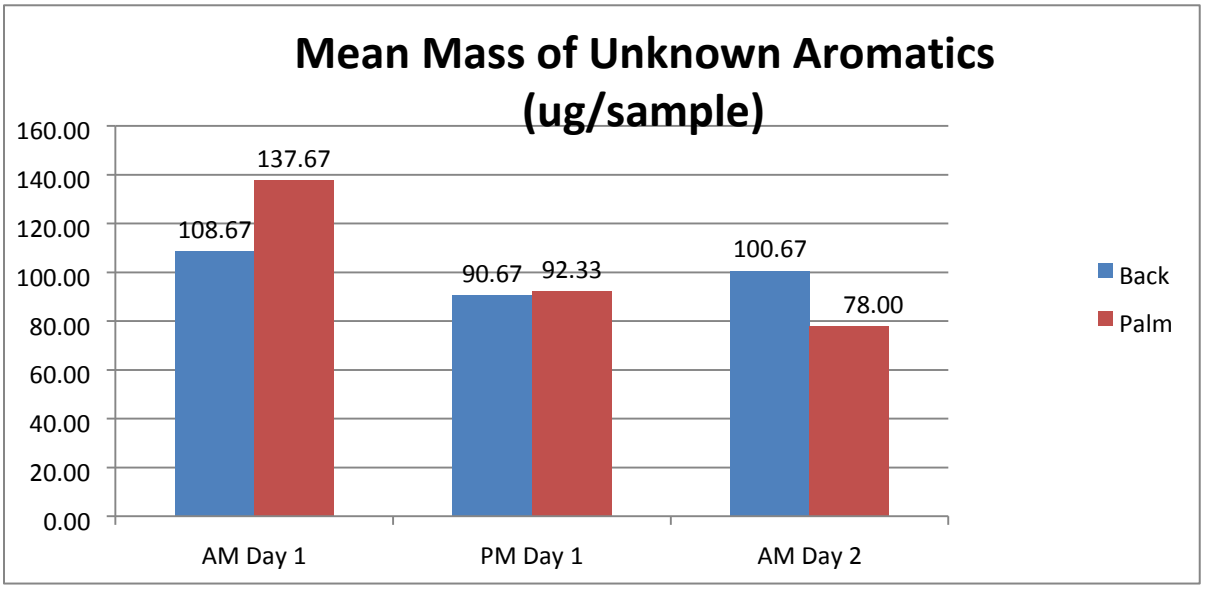


Figure 49: Mean Mass of Unknown Aromatics at Site B



8.4: Data Analysis

Each sample was to be classified as a "hit", or whether that particular kind of PPE was not effective (or whether the media contained an amount of pesticides that could not be contributed to contamination error) or not. In order to do this, it was necessary to determine the mass of the total amount of all of the compounds that came through the respirator cartridge that was not due to pre-existing contamination on the sampling media. The field blanks were looked at, and the mean mass for each of the field blanks was calculated, as well as the standard error of that mean for each of the kinds of samples. Any media that had a mass of solvents greater than that of 4 standard errors added to the average mass of the blank media was defined as a "hit". Four standard errors was used as this would give a 99.0 to 99.5% amount of confidence that anything greater than the mean plus the four standard errors would actually be media behind PPE that was not working effectively. However, this means that some of the blanks could also be classified as "hits", if they had a mass that was outside of the mean mass plus four standard errors. These blanks would be outliers, and not be considered to be the norm for blanks. On unknown aromatics for the respirators and non-aromatic hydrocarbons for the charcoal cloths, the upper limit of non-hits was 0. That means that the amount of those compounds that was detected on the blanks was zero, and therefore any media that had any mass at all of those compounds would be considered a "hit". See **Appendix P** for the calculation of the upper limit of non-hits.

A multiplier was calculated to compare the masses of the compounds in the respirator samples since the flow rates of the cartridge samples had some that were at 6 L/min and some that were 8 L/min. This multiplier was created by choosing a number close to the average total liters of air that was taken in at each sample for each type of media (2000 was chosen as the

multiplier for the charcoal cloths, and 330 was chosen as the multiplier for the charcoal tubes). The adjusted mass was calculated by dividing the multiplier by the total liters of air that was taken in in that sample, and then multiplied by the mass of the sample.

Adjusted Mass = Multiplier/Liters air x Reported Mass

Therefore, the adjusted mass was able to be comparable for various flow-rates. See **Appendix Q** for the calculations of the adjusted mass.

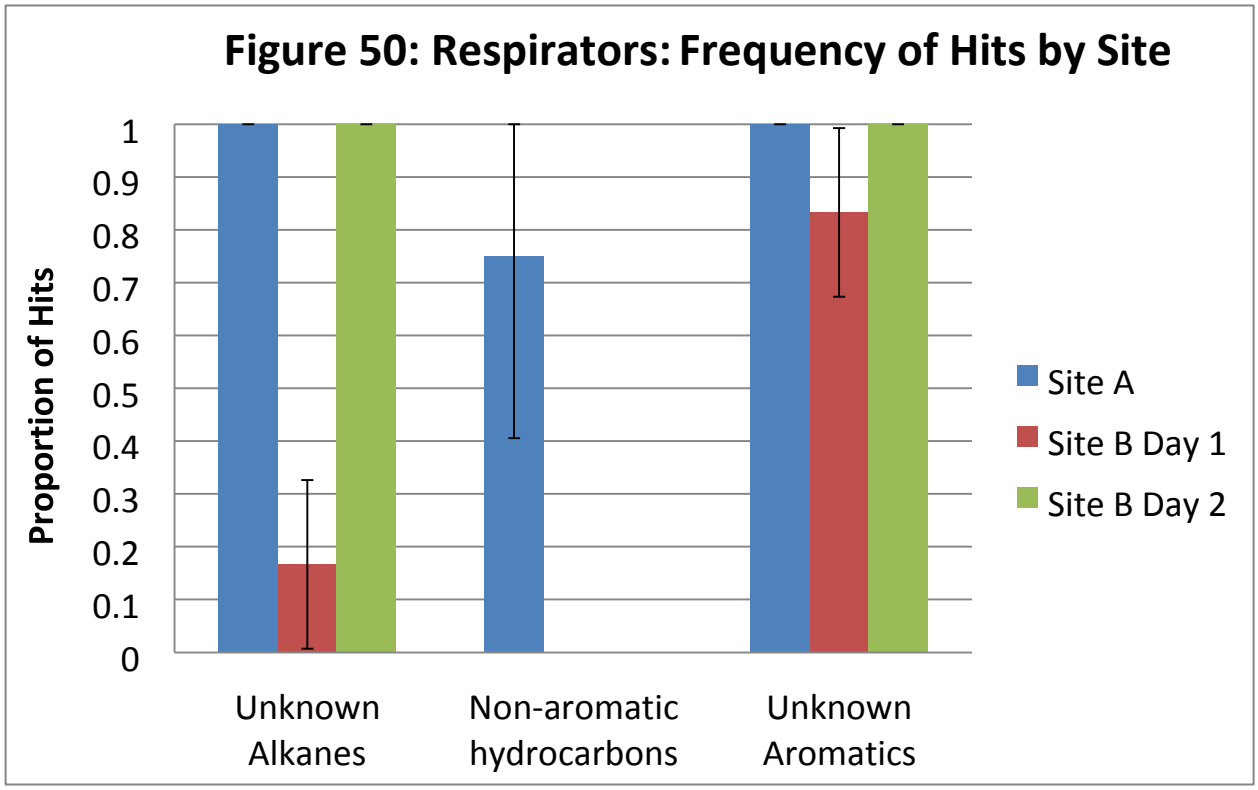
Once the adjusted mass was calculated, the adjusted mass for the combined front and back sections of each collected sample media, as well as the mass on the sample media for the gloves, was compared to the calculated upper limit from the mean and standard error the blanks.

The results are paired by ambient and cartridge samples for the respirators, as well as by AM and PM samples and by set, and by palm and back samples for the gloves, as well as by AM and PM samples. (An adjusted mass was not calculated for the glove sample since there was no concentration). Anything that is highlighted was a "hit", or was higher than this upper limit.

Then, the proportion of hits was calculated. The proportion of hits for each Site, each time, and for gloves, each location was calculated. This proportion is what percent chance each sample has of being contaminated based on the site it is at and the time that the sample is taken from, or the location of the sample (just for the gloves). A 95% confidence interval for each of the frequencies was calculated, and a bar charts with error bars were created.

8.4.1: Frequency of Hits

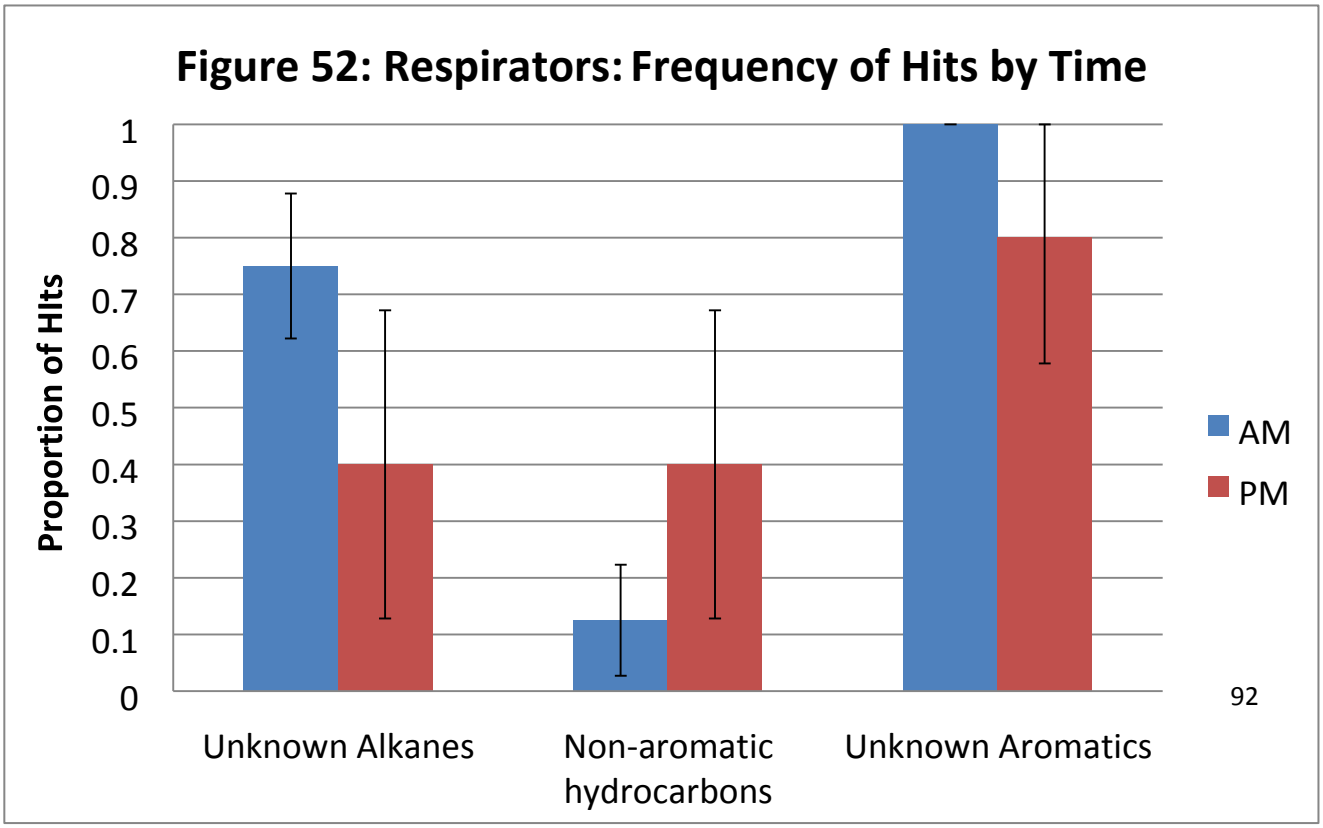
Looking at the Respirator Frequency of Hits by Site, (**Figure 51)** at Site A there was a high frequency in all of the compounds, including a 100% frequency of unknown alkanes and unknown aromatics. Site B did not have any frequency for non-aromatic hydrocarbons, but all sites and days had a frequency of unknown alkanes.

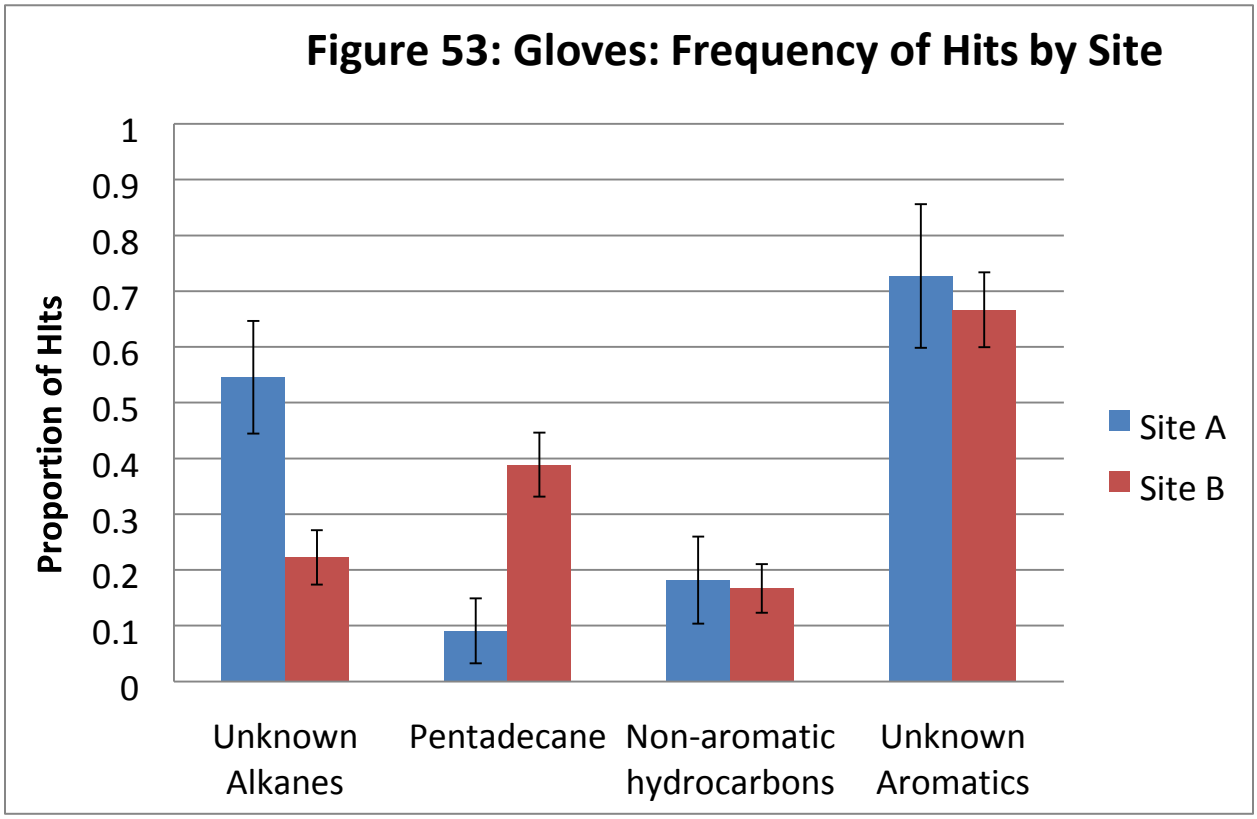


Looking at the respirator frequency of hits by time, (**Figure 52)** we would expect there to be a greater amount of his in the afternoon as compared to the morning, since this would show that there was breakthrough over time. However, this is not what we saw. Generally there was a high frequency of hits, but only in non-aromatic hydrocarbons was there an increase in the frequency of hits in the afternoon.

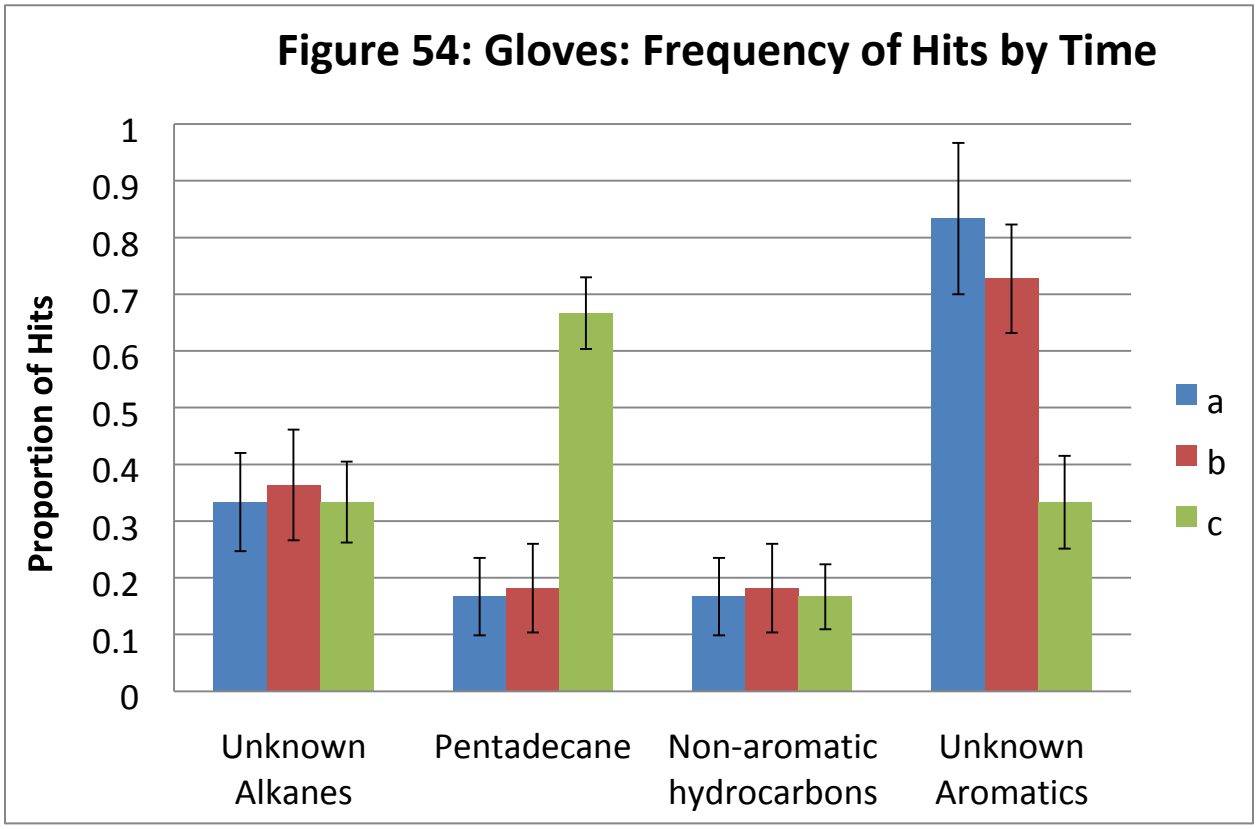
A single tailed p-test was performed, and on all three compounds, on unknown alkanes, non-aromatic hydrocarbons, and unknown aromatics, we reject the null hypothesis, and can state that there is a statistically significant difference between the frequency of hits in the media in the blanks and the frequency of hits in the media.

For the gloves, the frequency of hits by site (**Figure 53)** shows that generally there is a greater frequency of hits in Site A than there is in Site B, except for pentadecane. However, this frequency of hits is smaller than what showed up in the respirator results.

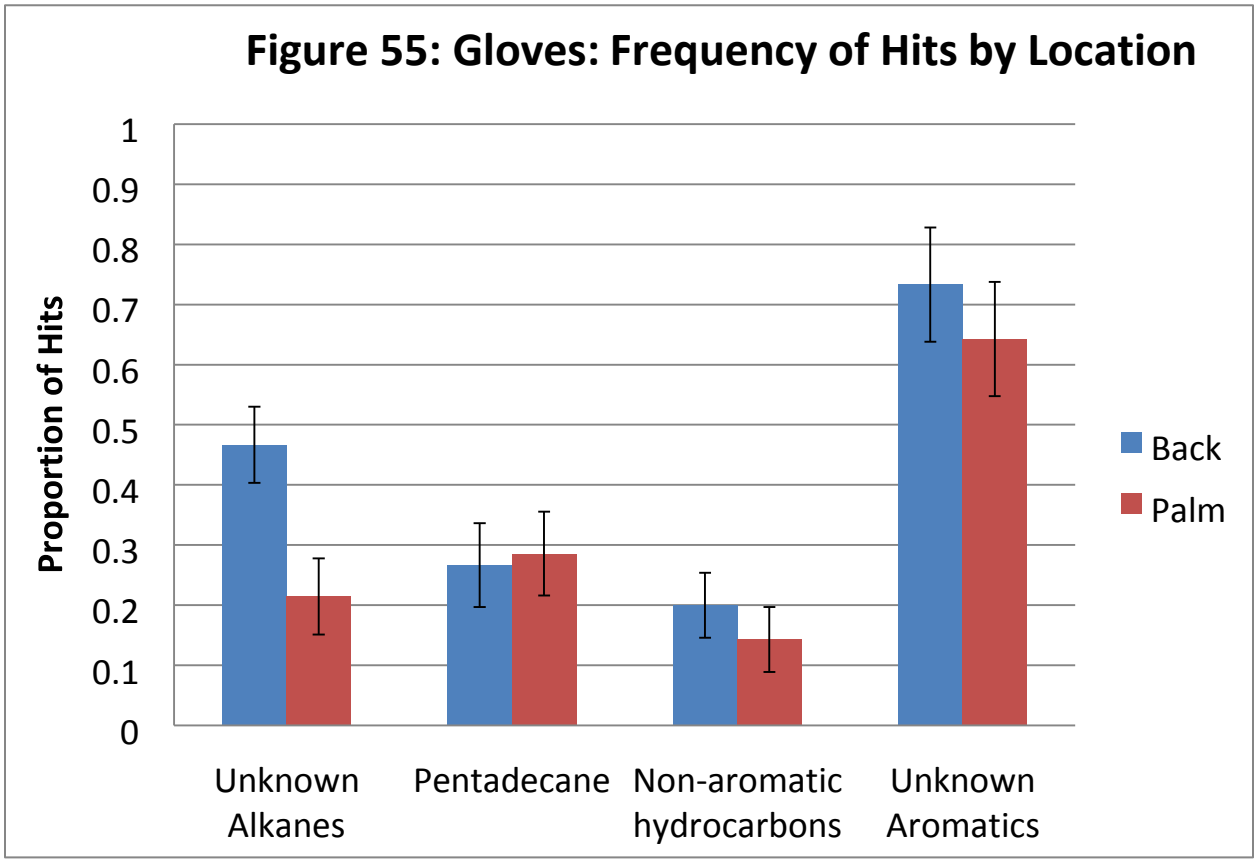




Looking at the frequency of hits by time, (**Figure 54)** we would expect that there would be more dermal exposure the longer the gloves are worn, because there would be a greater amount of breakthrough. However, except for pentadecane, this was not true. The frequency of hits for unknown alkanes and non-aromatic hydrocarbons did not seem to make a difference no matter what the time period was, and the frequency of hits or unknown aromatics actually seemed to decrease the longer the gloves were worn.



In the results that compared the frequency of hits by location (**Figure 55),** generally the back of the hand had a greater frequency of hits than the palm of the hand did. This may have been because the subject's hands were pronated while gripping the steering wheel, and therefore have more exposure on the back of the hand that on the palm of the hand.



A single tailed p test was performed for the gloves as well, and for all four compounds that we looked at regarding the gloves (unknown alkanes, non-aromatic hydrocarbons, unknown aromatics, and pentadecane), we should accept the null hypothesis, or there is not a statistically significant difference between the frequency of hits in the blanks as compared to the frequency of the hits in the media.

8.4.2: Mass to Mass Ratios

Since a standard multiplier was used for the ambient and cartridge samples of the respirator cartridges, a ratio of the standard multipliers was calculated, by dividing 2000 by 330 (cartridge/ambient ratio). This ratio could be used to equate the flow rates, by multiplying the ratio by the adjusted mass for the ambient sample. This enabled the ambient samples to be able

to be compared to the cartridge samples. Then, a mass-to- mass ratio was established by dividing the equated ambient mass by the adjusted cartridge mass. This ratio of expected over observed showed a rough value of what the protection was. If the resulting ratio was equal to 1, then there was no established difference between the mass of alkanes inside and outside of the respirator cartridge, and the cartridge offers no protection. If the mass-to-mass Ratios was 0, then no mass of compounds was found in the ambient samples. I the MTMR was -, then there was no mass of compounds that was found in the cartridge sample, and since nothing can be divided by zero, and a mass-to-mass ratio was unable to be calculated [**Table 39].** (In the table, anything highlighted in yellow is considered a "hit", that was established in section **8.4.1**).

Table 39: Mass to Mass Ratio

								Mass to Mass: Expected/Observed
Set	Set	Type	Time	ID	Combined	Hit	Equating Flow Rates	Estimated Protection Factor
A	11	Ambient	AM	501	410.00	1	2484.848485	3.4416184
		Cartridge	AM	503	722.00	1		
		Ambient	PM	505	1860.00	1	11272.72727	0.605409628
		Cartridge	PM	507	18620.00	1		
	12	Ambient	AM	537	240.00	1	1454.545455	2.760048301
		Cartridge	AM	539	527.00	1		
		Ambient	PM	541	220.00	1	1333.333333	4.004004004
		Cartridge	PM	543	333.00	1		
B	13	Ambient	AM	525	90.00	1	545.4545455	#DIV/0!
		Cartridge	AM	527	0.00	0		
		Ambient	PM	529	50.00	0	303.030303	60.60606061
		Cartridge	PM	531	5.00	0		
	14	Ambient	AM	573	20.00	0	121.2121212	20.2020202
		Cartridge	AM	575	6.00	0		
		Ambient	PM	577	40.00	0	242.4242424	26.93602694
		Cartridge	PM	615	9.00	0		
	15	Ambient	AM	609	20.00	0	121.2121212	1.534330648
		Cartridge	AM	611	79.00	1		
		Ambient	PM	613	0.00	0	0	-
		Cartridge	PM	615	0.00	0		
	16	Ambient	AM	630	200.00	1	1212.121212	71.30124777
		Cartridge	AM	631	17.00	1		
	17	Ambient	AM	632	480.00	1	2909.090909	153.1100478
		Cartridge	AM	633	19.00	1		
	18	Ambient	AM	634	150.00	1	909.0909091	50.50505051
		Cartridge	AM	635	18.00	1		

2000/330: 6.06 = Ratio of Standard Multiplier

Chapter 9: Discussion

9.1: Discussion of Results

Site A had a high frequency of hits for unknown alkanes, non-aromatic hydrocarbons, and unknown aromatics. Site B had a higher frequency of hits for non-aromatic hydrocarbons and unknown aromatics in the afternoon as compared to the morning, which may suggest that there was breakthrough after four hours of use. Generally, most of the frequencies for respirators indicate that there is a high probability of breakthrough occurring through the respirator cartridge. There seems to be a higher frequency of breakthrough at Site A than at Site B, on either day. On Site B, there seems to be a higher frequency of breakthrough in the afternoon, which suggests that the respirator cartridges are not providing protection for as long as they should.

For chlorpyrifos, there was a high frequency of breakthrough of chlorpyrifos and chlorpyrifos oxon even after the morning sample, which suggests that the respirators are not being very protective, and this frequency suggests that it is almost certain that there will be breakthrough. However, there were only three samples, so it is difficult to say for certain.

For the gloves, looking at all of the frequencies of the hits, generally there were greater frequencies of hits in Site A than in Site B, but the frequency of hits did not seem to increase with longer glove use. There seems to be slightly more hits on the back of the hand than on the palm of the hand. Also, there is an assumption of a steady state of permeation. Even some of the applications of the pesticides may have not been continuous, we are still assuming a steady of state of permeation for the glove results.

For the respirators, the results showed that there were some samples that were classified as “hits” in both the ambient and the cartridge matched pair, some that were classified as “hits” with just the ambient sample of the matched pair (which would indicate that the cartridge has a protective effect) and some that were classified as “hits” in just the cartridge set of the matched pair (which would indicate that the cartridge actually has a negative effect of breathing the mass of alkanes in; possibly due to the high concentration of alkanes that would be trapped inside the cartridge and then breathed in). There many reasons that this could happen; the charcoal in the cartridge could be migrating through. Since the retention time is directly related to volatility, the shorter the retention time that the solvents are able to be retained by the charcoal filter, the more volatile the particles that are being breathed in are. However, there is a possibility that this contamination could be minimalized by changing the cartridge out in the afternoon, so that the worker is not breathing in already absorbed and collected solvent particles at a high concentration.

Looking at the respirator results, it is obvious that there are some patterns that are present, but not definite patterns. The estimated protection factor that was calculated for the respirator cartridges generally shows that when both the ambient and cartridge matched sets had breakthrough (particularly in Site A), then the morning samples have a much greater protection rate than the afternoon samples. This is to be expected. However, in Site B, there was less incidences of breakthrough. When neither was contaminated, generally there was a similar estimated protection factor, or sometimes even a greater one in the afternoon. This could be due to some contamination of samples, or other confounding factors.

Although there are certainly some exceptions, overall, most of the samples have a relatively high estimated protective factor, which shows that wearing the cartridge is preferable

to not wearing any cartridge at all. This indicates that although the cartridges are not as ideally protective as they should be, they still are better than no protection whatsoever. One interesting point to note is that on the one matched pair where the cartridge sample was classified as a "hit", which would indicate that a workplace protection would be low, since it seems it was the opposite of protective to be wearing a respirator cartridge, the workplace protection factor was still close to 2. This is not a very high estimated protection factor, but it still indicates that there is some level of protection.

One interesting phenomenon is that several samples were found in which the cartridge samples had a higher amount of breakthrough than the ambient samples did. Human error, either with the field team or the EHS lab might be one possible explanation for this. Another explanation would be that solvents might be migrating through the charcoal cartridge and through the carbon cloth, as well as through the charcoal that is inside the respirator. The particles evaporate in the air, and this could cause this migrating through the pre-filters. With the higher flow rate of the cartridge pump, if these compounds are migrating, there is a chance that a cartridge could appear to be less protective than the ambient sample, however, in actuality, a cartridge would always be more protective, because a person's lungs would always be operating at a high flow rate (around 8 L/min), and so the cartridge would prove to be more protective. It is important to note as well that retention time indirectly corresponds to volatility, which means that the compounds that are being retained the least amount of time are the most volatile. Another explanation of this phenomenon could be the location of the samplers. There is a possibility that, although great care was taken to match the ambient and the cartridge samples as much as possible, that the cartridge samples could have gotten a greater exposure to pesticides due to the location on the tractor for some reason. This could have happened when the tractor turned, possibly brushing a high concentration of pesticides into the cartridge sample, or possibly

have something to do with the location of the nozzle that sprays pesticide on the tank (if it was closer to the cartridge sample this could have affected the results).

Looking at the results, the compounds that were expected to be analyzed in the lab did not show up. The analyzing of the oil sample from Site B showed that there were no aromatics that were found, and yet aromatics still showed up in the analyzing of the samples. This shows either that there was some problem with the lab, some contamination issues (such as residue being stuck inside the tank or the sprayer). There could be other sources for the aromatics that were found in the sampling media. It is possible that the fuel that the tractors use, which would contain benzene, has aromatics in it and is contaminating the sampling media, but this would obviously not show up in the bulk tank sample. It is possible that the sampling media themselves contained aromatics, and therefore those are showing up in the lab. Also, there is a possibility that some contamination in the lab or contamination in bringing the samples back from the field resulted in their containing aromatics.

The two sites that were sampled had very different conditions, and therefore very different results. At Site A, chlorpyrifos and horticultural oil was being sprayed, so both Trimethyl benzene and unknown alkanes were detected. In the second site, only horticultural oil was sprayed, and so only unknown alkanes were detected, and at much smaller quantities.

However, very small amounts of all compounds were found, so more study is needed.

Since for all of the compounds on the respirators the frequency of hits in the blanks was significantly different than the frequency of the hits in the media but for the gloves there was not a statistical difference, this suggests that for some reason either the samples on the gloves got

contaminated more easily or the samples from the respirators had a higher exposure, and therefore a higher frequency of contamination.

9.2: Limitations

Although there are many benefits to this project, there are many limitations as well. This is a pilot study, and therefore had some problems in the field as well as a fairly small sample size. However, sampling in this manner has never been done before, and could provide a solid methodology that could lead to future studies or be used in future studies.

Initially, the proposal of the project was to measure the amount of chlorpyrifos, as well as the amount of solvents and oils, that would break through the PPE that was worn (the respirators and the gloves). However, the spraying of the pesticides is very dependent on the weather. If there is too much rain, if the wind is too strong (causing drift of the pesticides), or if the weather is either too hot or too cold, then chlorpyrifos cannot be sprayed. Also, if the flowers have begun to open, then chlorpyrifos cannot be sprayed. Therefore, sometimes the farmers will end up not spraying any chlorpyrifos at all during a year. This is particularly difficult, since there are only a limited number of farms that it is possible to get contact with and that will allow sampling to take place. Also, many farms have stopped using chlorpyrifos altogether, since there are many hazards that are associated with it and many farms would rather not take the risks. Therefore, the window of opportunity, coupled with the sites that it is possible to sample at, caused the research to not be able to be done of chlorpyrifos this year. At Site A it was possible to sample for chlorpyrifos, but since sampling was not able to be done on Site B or on any other farm, as well ast the fact that the sampling done at Site A had many problems and therefore may not have had

the most accurate results, it was decided that the chlorpyrifos samples would not be the focus of this study.

On Site A, the sampling that was done on 4/2/2013, there were some problems with the method. Because it was the first time out in the field, and there were some major adjustments that needed to be made to the methodology of the field work, some of the sampling did not go as smoothly as the sampling at Site B. There were fewer tractors that were available to be sampled at Site A than at Site B, which could have caused some discrepancies in the samples. Also, the process was not set up as smoothly as it was at Site B (due to the fact that there was time prior to Site B, after seeing what it was like to be in the field, to create an improved field design plan so that things would run smoother). It is possible that there was some contamination in the change out, because there was chlorpyrifos that was being sprayed all around the area where the work station was set up, particularly in the afternoon. Also, on Site A, the preparation and set up was done in an open field, with exposures from all different pesticides and other chemicals around, whereas in Site B the preparation and set up was done in an enclosed space, that could be kept more (theoretically) free of contaminants. Also, because the only media that was being used at Site B was charcoal filters or charcoal tubes, (not PUFs), it was less complicated and therefore subject to fewer errors.

At Site B, (the sampling done on 4/12/2013 and 4/13/2013), the workers did not actually wear the type of cartridges that were used in the sampling. As oil is the only hazardous substance, NIOSH approved N95 dust masks were used as PPE. They did have an adjustable valve, but they were not the same as the OV cartridge with an R-95 pre-filter that was being used for the sampling in the respirator portion of the project.

A problem with the patches on the gloves is that because during the day the hands of the workers get sweaty, the stickiness on the back of the PermaTech charcoal patches tended to come off, and sometimes would get lost completely (as is the case with one sample) or would end up in the fingers of the gloves of the applicators, which is not the location which is supposed to be measured. It may cause some problems in the samples because of any kinks or bends or tears in the PermaTech charcoal patches.

On Site A, two of the samples were lost at the end of the day. One of the SKC personal pumps, Number 23, flow faulted after 286 minutes for unknown reasons. Therefore, the PM sample is subject to question. Also, Leland Legacy pump number 103 was gauged by the metal inside the polycarbonate case during its' run time due to the vibration of the tractor, and has stopped working. Because it stopped working completely, it is impossible to know how long it ran for. Therefore, the sample that was attached to it (which was a PUF filter used to measure chlorpyrifos) is also subject to question and may not be a good sample, and the air concentration of the chlorpyrifos cannot be calculated. In addition, the DryCal Calibrator labeled "Leland Pump" stopped working for unknown reasons on Site B, which caused it to be necessary to use the other Calibrator, which was not a high-flow calibrator, to calibrate the Leland Legacy Pumps.

This could possibly have caused some discrepancy in the calibration.

At Site A, 3/8" tubing was used to connect to the Leland Legacy Pump. This is the tubing that most fit over the pump, but it proved too loose in the field once the pump was subjected to vibrations from the tractor and dirt, grime, oils, solvents and chlorpyrifos, and therefore did not have as tight of a seal as it should have to completely prevent flow leakage. At site B, this was

rectified by using ¼" ID tubing to connect to the Leland Legacy pump, but the tubing could not be connected without the use of isopropyl alcohol and Q-tips. Another problem was that there could have been some leakage from the hose barb in the respirator cartridge to the ½" tubing that was connecting it. This was solved by placing a zip-tie, secured tightly, around the joint, but this was not done on all samples, which could lead to some discrepancy of samples.

When taking off the media for change out or for the end of the day, it is possible that there was some contamination of media that was present. Even though there was a "dirty" box and a "clean" box, occasionally things got mixed up in the frustrations with the lack of time and the contamination of the tractor. This could cause some contamination problems on the samples.

Even though this project can give a rough estimate of how long it takes before there is breakthrough on the both the gloves and the respirator cartridges, it does not give an exact time. As there are only two change outs for both types of PPE, the amount of time it takes to breakthrough cannot be narrowed down to any more than twice a day. Also, even though the goal of this project was to simulate lung use by having a sampling train with a respirator, it is unlikely that it will exactly and simulate it in a parallel manner. There will be some differences between the set up and actual human use of the personal protective equipment. There is also the possibility of bias among the workers because of the fact that they are being sampled, and may have behaved differently than they ordinarily do.

During the analysis for the solvents and oils, all of the unknown peaks are classified as pentadecane, even though it is uncertain if that is in fact what they are. It is possible that these peaks may need to be quantified later as another compound, but for our purposes we classifed all the unknown peaks as pentadecane. This shows that the MSDS sheets were not completely

accurate, as there were still unknown chemicals that were in the oil mix that were not listed on the MSDS sheets. Getting a small sample of all the products used should be done in the future so that this problem can be avoided. Also, aromatics were not distinguished from aliphatics based on retention time, since there was not an aromatic component in the samples. These aromatics, according to the analysis of the horticultural oil at Site B, should not have been present.

Another big limitation is that this project focused more on whether there was contamination at all, or whether the respirator or gloves were effective, as opposed to the actual amounts of the compounds. The sample size was not great enough to perform a solid statistical analysis.

As this project is a pilot study, there are many problems that can be found with it. However, it may give rise to other projects that can be used to test the PPE for difficult occupations, and it provides a clear methodology of a development of how this may be done, not just in agricultural settings, but in other occupations as well that use various types of PPE as well.

9.3: Recommendations

If a study like this were to be done in the future, there are a few items that should be changed. First of all, there was a great disconnection from the transition of lab preparatory work to actual work out in the field. It would have been helpful to have a time to go out in the field, possibly a month before the project was to take place, evaluate what was needed, and then still have time to create a suitable set up, while having a better understanding of how it was going to work in the field. Having no idea what going out into the field was going to be like ended up

hampering the effectiveness of the design of the project.It would be more useful if everyone was trained in every job that he or she was going to perform. There were some people who know what they were doing with regard to certain jobs more than others, and when the lesser informed people tried to be of assistance, they ended up just slowing everyone down or being in the way. Universal training would be useful. Also, it would be more helpful if there could be more continuity in the organizing of going out into the field. It can be difficult to plan when often what sampling that was supposed to happen could change at the last minute and be completely out of the researcher's control.

We only used two field blanks per day, or a total of six field blanks for each kind of media. As there was a great reliance on the average mass of the field blanks to determine contamination of the media, a larger sample size of field blanks would be useful, and would give us more confidence in establishing the mean mass of compounds that were collected on the field blanks. In future studies, around 10 field blanks per day would be helpful.

There are several additional studies that could be done to continue in the vein of the work of this study. More sampling should be done on chlorpyrifos, since the limited samples that we have show that the respirator cartridges are not as protective as they should be. More studies should be done to back this assumption up. Even though this project initially was to evaluate the effects of chlorpyrifos, not very many chlorpyrifos samples were collected. More data should be done on chlorpyrifos to see if the results that we gathered are consistent with other samples.

Also, since the sampling size was small for the horticultural oil as well, there could be should be more studies on the effects of the horticultural oil and more sampling should be done on the breakthrough of that.

There seems to be many confounding factors concerning why there is occasionally a greater amount of breakthrough in the cartridge samples than in the ambient samples. This should be analyzed more to find out the exact reasons for this breakthrough, and measures should be taken to prevent these confounding factors from interfering with the sampling, or just accounting for them in the analysis of the results.

Also, since the bulk sample collected from the tank was different than what was analyzed in the lab, more study should be done to find out the reason for this.

However, the set-up of the sampling train was a unique idea, and the creation of using a respirator cartridge to measure the amount of breakthrough is something that has not really been done before and could be translated to many other uses and studies. The sampling train could be used to test the respirator effectiveness for many jobs; not exclusively agricultural. This kind of set-up for both inhalation exposure and dermal exposure could be useful for sampling in many industries.

Chapter 10: Conclusions

This study paved the way for testing respirators in a unique way, and showed some data about testing gloves as well. However, all of the masses that were collected from the sampling media were very small. This study demonstrated that although wearing a cartridge is more protective than not wearing one, there is still amounts of solvents and particles that are getting through the respirator cartridge, into the workers breathing zone. This is particularly prevalent for the afternoon samples. Therefore, it is possible that the respirator cartridges are generally not being changed out enough to be completely protective for the duration of their use. For Site A, the cartridges did not seem to be as protective as they did at Site B. However, the sample size was very small and there may have been some contamination issues. More study and analysis is needed to continue to understand this data and its' implications. Although further study is needed, it is evident that the respirators that are currently being worn are not very protective. The workers should evaluate the types of respirators that they are wearing, and change to something more protective or provide a respirator cartridge change out more often. It does not appear that the longer that the gloves are worn, they will cause more breakthrough, although there is some breakthrough. Though wearing respirators and gloves is generally more protective than not wearing any at all, they are not fully protecting the worker from the hazards of pesticides.

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Chapter 13: Appendix

Appendix A: Comprehensive list of Materials

Respirator Cartridge Effectiveness Study

- **Materials for Media Preparation ○ Cutting charcoal tubes**

    - 1800/200 Charcoal Tubes (SKC product number 266-16-02)
    - Red Caps for Charcoal Tubes or Parafilm
    - Dish soap
    - Glass cutter
    - Safety Glasses
    - Glass resistant gloves
    - Glass receptacle
    - Paper towels

    - **Preparation of Charcoal Circles**

        - Charcoal cloth with no backing (Zorflex 100% activated woven carbon cloth)
        - 1.5" diameter Di-cut
        - Nitrile gloves (VWR 82026)
        - 37 mm cassettes (2) (SKC product # 225-36050LF)
        - Scissors
        - Acetone
        - Small crochet hook (.75 mm)
        - Ziploc bags
        - 4 mL vials (National Scientific- Waters Clear product # C4015-1)
        - Caps for 4 mL vials (National Scientific- Waters Clear product # B7815-13)
        - Small forceps (#08900- Fisher Brand; Medium Pointed, 4 ½ straight)
        - Thermolyne oven (EH lab; HSB)

    - **Preparation of Polycarbonate Case**

        - Polycarbonate Cases of various sizes (Storables and Fred Myer)
        - Drill
        - Safety Glasses
        - Rubber Gaskets

    - **Cutting of Charcoal Tube casing**

        Safety Glasses
        Hacksaw
        Tape Measure
        SKC 1800/200 mg Charcoal Tube (product number 266-16-02)
        ½" ID Rigid PVC Pipe (Home Depot model # 1120) Sharpie

- **Materials for DryCal Calibration in Lab**

    - DryCal Defender Calibrator (Model # 510-H) ○ 1,000 mL burette
    - Leland Legacy air sampler pump (SKC cat. Number 100-3002)
    - SKC sampler (Model 224-PCXR8) ○ Glass petri dish (wider than 1,000 mL burette) ○ Bubble solution (same as what is used for children's bubbles)
    - ¼" latex Rubber tubing
    - ¼" ID Tygon Tubing (Cole Parmer product # 63010-064) ○ 3/8" ID Tygon tubing (USP product # 054005) ○ ¼" to 3/8" reducing connector (Cole Parmer YO 30622-39) ○ Stopwatch
    - DryCal calibration data sheet
    - Lab stand ○ Glassware clamp ○ Pen

- **Materials for SKC Pump Calibration**

    - SKC personal pump (Model 224-PCR8) ○ DryCal Defender Calibrator (Model 510-H) ○ Flat head screwdriver, 5/62" ○ SKC 1800/200 mg Charcoal Tube (product number 266-16-02) ○ ¼" ID Tygon Tubing (Cole Parmer product # 63010-064) ○ 3/8" ID Tygon Tubing (USP product # 054005) ○ ¼" to 3/8" reducing connector (Cole Parmer YO 30622-39) ○ Data Sheet for Calibration
    - Lab tape
    - Sharpie

- **Materials for calibration of Leland Legacy Pumps**

    - **Calibration of Cartridge samples with cassettes**

        - Leland Legacy Air Sample personal pump (SKC cat. Number 100-3002)
        - DryCal Defender Calibrator labeled "Leland" (Model 510-H)
        - Leland Legacy Quick Guide laminated sheet
        - North Organic Vapor Respirator Cartridge (product # N 7500-1)
        - North R95 pre-tube with cap (product # 7506R95)
        - ¾" to ½" Hose barb (USP product # 1URN5)
        - 37 mm cassettes (SKC product # 225-3050LF)
        - 1.5" diameter charcoal cloth circles
          Porous Plastic Support pads (SKC product # PFSP37) White Urea
          Lure adapters (SKC product # 225-13-2)
          ¼" ID Tygon Tubing (Cole Parmer product # 63010-064)
          ½" ID Tygon Tubing (USP product # 057246)
          ¼" to 3/8" Reducing connector (Cole Parmer product # YO 30622-39)
          ¼" to ½" Reducing connector (Cole Parmer product # EW 30703-56)
        - Grey Case for Respirator Cartridge Calibration
        - Teflon tape
        - Data Sheet for calibration

- **Quality Control Materials**

    - Cut charcoal tubes that are capped ○ Red caps for charcoal tubes

- Prepared charcoal cloth circles in 4 mL vials (See **SOP 1.4**) ○ Nitrile gloves ○ Cooler ○ Ice ○ Labels ○ Tape ○ Aluminum Foil ○ Lab diaper ○ Small forceps ○ Safety Glasses
- Spiking solution (taken care of in the EHS lab)

- **Materials for Set-up of Sampling Trains**

  - **Ambient Sample with Charcoal Tube**

    - SKC 1800/200 mg Charcoal Tube (product number 266-16-02) ▪ SKC personal pump (Model 224-PCXR8)
    - ¼" ID Tygon Tubing (Cole Parmer product # 63010-064)
    - 3/8" Inner Diameter Tygon Tubing (USP product # 054005)
    - ½" ID cut PVC Pipe (Home Depot model # 1120)
    - Reducing connector ¼" to 3/8" (Cole Parmer)
    - Electrical Tape
    - Data Sheets

  - **Cartridge Sample with Cassettes**

    - North Organic Vapor Respirator Cartridge (product # N 7500-1)
    - North R95 pre-tube with cap (product # 7506R95)
    - ¾" to ½" Hose barb (USP product # 1URN5)
    - ½" ID Tygon Tubing (USP product # 057246)
    - ¼" Inner Diameter Tygon Tubing (Cole Parmer product # 63010-064)
    - 3/8" ID Tygon tubing (USP product # 054005)
      ¼" to 3/8" reducing connector (Cole Parmer YO 30622-39)
      ¼" to ½" Reducing connector (Cole Parmer product # EW 30703-56)
      37 mm cassettes (SKC product # 225-3050LF)
      2" Inner Diameter PVC Pipe (Home Depot)
      1.5" diameter charcoal cloth circles- pre-prepared in the lab Porous Plastic Support pads (SKC product # PFSP37)
    - White Urea Lure adapters (SKC product # 225-13-2)
    - Leland Legacy Air Sample personal pump (SKC cat. Number 100-3002)
    - Teflon Tape
    - Small forceps
    - Data Sheet for Calibrations

- **Set-Up in Polycarbonate Boxes**

  - Industrial Strength Velcro ○ Polycarbonate Case of various sizes ○ Both sampling trains

- **Materials for Field Work**

  - Ambient Air sampling train with 1800/200 mg charcoal tube (see **SOP 5.3.2**) ○ Respirator Cartridge sampling train with cassettes (see **SOP 5.3.4**) ○ Charging Station for Leland Legacy Pumps (Li-Ion 5) ○ Charging Station for SKC Pumps (Model 223-1000) ○ SKC

1800/200 mg Charcoal Tube (product number 266-16-02) ○ ½" ID PVC Pipe for charcoal tube casings ○ Flat head screwdriver- very small (5/62") ○ Phillips head screwdriver
  - Data sheets ○ Aluminum Foil ○ Zip ties
  - Polycarbonate plastic case ○ Masking Tape ○ Tin poles (4) ○ Alligator clamps ○ Duct Tape ○ Clock/Stopwatch
  - Acetone for rinsing PUF tube holders ○ Nitrile Gloves (VWR 82026)
  - 4 mL vials (National Scientific- Waters Clear product # C4015-1) and caps for 4 mL vials (National Scientific- Waters Clear product # B7815-13)with charcoal cloth circles (see **SOP 1.4)**
  - Small forceps

- **Materials for Storage and Transfer**

  - Cooler ○ Blue Ice ○ Dry Ice
  - Thermometer for cooler

Complete List of Materials for the Glove Project

- Glove Thickness
  - 0.050" Mitutoyo Dial Thickness Gage No. 7326S MIT-7326 range 0.050inch. Victor Machinery Exchange, Inc. Brooklyn, NY (http://www.victornet.com/tools/Thickness-Gages/222.html) ○ 15mil Best Nitri-Solve® Unsupported Nitrile Gloves Ref: 727. Showa Best Glove, Menlo, GA
  - 5mil nitrile gloves (size to fit tester)
  - Lab diaper

- Permeation ○ Permea-Tec™ Sensor Solvent, Part No 3050. CLI Laboratories, Inc. Des Plaines, IL ○ 15mil Best Nitri-Solve® Unsupported Nitrile Gloves Ref: 727. Showa Best Glove, Menlo, GA ○ 2" wide aluminum tape ○ General® 1" arch punch ○ Storage
  - Box to transport patches
  - Clear screw top vial 12x32 2mL with large opening, Supelco P/N 27265 ○ Solid cap, black polypropylene F217/PTFE lines 10-425 thread, Supelco P/N 28659-U ○ Frozen blue ice (5) ○ Cooler (1): to transport acetone ○ Dry ice
  - Styrofoam cooler (3): to transport QC samples, field samples, and dry ice
- Miscellaneous ○ Acetone ○ forceps
  - Tape
  - Chemical resistant marking pens ○ Sharpie pens
  - Paper
  - Ziploc bags (different sizes)
  - Scissors ○ Razor blades ○ Packing tape ○ Timer ○ Parafilm ○ Ruler ○ Tape measure ○ Pre made labels
  - Acetone squirt bottles ○ Kimwipes
  - 0.050" Mitutoyo Dial Thickness Gage No. 7326S MIT-7326 range 0.050inch. Victor Machinery Exchange, Inc. Brooklyn, NY (http://www.victornet.com/tools/Thickness-Gages/222.html)
  - ○ Beakers ○ Trash

bags ○ Blue lab
diapers

- Vial rack for 2 mL vials (3 to 4)
- Hair dryer
- Foil

Appendix B: Methods for PUF tubes and Chlorpyrifos

Even though the nature of the project resulted in not sampling with PUF tubes or for chlorpyrifos, standard operating procedures were made outlining the way that sampling would have taken place (and did take place at Site A). These SOPs were turned into methods and put in this appendix so that in any future studies, particularly ones involving sampling trains and PUF tubes, these Methods can be used.

Set-up of Sampling Train for Calibration with PUF Tube

The calibration of both kinds of pumps was different with the PUF tubes instead of the charcoal cloth circles and the charcoal tubes. For calibration of the ambient sample, the calibration jar was used, with a PUF that was labeled as "Calibration only" (**Figure 2).** This tube was attached to the black tubing on the inside of the lid, and then the lid to the calibration jar was replaced and screwed on tightly. The ¼" ID Tygon tubing that is attached to the center of the calibration jar lid (which should be connected to the PUF tube on the inside of the lid) was connected to the SKC personal pump, and the ¼" ID Tygon tubing attached to the L-shaped connecter on the calibration jar to the top inlet of the DryCal Defender. Then, the pump was turned on and allowed to run for one minute. A 5/62" screwdriver was used to adjust the pump to as close as 4.624 L/min as possible. The Defender DryCal was turned on, and "Enter" was clicked in order to select the "Measure" icon. The Defender was set to take single measurements by clicking the left arrow to select "Single". Three single flow rates were taken, until the average of the flow rates was in the 4.624 L/min range. In order to adjust the flow rate, the 5/62" screwdriver was turned clockwise to increase the flow rate or counterclockwise to decrease the flow rate until the flow rate was at the desired amount. Afterwards, the Defender DryCal was reset when the flow rate was in the desired range (which was 4.624 L/min) (**Figure 2).**

For the calibration of the PUF tube for the respirator cartridge sampling train, the R-95 prefilter and cap was detached from the plastic backing and attached securely to the North OV cartridge. Teflon Tape was wrapped around the threaded side of the hose barb. The hose barb was screwed into the opening of the cartridge, and an extension of ½" ID Tygon Tubing was attached to the extended end of the hose barb. Then, a ½" to ¾" reducing connector was attached to the Tygon Tubing. The ¾" ID Tygon Tubing was attached to the outside of the wide end of the PUF tube. A short amount of tubing was used so that the cartridge was as close to the PUF tube as possible. The other end of the PUF tube was connected to ¼" ID Tygon tubing, and then the ¼" Tygon tubing was connected to the inlet on the inside of the grey calibration case labeled "to media". Another extension of ¼" ID Tygon Tubing was attached to the outlet on the outside of the grey calibration case labeled "to pump". Then, this tubing was attached to a Leland Legacy Pump using isopropyl alcohol and a Q-tip on the inside of the tubing. Another extension of ¼" ID Tygon Tubing was attached to the outlet on the outside of the grey calibration case labeled "To DryCal". The DryCal labeled "Leland" was attached to the end of the ¼" Tubing. The calibration took place much in the same way as it did for the charcoal cloth circles in the cassettes. The pump was calibrated to 8 L/min. (**Figure 3)**

Figure 2: Calibration of PUF tube for Ambient Sampling Train

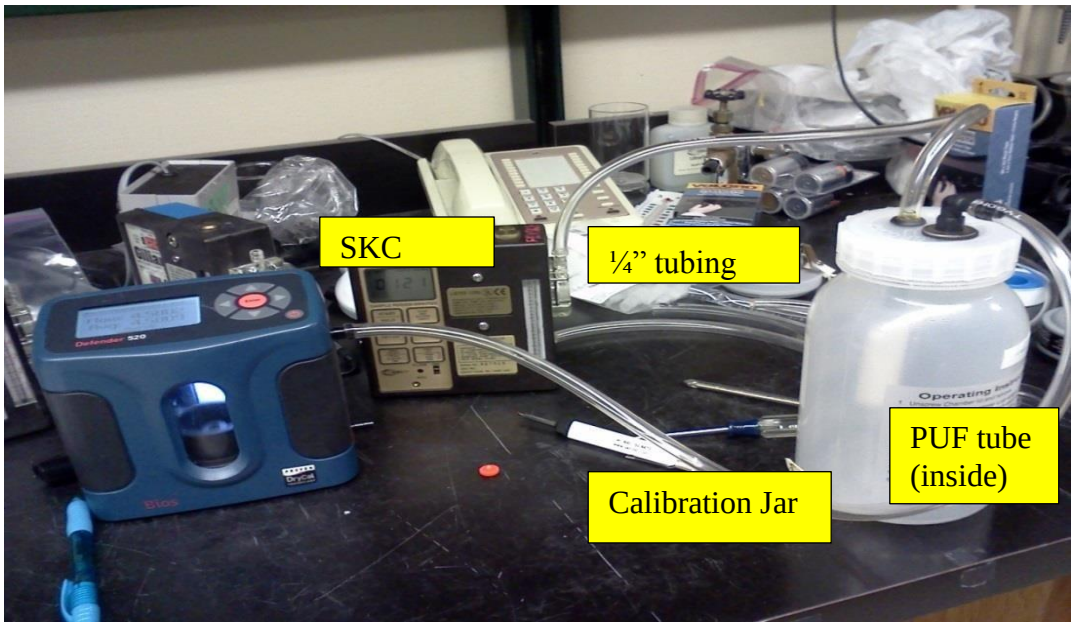
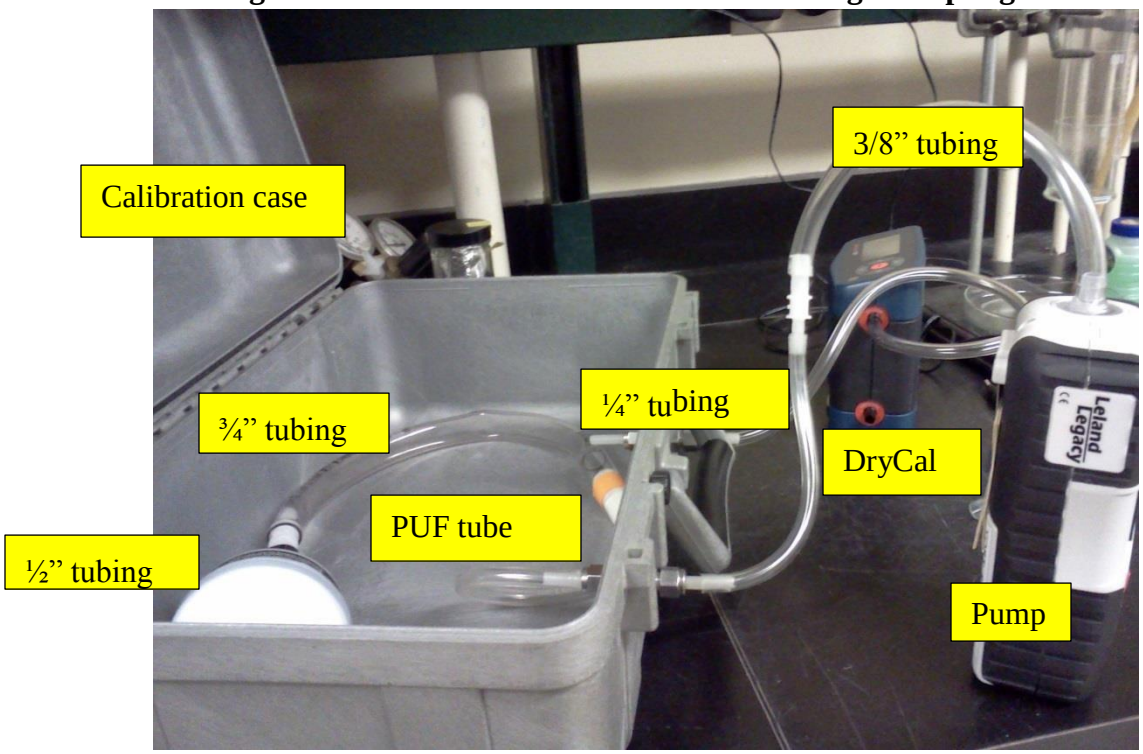


Figure 3: Calibration of PUF tube for Cartridge Sampling



In order to set up the sampling train in the field, there would have been four pumps in the polycarbonate box on the back of the tractor instead of just two (Two SKC pumps and two Leland Legacy pumps). The PUFs were set up to the pumps in a similar manner to how they were calibrated and how the charcoal samples were set up. For the cartridge sample (**Figure 4)**, the respirator cartridge was attached to a hose barb which was attached to an extension of ½" Tygon Tubing, which was then attached to a connector and connected to ¾" Tygon Tubing, which went around the outside of the large end of the PUF tube. On the other side of the PUF tube was ¼" Tygon Tubing which was connected to the Leland Legacy pump. This pump was set to run at 8 L/min, as the charcoal sample was. For the ambient sample (**Figure 5)**, a PUF was put in a PUF casing and connected with ¼" Tygon Tubing to an SKC pump, which was set to run at about 4.6 L/min, as that is the calculated flow rate to match the face velocity based on the

Figure 5: Sampling Train Set-Up for Ambient Sampling Train

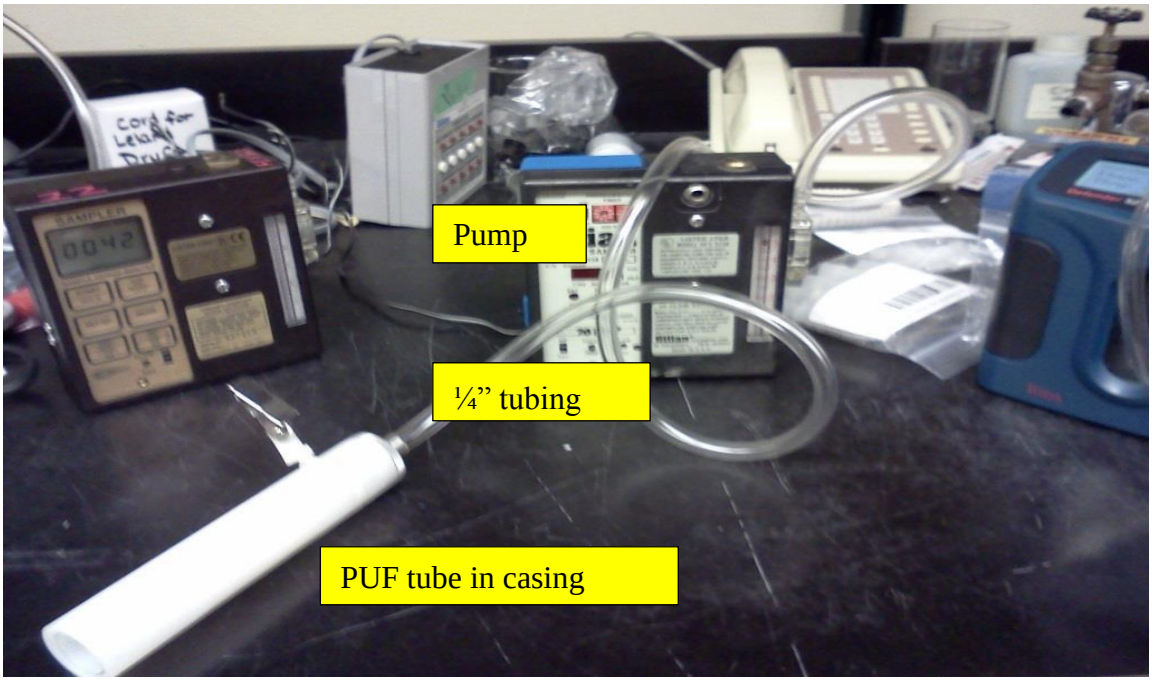
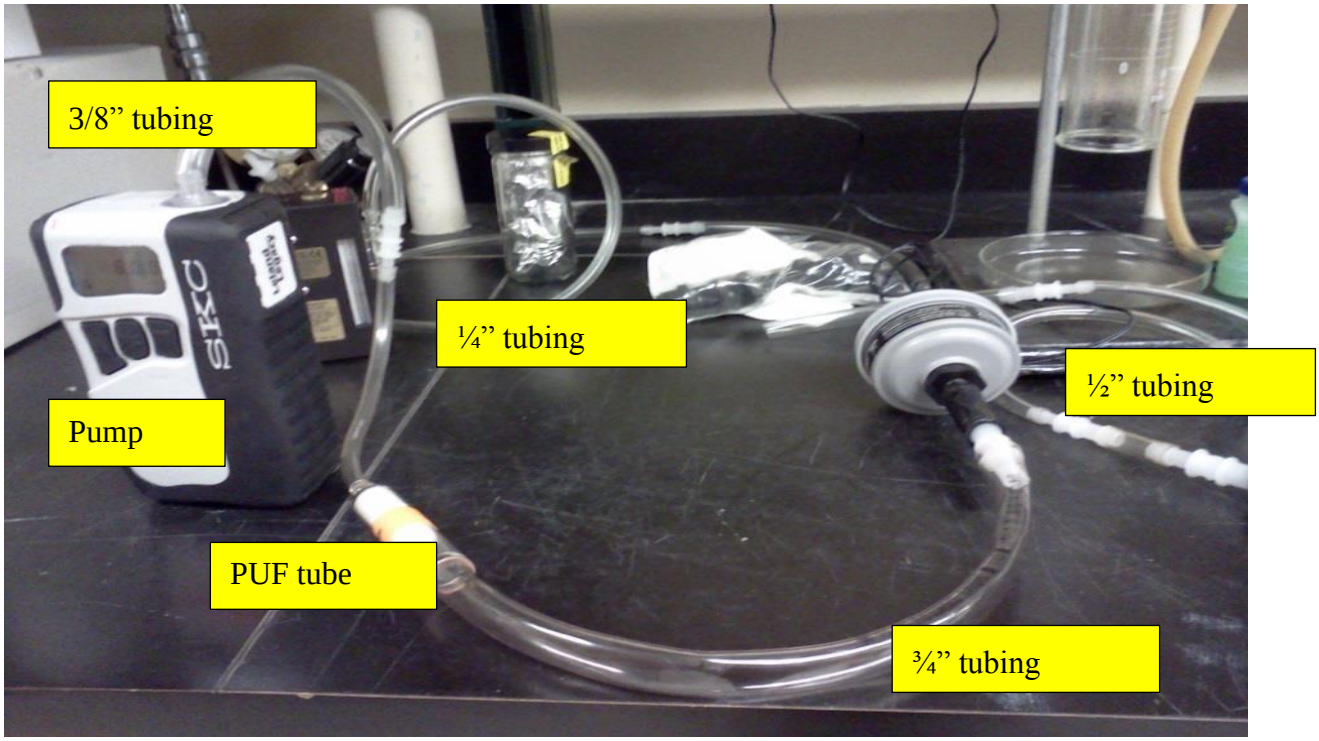


Figure 4: Sampling Train Set-Up for Cartridge Sampling Train



diameter of the PUF tube opening. These samples were set to run attached to the tractor, and were changed out in a similar manner to how the charcoal samples were changed out. One taken of the tractor, the PUF tubes were labeled, wrapped in aluminum foil, but back in their glass jars and in their cardboard boxes, and then put in the dry ice to take back to the lab. In the lab, Chloryrifos and chlorpyrifos oxon was analyzed for.

Appendix C: Calculations for Flow Rate and Face Velocity

Face Velocity= Flow rate (Q)/ Area (A) diameter
(d) = radius(r) /2
Area (A) = πr^2
1 L = 1000 cm^3
Flow Rate for Sedentary Tractor Driver= 8 L/min

Table 3: Measurements of Media

	Respirator cartridge (cm)	Charcoal Tubes
radius (cm)	1.25	0.45
diameter (cm)	2.5	0.9
area (cm^2)	4.9	0.64

Table 4: Calculations of Flow Rates for Ambient Sample with Charcoal Tube

Face velocity of cartridge	face velocity = Q/A 8 L/min/ 4.9 cm^2 8 L/min = 8000 cm^3/min 8000 cm^3/min/ 4.9 cm^2 1632.65
	1632.65 cm/min
Face velocity of cartridge = Face velocity of charcoal tube	
Face velocity of Charcoal tube	1632.65 cm/min
Flow Rate of Charcoal Tube	face velocity = Q/A 1632.65 cm/min = Q / 0.636 cm^2 Q= 1632.65 cm/min*0.636 cm^2 1038.367347 1038.38 cm^3/min 1038.38 cm^3/min * 1 L/1000 cm^3
	1.038 L/min

Table 5: Summary of Flow Rates of Ambient Air Samples with Charcoal Tubes

	Charcoal Tubes	Respirator cartridge (cm)	
radius (cm)	0.45	1.25	
diameter (cm)	0.90	2.5	
area (cm^2)	0.636	4.9	
Face Velocity (cm/min)	1632.65	1632.65	
Flow Rate (L/min) for Ambient			**1.038**

Table 6: Summary of Flow Rates of Cartridge Samples with Cassettes

	Charcoal Cloth	Respirator cartridge (cm)	
radius (cm)	0.45	1.25	
diameter (cm)	0.90	2.5	
Face Velocity (cm/min)	1632.65	1632.65	
Flow Rate from inhalation rate of tractor drivers (L/min)			**8.00**

Table 7: Summary of Flow Rates of Cartridge Samples with PUF Tubes

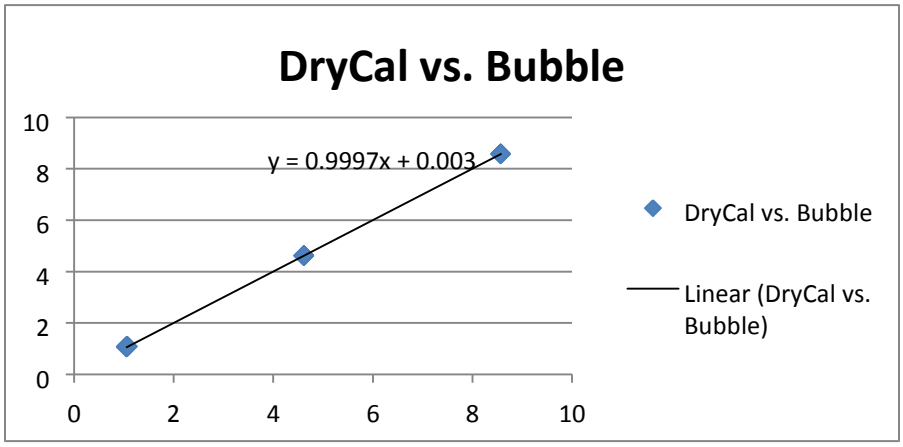
	PUFs	Respirator cartridge (cm)
radius (cm)	0.950	1.25
diameter (cm)	1.90	2.50
area (cm^2)	2.83	4.90
Face Velocity (cm/min)	1630	1630
Flow Rate (L/min)	4.62	8.00

Appendix D: Calibration of the Defender DryCal

Table 8: DryCal Flow Rate and Bubble Burette Flow Rate

Pump Number	Pump Speed	Time	DryCal flowrate	Avg flowrate	Bubble flowrate	Average bubble flowrate
129609	1.0561	0.933333	1.0714	1.058866667	1.071428571	1.065162907
	1.0561	0.95	1.0526		1.052631579	
	1.0561	0.933333	1.0526		1.071428571	
	4.61	0.216667	4.6147	4.6147	4.615384615	4.615384615
	4.61	0.216667	4.6147		4.615384615	
	4.61	0.216667	4.6147		4.615384615	
	8.04	0.116667	8.57	8.57	8.571428571	8.571428571
	8.04	0.116667	8.57		8.571428571	
	8.04	0.116667	8.57		8.571428571	
113833	1.06	0.933333	1.0714	1.0714	1.071428571	1.071428571
	1.06	0.933333	1.0714		1.071428571	
	1.06	0.933333	1.0714		1.071428571	
	4.61	0.216667	4.6147	1.538233333	4.615384615	4.615384615
	4.61	0.216667	4.6147		4.615384615	
	4.61	0.216667	4.6147		4.615384615	

Figure 7:Graph of DryCal verses Bubble Burette



The line of best fit is
y= .9997x +.0003
The r^2 value is 1

Appendix E: Number of Samples Used

Table 9: Amount of Each Kind of Media Used for Respirators

	Field Samples			Quality Control			Total Per Day
	# of Sets	Change outs	**Field samples per day**	Level of Spike		**Total QC**	11
Day 1	3	2	6	High Spike	1	5	
				High Spike	1		
				Low Spike	1		
				Blank 1	1		
				Blank 2	1		
Day 2	3	2	6	Blank 1	1	2	8
				Blank 2	1		
Day 3	3	2	6	High Spike	1	5	11
				High Spike	1		
				Low Spike	1		
				Blank 1	1		
				Blank 2	1		
Totals			18			12	30
Blanks for lab							6
Blanks for Calibration Extras							1
							13
Grand Total							**50**

Table 10: Total Number of Samples for Gloves

	Field Samples				Quality Control			Total Per Day
	Subjects	Patches Per Subject	Change outs	**Total per day**	Level of Spike		**Total QC**	
Day 1	3	2	2	12	High Spike	1	5	11
					High Spike	1		
					Low Spike	1		
					Blank 1	1		
					Blank 2	1		
Day 2	3	2	2	12	Blank 1	1	2	8
					Blank 2	1		
Day 3	3	2	2	12	High Spike	1	5	11
					High Spike	1		
					Low Spike	1		
					Blank 1	1		
					Blank 2	1		
Totals				36			12	48
Blanks for lab								6
Extras								16
Grand Total								**70**

Appendix F: Glove Measurements

Table 11: Glove Thickness

Subject ID	Glove Size	Domniant Hand	Glove Thickness					
			Palm			Back		
			#1	#2	#3	#1	#2	#3
1	9	Right	0.0173	0.0167	0.0166	0.0165	0.0172	0.0171
2	9	Right	0.0169	0.0161	0.0166	0.0172	0.0175	0.0172
3	9	Right	0.0170	0.0173	0.0171	0.0179	0.0178	0.0171
4	10	Right	0.0161	0.0159	0.0154	0.0167	0.0164	0.0168
5	10	Right	0.0163	0.0156	0.0162	0.0159	0.0162	0.0164
6	10	Right	0.0160	0.0169	0.0167	0.0163	0.0166	0.0157

Appendix G: Calibration Data

Table 12: Calibration Data from Ambient Sample with SKC Personal Pump

Date	Time	Pump Number	Pump Type	Target Flowrate	Average Flowrate	Media	Pre/Post
4/1/2013	20:52	33	SKC	1.0 L/min	1.0566 L/min	charcoal tube	pre
4/1/2013	20:59	21	SKC	1.0 L/min	1.0537 L/min	charcoal tube	pre
4/2/2013	17:00	33	SKC	1.0 L/min	1.02 L/min	charcoal tube	post
4/2/2013	17:13	21	SKC	1.0 L/min	1.04 L/min	charcoal tube	post
4/11/2013	20:12	33	SKC	1.037 L/min	1.036 L/min	charcoal tube	pre
4/11/2013	20:42	22	SKC	1.037 L/min	1.03424 L/min	charcoal tube	pre
4/11/2013	20:42	23	SKC	1.037 L/min	1.0548 L/min	charcoal tube	pre
4/11/2013	20:45	32	SKC	1.037 L/min	1.013 L/min	charcoal tube	pre
4/12/2013	16:49	33	SKC	1.037 L/min	1.02 L/min	charcoal tube	post
4/12/2013	16:47	23	SKC	1.037 L/min	1.04 L/min	charcoal tube	post
4/12/2013	16:48	32	SKC	1.037 L/min	1.02 L/min	charcoal tube	post
4/12/2013	19:02	32	SKC	1.037 L/min	1.05 L/min	charcoal tube	pre
4/12/2013	19:03	22	SKC	1.037 L/min	1.028 L/min	charcoal tube	pre
4/12/2013	19:04	23	SKC	1.037 L/min	1.043 L/min	charcoal tube	pre
4/12/2013	19:05	33	SKC	1.037 L/min	1.008 L/min	charcoal tube	pre
4/13/2013	12:25	32	SKC	1.037 L/min	1.0249 L/min	charcoal tube	post
4/13/2013	12:23	23	SKC	1.037 L/min	1.028 L/min	charcoal tube	post
4/13/2013	12:27	33	SKC	1.037 L/min	1.024 L/min	charcoal tube	post

Table 13: Calibration Data from Cartridge Sample with Leland Legacy Pump

Date	Time	Pump Number	Pump Type	Target Flowrate	Average Flowrate	Media	Pre/Post
4/1/2013	19:52	104	Leland	6 L/min	6.02 L/min	Cassette	Pre
4/1/2013	19:59	102	Leland	6 L/min	6.05 L/min	Cassette	Pre
4/1/2013	20:05	105	Leland	6 L/min	6.00 L/min	Cassette	Pre
4/2/2013	16:50	104	Leland	6 L/min	5.7 L/min	Cassette	Post
4/2/2013	17:04	102	Leland	6 L/min	5.75 L/min	Cassette	Post
4/11/2013	20:30	104	Leland	8 L/min	8.0115 L/min	Cassette	Pre
4/11/2013	20:38	101	Leland	8 L/min	8.1719 L/min	Cassette	Pre
4/11/2013	20:42	102	Leland	8 L/min	7.9871 L/min	Cassette	Pre
4/12/2013	16:51	104	Leland	8 L/min	7.8 L/min	Cassette	Post
4/12/2013	16:52	101	Leland	8 L/min	7.89 L/min	Cassette	Post
4/12/2013	16:50	102	Leland	8 L/min	7.64 L/min	Cassette	Post
4/12/2013	18:32	104	Leland	8 L/min	7.98 L/min	Cassette	Pre
4/12/2013	18:54	102	Leland	8 L/min	8.04 L/min	Cassette	Pre
4/12/2013	18:56	101	Leland	8 L/min	8.04 L/min	Cassette	Pre
4/12/2013	18:57	105	Leland	8 L/min	7.92 L/min	Cassette	Pre
4/13/2013	12:14	104	Leland	8 L/min	7.88 L/min	Cassette	Post
4/13/2013	12:18	102	Leland	8 L/min	7.79 L/min	Cassette	Post
4/13/2013	12:21	101	Leland	8 L/min	7.87 L/min	Cassette	Post

Appendix H: Table of Contents from Field Manuals

1. Researchers' Names and Contact Information
2. Timeline and Daily Checklist
3. Objective and Purpose of Study
4. Instrument Manuals
    a. Defender DryCal
    b. SKC personal pump
    c. Leland Legacy Pump
5. Checklists
    a. List of Materials
    b. Packing List
6. In lab preparation
    a. SOP 1
7. Calibration
    a. Calibration for Calibrator
        i. SOP 2
        ii. Data Sheets
    b. Calibration for pumps
        i. SKC Pump
            1. SOP 3 ii. Leland Legacy pumps
                1. SOP 4
            iii. Data Sheets
8. Set-Up of Sampling Trains
    a. SOP 5
9. Field Sampling
    a. SOP 6
    b. Data Sheets
10. Gloves
    a. Glove Description
    b. Permeatic Solvents
11. Quality Control Blanks/Spikes
    a. SOP 7
    b. Table for Spiking amounts
12. Storage and Transport
    a. SOP 8
13. Labeling
    a. Labeling Instructions
    b. Labels
14. Chemical Information
    a. Lorsban
        i. MSDS Sheet for Lorsban 4-E
        ii. Specimen Label for Lorsban 4-E
    b. Supreme Oil
        i. MSDS Sheet for Supreme Oil
        ii. Specimen Label for Supreme Oil
    c. Acetone
        i. MSDS Sheet for Acetone

15. General Health and Safety
    a. Personal Safety and Welfare
    b. PPE and Safety Supplies
    c. UW policy for Workplace Violence
    d. UW vehicles

Appendix I: Data Sheets

Staff Initials:_____ Site _____ Tractor _____ Date _____ Temperature _____ Barometric Pressure_____ Page ___/____

Respirator Cartridge Effectiveness Study-Personal Air Sampling Data Sheet

Sample_ID	Pump #	Chk_flow	Chk_flw time	Media on trctr time	Media off trctr time	Chk_flw or Cal_flw	Chk_flw time or stop_flw time	Run time	Comments

Filled out by:
Date Site ID Day# SubjectID Glove #

PS PUF (Solvents) Change Out (Gloves)

Charcoal Patches			Notes
Rep #	On time	Off time	

Terms:

CHR Rep#: The first set of Permeatec sensors is 1. The second set is 2, and so on.

CHR On/Off Time: Time Permeatec Rep was placed onto and removed from the subject. Glove G#: This corresponds to the Glove Number on glove.

Appendix J: Supplies

Table 14: Respirator Supplies

	Sampling Train Supplies	General	Attachment/Removal to/from Tractor	Miscellaneous
Ambient	SKC Pump ¼” Tubing ¼” to 3/8” Reducing Connector 3/8” Tubing Charcoal Tube PVC Pipe Casing	Red Caps/Parafilm Plastic Bags Glass Cutter Safety Glasses Broken Glass Container Electrical Tape	Polycarbonate Case Rubber Gaskets Metal things XXX Velcro Sampling Trains Zip Ties Aluminum Foil Blue Masking Tape Wire cutters Scissors Exacto Knife	Litter Boxes Clorox Wipes Lab Diapers Labels Kim Wipes Dish soap Trash Bags Lab Tape Allen Wrench
Cartridge	Leland Legacy Pump ¼” Tubing White Urea Leur 3 Piece Cassette 2 Porous Plastic Support Pads 2 Charcoal Cloth circles (packaged in vials) PVC Pipe ¼” to ½” Reducing Connector ½” Tubing ¾” to ½” Hose Barb OV Cartridge with R-95 Pre-filter	Isopropyl Alcohol Q-tips Flat head screwdriver Forceps Acetone Plastic Beakers Kim Wipes 4 mL Vials Plastic Bags Electrical Tape Zip Ties Parafilm Teflon Tape		

Table 15: Glove Supplies

Glove Testing Supplies	General
15 mil Nitrile Gloves of the correct size PermaTech patches Aluminum Foil Tape Vials for Sampling Media ParaFilm	5 mil Nitrile Gloves Forceps Lab Diapers Acetone Labels

Appendix K: Quality Control Spiking

Table 16: Quality Control Spiking

Media	Day 1	Day 2	Day 3	Day 4		
Charcoal tubes- ambient	High High dup Low Field Blank Field Blank	Field Blank Field Blank	High High dup Low Field Blank Field Blank	Field Blank Field Blank	**O-xylene** High Spike Low Spike **Pentadecane** High Spike	200 ug 50 ug 200 ug
Charcoal cloth circles- cartridge	High High dup Low Field Blank Field Blank	Field Blank Field Blank	High High dup Low Field Blank Field Blank	Field Blank Field Blank	Low Spike **1,2,4 Trimethylbenzene** High Spike Low Spike	50 ug 200 ug 50 ug

Appendix L: Explanation of Labels

: Explanation of a respirator label

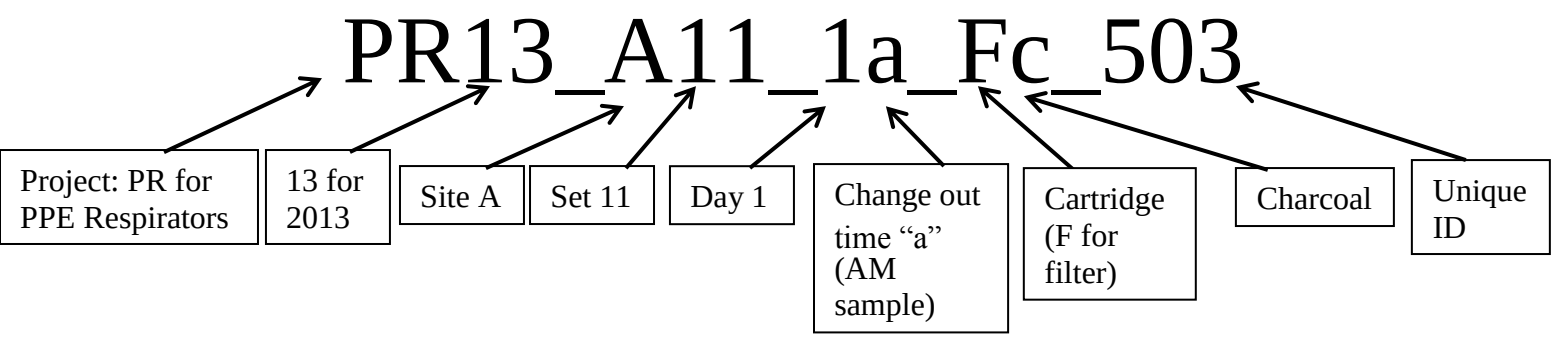


Figure 25: Explanation of a Glove Label

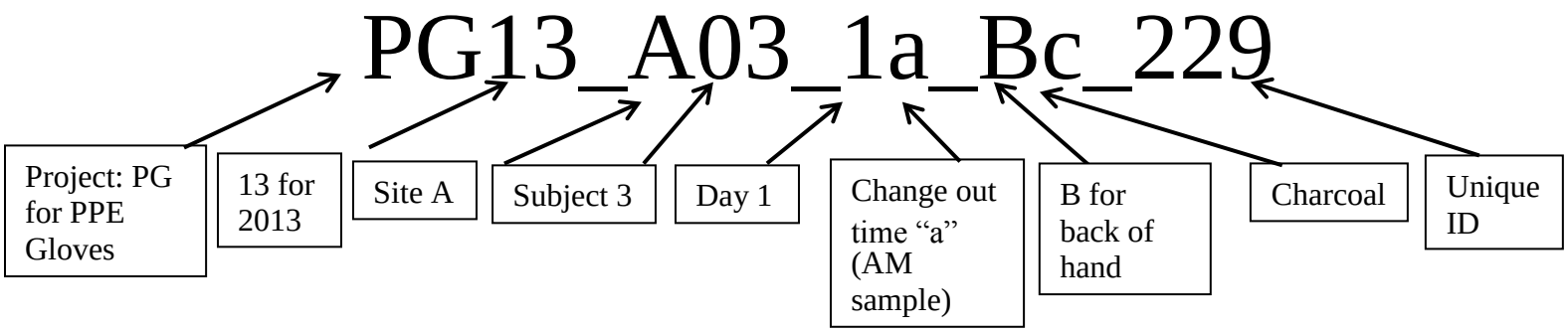
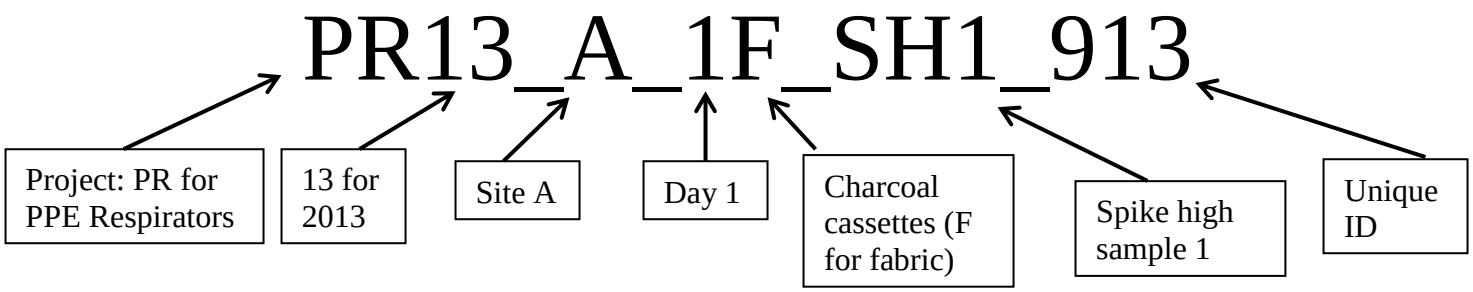


Figure 26: Explanation of a Quality Control



Appendix M: Pictures of Field Work

Figure 27: Abigail and Maria changing out media on a tractor during lunch break

Figure 28: Pablo and Miyoko changing out media on a glove during lunch break

Figure 29: Sampling Box on the back of a tractor

Figure 30: Mixing and Loading Station

Figure 31: Lime Sulfur being poured

Figure 32: Pouring Pesticide into Applicator on Back of Tractor

Figure 33: Field Team: From Left, Miyoko Abigail, Maria, Kit and Pablo

Appendix N: Demographic Data

Table 17a: Demographic Data for Respirators

Set	# Tanks	Tractor Type	Sprayer Type	Product Name	EPA Reg #	Pest.	App Rate
11	8	New Holland TN 95FA	airblast	1) Microthiol Disperss 2) Warhawk 3) Omni Supreme Spray	70506-187 34704-857 5905-368	1) Spider mite, Two spotted mite 2) Lygus bug 3) San Jose' Scale	10 lb/acre 2 Qt/acre 5 gal/acre
12	7	New Holland TN 95FA	airblast	1) Microthiol Disperss 2) Warhawk 3) Omni Supreme Spray	70506-187 34704-857 5905-368	1) Spider mite, Two spotted mite 2) Lygus bug 3) San Jose' Scale	10 lb/acre 2 Qt/acre 5 gal/acre
13	3	New Holland TN 4040Y	Stainless Turbo Mist	1) Lime Sulfur 2) Supreme Oil	71096-6 2935-405	1) Mildew 2) San Jose Scale, European Red Mite	6 gal/acre 3 gal/acre
14	3 & 50 gallons	New Holland TN 4040Y	Stainless Turbo Mist	1) Lime Sulfur 2) Supreme Oil	71096-6 2935-405	1) Mildew 2) San Jose Scale, European Red Mite	6 gal/acre 3 gal/acre
15	3.5	New Holland TN 4040Y	Stainless Turbo Mist	1) Lime Sulfur 2) Supreme Oil	71096-6 2935-405	1) Mildew 2) San Jose Scale, European Red Mite	6 gal/acre 3 gal/acre
16	1 & 240 gallons	New Holland TN 4040Y	Stainless Turbo Mist	1) Lime Sulfur 2) Supreme Oil	71096-6 2935-405	1) Mildew 2) San Jose Scale, European Red Mite	6 gal/acre 3 gal/acre
17	2 & 350 gallons	New Holland TN 4040Y	Stainless Turbo Mist	1) Lime Sulfur 2) Supreme Oil	71096-6 2935-405	1) Mildew 2) San Jose Scale, European Red Mite	6 gal/acre 3 gal/acre
18	2.5	New Holland TN 4040Y	Stainless Turbo Mist	1) Lime Sulfur 2) Supreme Oil	71096-6 2935-405	1) Mildew 2) San Jose Scale, European Red Mite	6 gal/acre 3 gal/acre

Table 17b: Demographic Data for Respirators

Set	Concentration Prod	Sprayer Tank Size	Comments
11	80% 44.90% 98%	400 gallons	First Day Spraying. Stopped Spraying chlorpyrifos today and will continue spraying this insecticide later- (maybe April 5-2013)
12	80% 44.90% 98%	400 gallons	Stopped Spraying today (April 2-2013). They will continue spraying chlorpyrifos later (maybe on April 52013)
13	28% 99%	400 gallons	
14	28% 99%	400 gallons	
15	28% 99%	400 gallons	
16	28% 99%	400 gallons	
17	28% 99%	400 gallons	
18	28% 99%	400 gallons	

Table 18: Demographics for Gloves

Age	Sex	Ethnicity	Race	Height (in)	Weight	Primary Language	Seasons in Industry	Seasons with Orchard	Gloves Underneath?
34	M	Hispanic or Latino	White	71	-	Spanish	4	4	No
37	M	Hispanic or Latino	White	69	-	Spanish	11	1	Yes- Cloth Gloves
21	M	Hispanic or Latino	White	63	37.1 kl	Spanish	6	2 weeks	No
25	M	Hispanic or Latino	Unknown	69.5	96.5 kl	English	2	1	Yes- Nitrile Gloves
24	M	Hispanic or Latino	Unknown	67	92.2 kl	Spanish	4	1	Yes- Latex
21	M	Hispanic or Latino	White	69.5	93.1 kl	Spanish	1	2	Yes-Latex

Appendix O: Quality Assurance from Lab

Table 19: Quality Assurance for Charcoal Cloth Circles (ug/sample)

Parameter	p-Xylene (ug/sample)	o-Xylene (ug/sample)	Cumene (ug/sample)	1,2,4-Trimethyl benzene	Pentadecane	Unknown Alkanes
R^2, calibration	1.0000	1.0000	1.0000	0.9999	1.0000	NA
Reporting Limit, (ug)	2	2	1	2	1	1
SR Efficiency	86%	86%	91%	88%	87%	NA

Table 20: Quality Assurance for Charcoal Cloth Tubes

Parameter	p-Xylene	o-Xylene	Cumene	1,2,4-Trimethyl benzene	Pentadecane	Unknown Alkanes	Non-aromatic hydrocarbons
R^2, calibration	0.9998	0.9999	0.9999	0.9996	0.9998	NA	NA
Reporting Limit, Front (ug)	2	2	2	2	5	10	5
Reporting Limit, Back (ug)	1	1	1	1	2	NA	2
SR Efficiency	74%	77%	81%	72%	68%	NA	NA

Table 21: Quality Assurance for Glove Charcoal Cloth Circles at Site A

Parameter	p-Xylene (ug/sample)	1	Cumene (ug/sample)	1,2,4-Trimethyl benzene	Pentadecane	Unknown Alkanes
R^2, calibration	1.0000	0.9999	0.9999	0.9996	0.9998	NA
Reporting Limit (ug)	2	2	0.6	2	8	NA
SR Efficiency	97%	77%	103%	96%	92%	NA

Table 22: Quality Assurance for Glove Charcoal Cloth Circles at Site B

Parameter	p-Xylene (ug/sample)	o-Xylene (ug/sample)	Cumene (ug/sample)	1,2,4-Trimethyl benzene	Pentadecane	Unknown Alkanes
R^2, calibration	1.0000	1.0000	1.0000	0.9999	1.0000	NA
Reporting Limit (ug)	2	2	0.6	2	6	NA
SR Efficiency	108%	107%	108%	104%	106%	NA

Appendix P: Calculations of Upper Limit of Non-Hits

Table 34: Charcoal Tube Blanks

Charcoal Tubes (in ug/sample)							
ID	Site	Mass of Unknown Alkanes	Average	Average Total (ug/sample)	Standard Deviation	Standard Error	Upper Limit
901	A	100 90					
902							
			95		7.071067812	5	105
916	B	0					
917		10					
937		70 0					
938							
			20		33.67	16.83	87.33
	Totals			45	46.80	19.10	83.21

Table 35: Charcoal Cloth Blanks

Charcoal Cloths							
ID	Site	Mass of Unknown Alkanes (ug/sample)	Average	Average Total (ug/sample)	Standard Deviation	Standard Error	Upper Limit
911	A	3					
912		2					
			2.5		0.707106781	0.5	3.5
920	B	0					
921		22					
932		3					
933		0					
			6.25		10.59481005	5.297405025	27.4396201
Totals				5	8.438009244	3.444802849	11.8896057

Table 36: Gloves Blanks:

Charcoal Cloth for Gloves (ug/sample)							
ID	Site	Mass of Unknown Alkanes	Average	Average Total	Standard Deviation	Standard Error	Upper Limit
401	A	1246					
402		1048					
			1147				
413	B	1270					
414		1220					
415		993					
416		1250					
			1183.25				
				1171.166667	119.0637084	48.60755543	1268.381778

Appendix Q: Calculations of Adjusted Mass

Table 37: Adjusted Mass for Ambient Samples

Ambient Sample- Charcoal Tube					
ID	Unknown Alkanes (ug/sample)	Total Run Time (min)	Flow Rate (L/min)	Total Liters air	Adjusted Mass Unknown Alkanes (ug/sample)
501	410	283	1.2	339.6	398.41
505	1860	260	1.20	312.00	1967.31
537	240	264	1.10	290.40	272.73
541	220	290	1.10	319.00	227.59
525	90	358	1.02	365.16	81.33
529	50	265	1.02	270.30	61.04
573	20	362	1.02	369.24	17.87
577	40	260	1.02	265.20	49.77
609	20	368	1.05	386.40	17.08
613	0	260	1.04	270.40	0
630	200	355	1.04	367.60	179.54
632	480	389	1.04	405.57	390.56
634	150	391	1.04	404.69	122.32

Table 38: Adjusted Mass for Cartridge Samples

Cartridge Sample- Charcoal Cloth					
ID	Unknown Alkanes (ug/sample)	Total Run Time (min)	Flow Rate (L/min)	Total Liters air	Adjusted Mass Unknown Alkanes (ug/sample)
503	722	284	6.80	1931.20	747.72
507	18620	305	5.70	1738.50	21420.77
539	527	264	6.60	1742.40	604.91
543	333	291	5.75	1673.25	389.03
527	0	361	7.92	2859.12	0
531	5	262	7.80	2043.60	4.89
575	6	365	7.97	2909.05	4.13
579	9	290	7.89	2288.10	7.87
611	79	369	7.87	2904.03	54.41
615	0	289	7.64	2207.96	0
631	17	357	7.96	2841.72	11.96
633	19	370	7.95	2941.50	12.92
635	18	347	8.07	2800.29	12.86