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United States Department of Agriculture
Animal and Plant Health Inspection Service

Miami, Florida

Max Kiefer

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Max Kiefer, CIH of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by John Decker and Anne Krake. Desktop publishing by Pat Lovell.

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

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Max Kiefer, CIH

SUMMARY

The National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation (HHE) from the USDA, Animal and Plant Health Inspection Service (APHIS), in Miami, Florida. The primary concern noted in the request was employee handling of plant material treated with unknown pesticides. Although no adverse health problems were reported, the request asked NIOSH to evaluate the potential for USDA employee exposure to pesticides present on imported commodities (plants, fruit/vegetables, cut flowers, etc.). Additionally, NIOSH was asked to review methyl bromide fumigation procedures at the Maritime and Cargo operations. This request was similar to an HHE (HETA 94-0353-2629) NIOSH was conducting at the USDA Plant Inspection and Quarantine Station (PIQS) in Miami, Florida.

On May 7-9, 1996, NIOSH investigators conducted an initial site visit at the APHIS operations in Miami, Florida, in conjunction with a follow-up survey to the PIQS. The objectives of this visit were to review the commodity inspection process; obtain samples from various imported cut flowers, plants, fruits, and vegetables; conduct personal monitoring to assess potential skin exposure to pesticides; and collect air samples to assess exposure to pesticides identified on the foliage samples.

On May 7-8, environmental monitoring was conducted to assess pesticide residues on plant material undergoing inspection at various import broker warehouses (Cargo operation). The potential for hand exposure to dislodgeable residue on imported commodities and during the fumigation of an aircraft was evaluated with sampling glove monitors worn by plant inspectors. Personal air samples for pesticides were collected during various inspections. On May 9, environmental monitoring was conducted at the USDA Maritime operations to assess pesticide residues on imported fruits and vegetables, and evaluate potential worker exposure. Policies and procedures regarding methyl bromide fumigation at the Maritime and Cargo facilities were reviewed.

Pesticide residues were detected on 30 of the 37 samples (81%) collected from commodities inspected by Cargo employees at various importer warehouses. Eighty-six total compounds comprising 18 different pesticides were detected on the samples. The fungicide benomyl was the most commonly detected pesticide and was also the compound found at the highest concentrations. Several classes of pesticides were detected, including organophosphate, carbamate, pyrethrin, and organo-chlorine. Based on pesticide function, 62 of the 86 (72%) compounds detected on the samples were fungicides (benomyl, captan, chlorothalonil, vinclozolin, and zineb). On some samples visible residue was observed but none of the monitored pesticides were found. Some samples with no visible evidence of residue had the highest concentrations of pesticide. No detectable pesticide residues were found on surface wipe samples collected from desk tops in the main USDA Cargo office.

Pesticide residue was detected on all glove samples analyzed. Fourteen different pesticides were found on the glove samples. Several pesticides detected on the gauze samples were not found on the glove monitors. Conversely, some compounds not detected on the gauze wipe samples were found on the corresponding glove sample.

At the Maritime operations, detectable levels of pesticide residues were found on 4 of 10 (40%) samples, and 6 different compounds were detected (3 of the 6 compounds (50%) detected were fungicides). The highest concentration of residue detected was the fungicide metalaxyl, found on a cantaloupe imported from Guatemala. Residue was detected on all four glove pairs analyzed and 7 different pesticides were detected. As with samples collected during the Cargo inspections, there was not a good correlation between compounds detected on the dislodgeable residue samples and the corresponding glove samples. Only 11 of the 19 (57%) compounds detected on the glove samples were also measured on the corresponding gauze sample. Because none of the dislodgeable residue samples from the Maritime operations indicated the presence of an organo-phosphate pesticide, the personal air samples collected during this survey were not analyzed.

USDA-APHIS employee involvement with fumigation entails oversight of the treatment contractors, determining the proper treatment dose and contact time, and monitoring the treatment. APHIS personnel have direct reading colorimetric detector tubes for monitoring methyl bromide, and self-contained breathing apparatus available in the event of an emergency. Although remote monitoring is conducted for methyl bromide inside the fumigation tents, there is no continuous methyl bromide detector inside the Maritime monitoring trailer to notify personnel in the event of a leak within the trailer.

The use of gloves to protect against pesticide residues is not uniform as some employees did not wear gloves during inspections. An inspector's decision to wear gloves during an inspection seemed to be based on the presence of visible residue or unusual odor. The results of this survey indicate that the presence of visible residue on plant material should not be used as criteria for determining if gloves should be worn.

The monitoring results indicate USDA-APHIS inspectors are at potential risk for skin exposure to pesticides during the handling of imported commodities. Dislodgeable pesticide residues were found on 91% of the cut flower samples and 31% of the produce samples. Measurable quantities of pesticides were found on cotton glove monitors worn by inspectors. No pesticides were found on any air samples. The cotton glove monitors were worn over the inspectors vinyl or latex glove (when worn) and these results only provide information on the potential for exposure if protective gloves are not used. The efficacy of the disposable gloves to prevent contact with pesticide residues was not evaluated during this project. The presence of visible residue on plant material was not a good indicator that a pesticide would be detected. Suggestions to reduce the potential for exposure are in the Recommendations section of this report.

Keywords: SIC 9641 (Regulation of Agricultural Marketing and Commodities). Pesticide Residue, Plant and Commodity Inspection, Ornamental Plant Imports, Cut Flower Industry, Skin Exposure, Leaf Sampling.

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INTRODUCTION

NIOSH received a management request from the United States Department of Agriculture (USDA) Animal and Plant Health Inspection (APHIS) in Miami, Florida, to evaluate the potential for worker exposure to pesticides during inspections of imported plants at the Cargo and Maritime operations. NIOSH was also asked to evaluate the USDA-APHIS methyl bromide fumigation facilities and procedures. No reported health problems were received with the request.

NIOSH investigators conducted a site visit at the Miami Cargo and Maritime operations on May 7-9, 1996, in conjunction with a similar evaluation at the USDA Plant Inspection and Quarantine Station (PIQS) in Miami, Florida (HETA 94-0353-2629). Prior to the site visit, information was solicited to determine pesticides that may have been applied to plants in the host countries, and analytical methods for measuring pesticide residues on foliage were developed and refined. During the site visit, dislodgeable residue (foliage) samples were collected, and the potential for skin exposure was assessed using glove monitors. Personal air samples were collected to evaluate inhalation exposure. Work practices during the plant inspection process were assessed.

A letter describing preliminary findings and recommendations was provided to PIQS management on September 6, 1996.

BACKGROUND

Process Description

The main USDA-APHIS Air-Cargo operations office is located at the Miami International Airport. USDA Cargo employees are responsible for inspecting air-delivered imported cut flowers (e.g., roses, chrysanthemums, carnations, etc.) and produce (fruit and vegetables). In addition to the Cargo operation, two other USDA groups in Miami are responsible for inspecting imported plants, cut flowers, and produce. The other two groups are Plant Inspection and Quarantine (live ornamental plants), also located at the Miami Airport but at a separate facility, and the Maritime operations (produce), located at the Port of Miami. Some inspectors are represented by the National Association of Agricultural Employees (NAAE), Local #8.

The objectives of the imported commodity inspection are to ensure the plants and produce are free of disease and infestation (microbiological, insect, and noxious weed), and are not an endangered or threatened species. This inspection is required prior to releasing the products into U.S. trade markets. Plants are imported from many South American and Caribbean countries, as well as from the Far East, and Europe. Exporters are not required to label or provide information about whether a plant shipment has been treated with a pesticide.

Cargo Operations

Ninety-five percent of cut flowers imported into the U.S. pass through the Cargo operations station in Miami. The peak season for cut flower imports is between October and the end of May, especially during Valentine and Mothers Day holidays. In contrast to the PIQS station, where import brokers bring the plants to the PIQS facility for inspection, USDA Cargo personnel travel to the individual brokers' warehouse to conduct the inspection. When an imported commodity arrives in the U.S.A., customs personnel issue a provisional release to the importers on the condition that the plants are approved by the USDA. The import broker or freight forwarder is then responsible for initiating the request for an inspection. Inspection time per shipment may range from 30 minutes to 1 hour depending on the size of the shipment and experience with the particular commodity (only a sample of the shipment is inspected). Daily logs are kept noting the size of the shipment, plant type, country of origin, and the name of the exporting grower or firm. During inspections there is considerable handling of the plants and close visual evaluation using magnifying glasses. After passing inspection, the plants are released to the importer where they may be distributed throughout the U.S.A. If a shipment does not pass inspection (insect infestation or plant disease is detected), the broker has the option of returning the entire shipment to the country of origin, destroying the plants in a gas-fired incinerator, or treating the plants on-site at a methyl bromide fumigation station.

During the NIOSH site visit, there were approximately 16 inspectors working at the Cargo operations, with 6-8 in the field at any given time. However, because the demand for inspections was very high, several Florida Department of Agriculture personnel had been assigned to the Cargo office, and there were plans to hire additional inspectors. The standard inspection service is operated from 8:00 a.m. - 4:30 p.m., Monday through Friday. However, because of the perishable nature of the imported material, service is available 24 hours per day on an on-call basis. During the NIOSH visit, the Cargo office was receiving 60-80 calls for inspections each day.

Maritime Operations

USDA-APHIS Maritime operations personnel are responsible for inspecting imported commodities shipped into the Port of Miami. During the NIOSH visit, 12 inspectors were stationed at the Maritime operations, which has offices located in the main shipyard area. As with the Cargo operations, because of the high demand for inspections, additional personnel had been assigned from the Florida Department of Agriculture to assist with the workload. Inspections primarily consist of large shipments of imported fruits and vegetables. The commodity importers schedule the inspections and are expected to have all arrangements (paperwork, commodity availability) in place prior to the inspection.

Commodity shipments are typically off loaded from the shipping vessel in semi-truck trailers, most of which are refrigerated. After the trailers are removed, they are kept within the shipyard and lined up on each side of a long concrete platform. Because of the large shipments (e.g., 40-50 trailers of produce), inspections are generally conducted as a team. Dock workers and the commodity brokers will then move a sample from each trailer onto the concrete platform where the inspection is conducted. Inspectors typically do not go inside the trailers. As with the other USDA plant inspection groups, considerable manual handling of the product is required. The extent of the inspection for each commodity will vary depending on the product and experience with the particular importer or host country. According to USDA personnel, many of the shipments had been previously fumigated prior to delivery to the Port of Miami.

Shipments not passing inspection are tagged for quarantine. The trailers are then moved to the Maritime fumigation station for treatment with methyl bromide.

APHIS Pesticide Residue Concerns

Although no illnesses among APHIS inspectors have been reported, there have been complaints of visible residue on some plant shipments. Disposable latex and vinyl gloves are available for use and some inspectors use them during inspections. The gloves are typically discarded after each inspection, and a new pair donned prior to the next shipment. Respiratory protection or special clothing is not required to be worn during routine plant inspections.

Methyl Bromide Fumigation

At the Cargo and Maritime operations, methyl bromide fumigation of quarantined commodities is conducted on a daily basis. 100% methyl bromide (without the common additive chloropicrin) dispensed from cylinders, is used for the treatments. When an inspection determines the commodity must be quarantined and treated, the import brokers will arrange for and conduct the fumigation. USDA-APHIS personnel, however, are required to witness and monitor the treatment to ensure it is conducted properly. USDA-APHIS personnel also designate the necessary fumigant concentrations, contact time, and safety precautions. APHIS has designated a fumigation coordinator to oversee all aspects of commodity treatments.

Cargo

The methyl bromide fumigation facility for the Air-Cargo operation is located within a secured, fenced area adjacent the Miami airport. Fumigation takes place on an open-sided covered concrete tarmac and is operated by contractors. The quarantined commodity is placed on wooden pallets and covered with a tarpaulin. Sand snakes are used to seal the tarp edges to the concrete pad. Polyethylene tubing from 50 lb methyl bromide cylinders is routed under the tarpaulin. Methyl bromide concentrations underneath the tarp are monitored with a continuous detector to ensure adequate treatment levels. USDA personnel calculate the gas amount and fan placement for ventilating the commodity after treatment. Treatment time is typically 2 hours, followed by a 2 hour aeration time. During the NIOSH visit, a fumigation trailer was being installed that would replace the tarpaulin method. This system would provide for better fumigation control, containment, and ventilation.

Maritime

The Maritime fumigation operation is located in a fenced open area within the shipyard and is designed for much larger treatments than the Cargo operation. There are 14 fumigation stations with concrete pedestals on each side (28 total) where the semi truck trailer containing the commodity is positioned prior to treatment. After positioning the trailer, the fumigation contractor places a tarpaulin over the entire container and seals the tarp to the concrete pedestal with sand snakes. Methyl bromide is delivered from 50 lb cylinders via tubing into the covered container. Tygon and polyethylene lines from each treatment station are placed in various areas within the trailer being fumigated to measure gas concentrations during treatment. This tubing is routed underground to an adjacent facility housing a continuous monitoring system. The type of commodity and temperature dictate the treatment concentration and duration. A maximum treatment consists of 6-8 lbs of methyl bromide per 1000 cubic feet of treatment space with a contact time of 12 to 72 hours. Fumigation contractors are responsible, under USDA supervision, for installing the fumigant, aerating the trailer after treatment (3 hour aeration time), and removing the tarp.

METHODS

Foliage Residue

To evaluate dislodgeable pesticide residues on imported plants, a necessary first step was determining the agricultural chemicals that may have been applied. Measuring a known material is more analytically feasible (the specific method for a compound can be selected) than identifying and quantifying an unknown substance. This is particularly true for pesticides, which encompass a wide variety of complex chemical classes. To obtain this information, the literature was researched for similar studies, and information on grower application practices in host countries was requested from plant brokerage firms in south Florida. Existing sampling and analytical methods for assessing pesticides on foliage were identified and reviewed.[1,2,3,4] To determine the optimum method, two techniques (leaf punch and leaf wipe) for sample collection and analysis were field tested in February 1995 at a greenhouse where applications of known pesticides had occurred. The sampling and analytical methodology was further refined after a June 1995 survey at the USDA Plant Inspection and Quarantine Service facility in Miami, Florida (HETA 95-0353-2629). Efforts to obtain application information from major plant brokerage firms were unsuccessful as the importing brokers generally did not know what pesticides were applied by the off-shore growers. *Appendix A* provides details on the analytical methodology used for measuring pesticide residues on plant surfaces.

Because techniques for assessing foliar surfaces for a broad array of potential pesticides in multiple chemical classes were not available, a list of 15 pesticides (*Appendix B*) considered most likely to be present, and of higher concern from a toxicological standpoint, was selected. This list provided a baseline for analysis of the foliage samples. Included in this list were compounds from several chemical classes (organophosphate, organochlorine, pyrethroid, carbamate). For some classes of pesticides, the analytical method was conducive to measuring additional compounds within that chemical class (e.g., organophosphate, organochlorine), and the samples were analyzed for additional pesticides beyond the list of 15. A complete list of the pesticides measured on the foliar samples is presented in *Appendix A*.

The dislodgeable residue samples were obtained with pre-extracted 3" X 3" polyester gauze (NuGauze®) moistened with technical grade (99%) isopropyl alcohol. To prevent cross-contamination, NIOSH investigators wore a new pair of disposable latex gloves for each sample collected. To obtain the sample, both sides of five plant leaves were wiped using firm pressure. In some cases the flower, stalk, or fruit/vegetable (e.g., Dracena or corn plant, cantaloupe) had to be wiped. When possible, two or more samples were collected from each commodity shipment.

Thirty-seven gauze wipe samples were collected from cut flowers, fruit, and vegetables from various warehouses inspected by Cargo personnel. Ten dislodgeable residue samples were collected during the inspection of a large (36 semi-trailers) shipment of produce at the Maritime facility. Two wipe samples were also collected from various surfaces (desks) at the main USDA-APHIS office. For each sample, the plant type, country of origin, presence of any visible residue or odor, and any shipping notations of pesticide applications were recorded. Samples were placed in labeled amber jars and stored in a freezer prior to shipment, and were shipped cold via overnight express to the NIOSH contract laboratory for analysis. Blank gauze wipes were submitted with the samples. Each sample was analyzed for the presence of 60 separate pesticides (*Appendix A*)

During the analysis, additional compounds were suspected to be present on some of the gauze wipe samples. For these samples, an additional analytical step entailing gas chromatography-mass spectroscopy detection (GC-MSD) was used to identify additional pesticides.

Skin Exposure Assessment

Eighteen pairs (36 total) of pre-extracted sampling glove monitors made of polyester (65%) and cotton (35%) were used to assess the potential for skin contact to various pesticides during commodity inspections. For those workers using disposable protective gloves during plant inspections, the sample glove monitors were worn over the worker's disposable gloves. A different set of glove monitors were used for each batch of plant material inspected. Sampling time, name and country of origin of the inspected material, and the presence of unusual odor or residue was recorded for each sample set. After sampling, the glove monitors were placed in labeled amber jars and sealed with teflon®-lined caps. NIOSH investigators wore gloves to protect the sampling glove monitors from contamination. Left and right gloves were placed in separate jars for each test subject and stored in a freezer until shipment. The samples and field blanks were then shipped via overnight delivery to the NIOSH contract laboratory (DataChem, Salt Lake City, Utah) for analysis. The glove monitors were analyzed for pesticides identified on the corresponding dislodgeable residue samples.

Air Monitoring

Five personal breathing zone air samples were collected to determine the presence and concentration of organo-phosphate pesticides detected on the corresponding wipe samples. All samples were placed on hold until after the foliage samples had been analyzed. Two of the samples were collected during Cargo inspections, two during Maritime inspections, and one sample during the fumigation of an aircraft cargo bay. Although the pesticide (d-phenothrin) used for the aircraft treatment was not an organophosphate, the use of this material had not been anticipated and a sample was collected in the event that analysis was possible. Calibrated air sampling pumps were worn by plant inspectors and connected via tubing to collection media placed in the workers' breathing zone. The air samples were collected using OVS-2 (OSHA Versatile Sampler) sorbent tubes at a flow rate of 1 liter per minute. The samples were desorbed and analyzed according to NIOSH fourth edition analytical method 5600.[5] Monitoring was conducted for the duration of the activity. After sample collection, the pumps were post-calibrated and the samples submitted to the NIOSH contract laboratory (DataChem, Salt Lake City, Utah) for analysis. Field and media blanks were submitted with the samples.

EVALUATION CRITERIA

General

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs)[6], (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs™)[7] and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs).[8] In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to-10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Skin Exposure

Exposure standards, guidelines, or recommendations by NIOSH or regulatory agencies have not been established for pesticides on skin or work clothes.

However, skin exposures to pesticides are often considered to be a more important portion of total exposure than inhalation.[9,10,11] Pesticide applications generally entail considerable contact during mixing, spraying, and handling of treated crops. Loosely bound residues on plant material can be a major source of exposure for workers.[2,12] In general, hand exposure represents a major fraction of total dermal exposure.[13] Evaluation of the amount of material potentially available for absorption can provide estimates of skin exposure. Additionally, these types of assessments are useful for evaluating the need for and efficacy of control measures, as well as personal protective equipment. In some cases, where there is information on skin permeability and there is inhalation and biological monitoring data, skin contact assessments can theoretically provide more quantitative information on absorption or dose via the skin route. There are numerous techniques available to estimate the potential for skin contact; however, there is no standard protocol for the assessment of the degree of skin contact or the interpretation of data.

Pesticides

A pesticide is any substance or mixture intended to prevent, destroy, repel, or mitigate insects (insecticide, miticide, acaricide), rodents (rodenticide), nematodes (nematocide), fungi (fungicide), or weeds (herbicide), designated to be a "pest." For each type of pesticide there are numerous modes of action, chemical classes, target organs, formulations, and physicochemical properties. Pesticide toxicity is equally diverse, and even within a similar chemical class, individual compounds ranging from extremely toxic to practically nontoxic can be found.[14] As such, generalizations about the toxicity of pesticides cannot be made without considerable qualification and explanation. In the United States, regulatory responsibility to protect public health and the environment from the risks posed by pesticides lies with the Environmental Protection Agency (EPA) Office of Pesticide Programs. Currently, there are 620 active ingredients (AI)* in approximately 20,000 EPA registered pesticide products.[15] In the United States alone, over one billion tons of pesticide products are used each year.[15]

Organophosphate Pesticides

A variety of organophosphate chemicals are commonly used as insecticides because they are biodegradable as well as effective. Organophosphate chemicals, however, can cause adverse health effects in exposed humans through the inhibition of cholinesterase (ChE) enzymes. Symptoms after exposure to organophosphate chemicals usually appear quickly, often within a few minutes to two or three hours.[14]

Organophosphate insecticides typically cause illnesses in humans by binding to and inhibiting acetylcholinesterase (A-ChE) at nerve endings. A-ChE is a ChE enzyme that metabolizes, and thus controls, the amount of acetylcholine (nerve impulse transmitter) available for transmitting nerve impulses. Inhibition of A-ChE causes acetylcholine to accumulate at nerve endings, resulting in increased and continued acetylcholine stimulation at those sites. Symptoms of A-ChE inhibition include the following:
The organophosphate-ChE bond is stable and largely irreversible, so recovery of ChE activity depends on the generation of new ChE. ChE inhibition, therefore, can sometimes last for months.

ChE inhibition can be measured as decreases in ChE activity. Red blood cell cholinesterase (RBC-ChE), like ChE in nerve tissues, is an A-ChE. Its rate of regeneration nearly parallels that of A-ChE in nerve tissues, making its measurement a useful method of biologically monitoring exposure to organophosphate insecticides. A significant decrease

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**Active Ingredient is the material, or component, present in a pesticide formulation responsible for killing or controlling the target pest. Pesticides are regulated primarily on the basis of active ingredients, often expressed in terms of percent, pounds per gallon, etc.*

in RBC-ChE activity indicates either a recent excessive exposure or repeated exposures to amounts sufficient to depress ChE activity before recovery is complete. Other types of cholinesterase, such as plasma cholinesterase or pseudocholinesterase (P-ChE), are more sensitive to organophosphate inhibition. P-ChE activity, however, returns to baseline values earlier than RBC-ChE activity. Therefore, P-ChE values may not reflect the severity of toxicity unless blood specimens are obtained soon after exposure. P-ChE activity can also be affected by factors unrelated to organophosphate exposure, including medical conditions such as liver disease.[16] P-ChE activity is clinically useful in monitoring cases of severe organophosphate poisoning, but its use in monitoring workplace exposures is limited.

The range of toxicity and potential health hazard varies widely among organophosphate pesticides. The hazard associated with each is also dependent on other factors, including frequency of use, concentration, formulation, physical and chemical properties, and the efficacy of personal protective equipment against the particular compound.

Carbamate Pesticides

Exposure to carbamate insecticides can also cause ChE inhibition and its related symptoms. Unlike the organophosphate-ChE bond, however, the carbamate-ChE bond is rapidly broken, and carbamate are considered to be reversible ChE inhibitors. As such, the effects of carbamate exposure last for a much shorter time than that of organophosphate exposure. For this reason, biological monitoring of RBC-ChE activity may not necessarily reflect exposure to carbamate insecticides, and there is a greater span between the dose that will produce symptoms and the lethal dose.[14] As with the organophosphates, there is a wide range of acute toxicities among the carbamates. Unlike the organophosphates, however, most carbamates have low dermal toxicity and are only slightly absorbed through the skin (a notable exception to this is the pesticide aldicarb [Temik®]).[14,17]

Synthetic Pyrethroid Pesticides

Synthetic pyrethroid insecticides are chemically similar to natural pyrethrins. Pyrethrins are the active insecticidal ingredient in pyrethrum, which is the extract of chrysanthemum flowers and one of the oldest insecticides known to man.[14,17] Synthetic pyrethroids have been modified to increase their stability in the natural environment, and make them suitable for use in agriculture.

Certain pyrethroids have been shown to be highly neurotoxic in laboratory animals when administered intravenously or orally.[17] Systemic toxicity by inhalation or dermal absorption is low, and there have been very few reports of human poisonings by pyrethroids. Very high absorbed doses could result in incoordination, tremor, salivation, vomiting, and convulsions.[17] Some pyrethroids have caused sensations described as stinging, burning, itching, and tingling - with progression to numbness, when contact with the skin occurs. Sweating and exposure to the sun can enhance this discomfort. Pyrethroids are not cholinesterase inhibitors.

Organochlorine Pesticides

Because of their persistence in the environment and biologic media, the use of many organo-chlorines such as DDT, dieldrin, mirex, and chlordane have been banned or sharply curtailed in the United States. The major toxic action of organo-chlorine pesticides is on the nervous system, which, in cases of severe poisoning can manifest as convulsions and seizures.[17] Early signs of poisoning may include headache, dizziness, nausea, vomiting, and mental confusion. Following exposure to some organo-chlorine pesticides, a large part of the absorbed dose may be stored as the unchanged parent compound in fat tissue. As a class of compounds, organo-chlorine pesticides are often considered less acutely toxic, but with a greater potential for chronic toxicity, than the organo-phosphate or carbamate pesticides.[14] As with the other pesticide classes, however, there is a wide range of acute toxicities of individual organo-chlorine compounds. Organochlorine pesticides are not cholinesterase inhibitors.

Methyl Bromide

Methyl bromide is a colorless, non-flammable gas which is odorless and tasteless at low concentrations.[18] Odor thresholds reported for methyl bromide range from a low of 20 parts per million (ppm) to a high of 1,000 ppm.[19] Methyl bromide is a severe pulmonary irritant and neurotoxin. Short-term exposure can cause headache, dizziness, nausea, vomiting, blurred vision, slurred speech, convulsions, and death. Short-term exposure to high concentrations can cause lung irritation resulting in congestion with coughing, chest pain, and shortness of breath; lung effects may be delayed in onset.[20]

Prolonged or repeated exposure to methyl bromide can cause a variety of central nervous system symptoms including visual disturbances, slurred speech, numbness of the arms and legs, confusion, shaking, and unconsciousness.[20] The onset of neurological signs and symptoms may be delayed for several hours to a few days after exposure.[21] Although inhalation is by far the most significant route of exposure, skin contact can also be a important exposure pathway, and precautions should be taken to avoid contact. Methyl bromide can become trapped inside clothing and cause skin injury. Loose fitting long-sleeved shirts, long pants, and socks should be worn by applicators and handlers.[22,23]

Methyl bromide is used as a broad-spectrum agricultural pesticide throughout the world. In the U.S., about 28,000 tons of methyl bromide are used annually, primarily for soil fumigation (87%), commodity and quarantine treatment (8%), and structural fumigation (5%). Because of acute toxicity, the EPA has classified methyl bromide as a restricted use pesticide (RUP). As such, methyl bromide is not available for use by the general public and can only be purchased or used by certified pesticide applicators or persons under their direct supervision.

Most of the published literature concerning adverse health effects and/or exposure experienced by individuals exposed to methyl bromide is associated with its use as an agricultural fumigant.[24, 25,26,27,28] An extensive review has compiled reports from 1953 to 1981 of 60 fatalities and 301 cases of systemic poisoning resulting from the use of methyl bromide as a fumigant.[29] A report was also published which contains descriptions of six severe intoxications and four fatalities that occurred in California between 1957 and 1966 in the food processing industry; the principle products handled were nuts, fruits, and grains.[24] Air concentrations of methyl bromide were not monitored routinely in any of the work areas. However, attempts to reconstruct conditions at two work sites estimated exposure concentrations of approximately 100 ppm.

Two articles have been published which contain descriptions of exposure monitoring conducted during soil fumigation in Belgian greenhouses.[25,26] Methyl bromide concentrations during application ranged from 30 to 3000 ppm. Soil injection of methyl bromide in closed areas (e.g., greenhouses) was officially prohibited in Belgium in 1979 following investigations disclosing very high exposure concentrations and severe poisoning symptoms in a dozen cases.[28]

A report has also been published concerning four workers who developed acute respiratory and/or neurologic symptoms during removal of plastic sheets 10 days after injection of methyl bromide into the soil.[27] The fumigant contained 98% methyl bromide and 2% chloropicrin, and was injected into six acres of soil at a rate of 350 pounds per acre by an experienced fumigation company. The weather had been cool (About 30-45° F), but became warm (about 75° F) and humid during the second day. Although the addition of chloropicrin is designed to act as a warning agent, no immediate irritant symptoms or odor were reported by the affected workers. The author concluded that the addition of 2% chloropicrin cannot be relied on to warn workers of the presence of methyl bromide, since it may not be detected despite significant or even toxic concentrations of methyl bromide in the air.[29,30]

A report was published of an evaluation of neurobehavioral functions in soil fumigators exposed to methyl bromide at an average concentration of 2.3 ppm.[28] Fumigators using methyl bromide reported a significantly higher prevalence of 18 symptoms consistent with methyl bromide toxicity than did non-exposed individuals (referents). Methyl bromide fumigators did not perform as well as referents on 23 of 27 behavioral tests chosen to reflect methyl bromide effects, and were significantly lower on one test of finger sensitivity and one of cognitive performance. The authors concluded that the results of their study suggested that even low levels of methyl bromide found in fumigation can produce slight neurotoxic effects.[28]

The ACGIH TLV for methyl bromide is 5 parts per million (ppm) as an 8-hour TWA.[7] The ACGIH has also assigned a skin notation to methyl bromide, indicating that the cutaneous route may significantly contribute to the overall exposure. Methyl bromide has also been placed on the ACGIH notice of intended changes list for 1996, with a proposed lowering of the TLV to 1 ppm.[7] The current OSHA PEL for methyl bromide is 20 ppm.[8] OSHA had revised their PELs in 1989 and had adopted a PEL for methyl bromide of 5 ppm as a Ceiling Limit, but these PELs were vacated by the Court of Appeals in 1992. Based on tumorigenic studies and carcinogenic response in rats, NIOSH considers methyl bromide to be a potential occupational carcinogen and recommends reducing exposure to the fullest extent feasible.[31,6] Five ppm is the current clearance level recommended by methyl bromide manufacturers for commodity fumigation.[22,22]

A recent risk assessment conducted by the California Department of Pesticide Regulation (CaDPR) evaluated the toxicological significance of methyl bromide levels in air after structural and agricultural fumigations. This assessment resulted in establishing a significantly lower acceptable human exposure level for acute exposure. The new level was calculated to be 0.21 ppm as a 24-hour time-weighted average. As a result of this new reduced exposure level, CaDPR revised their methyl bromide use requirements and use practice restrictions.[32]

Methyl bromide is a potent ozone depleting substance and is considered a significant threat to stratospheric ozone. The Montreal Protocol of 1991 determined the use of methyl bromide should be restricted and eventually prohibited. The U.S. Clean Air Act requires that production and importation of substances defined by the Montreal Protocol as significant ozone depleting agents be phased out within 7 years. The Environmental Protection Agency has set January 1, 2001, as the phase-out target for methyl bromide. After this date, all uses of methyl bromide, including plant quarantine, will be banned. As a result, significant efforts to identify and evaluate viable alternatives have been underway for some time. Both the USDA and the EPA have established programs to evaluate methyl bromide alternatives.

RESULTS AND DISCUSSION

USDA-APHIS inspectors were aware of the potential for exposure to residual agricultural chemicals on imported plants, and gloves (disposable latex, cloth) are provided for employees to use. The use of the protective gloves is not mandatory, however, and some inspectors elected not to wear them when handling plants and plant products. Cloth gloves are used primarily for protection from plant thorns or allergic reactions (dermatitis) from plant contact. The decision to wear gloves during an inspection seems to be based in part on the presence of visible residue on the plants, unusual odor, or historical experience with the commodity. Although these are prudent measures, pesticide contamination may still be present in the absence of visible residue, and the senses should not be the sole determinant for using precautions.

Cargo Operations

Two of the six inspectors monitored wore disposable latex or vinyl gloves during inspections. One inspector wore a disposable dust/mist respirator during plant inspections. Inspection activity was very high during the NIOSH site visit and numerous shipments were evaluated.

Dislodgeable Residue

The results of the dislodgeable residue sampling are shown in Tables 1 (May 7, 1996) and 2 (May 8, 1996) at the end of this report. As depicted in the tables, pesticide residues were detected on 30 of the 37 foliage samples (81%) collected from commodities inspected at various importer warehouses. Eighty-six total compounds comprising 18 different pesticides were detected on the samples (Figure 1). The fungicide benomyl was the most commonly detected pesticide, and was found on 23 of the 30 (77%) samples that detected residue. Benomyl was also the compound found at the highest concentrations. The highest concentration detected was 5400 micrograms (µg), from a wipe sample of cut chrysanthemums imported from Columbia (Table 2, sample # 40). The detected residues encompass several classes of compounds, including organophosphate, carbamate, pyrethrin, and organo-chloride (Table 6). From the standpoint of pesticide action, 62 of the 86 (72%) compounds detected on the samples were fungicides (benomyl, captan, chlorothalonil, vinclozolin, and zineb).

The majority (26) of the commodities inspected were imported from Columbia, South America. Four samples were collected from Costa Rica, and three samples from Guatemala commodities. One sample each was obtained from Trinidad, Dominican Republic, Bolivia, and the Honduras.

As noted in Tables 1 and 2, the presence of visible residue was not a good indicator that a pesticide would be detected. On some samples (e.g., #34), visible residue was noted and none of the monitored pesticides were found. Conversely, some of the samples (#19, #32) with no visible evidence of residue had the highest concentrations of pesticide. Thirty-one of the 37 dislodgeable residue samples (84%) collected during Cargo inspections were from cut flowers (Figure 2), with the remainder of the samples obtained from produce (e.g., squash, spice, etc). Pesticide residues were detected on 29 of the 31 (94%) cut flower samples, and on 1 of the 6 (17%) produce samples. The fungicides

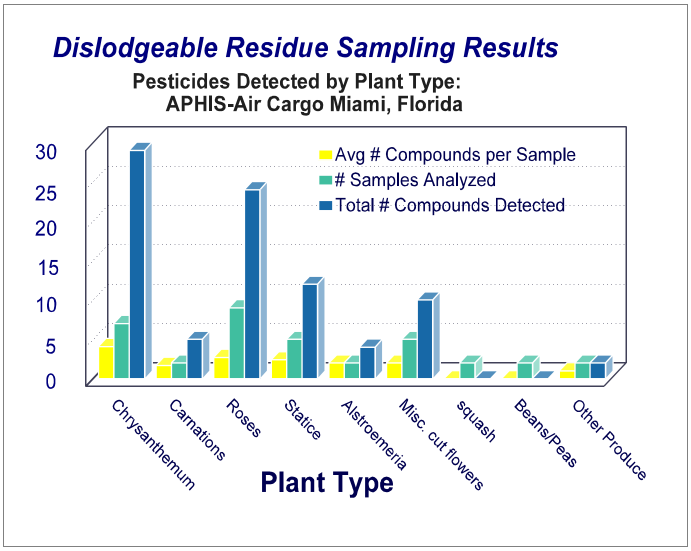

Figure 1

chlorothalonil and metalaxyl (Subdue®) were found on spices imported from Costa Rica.

On the morning (08:00) of May 8, two surface wipe samples were collected from desk tops in the main USDA Cargo office. An area of approximately 0.7 ft^2 (9" X 11") was sampled. The samples were analyzed for the same compounds as the dislodgeable residue samples. No detectable pesticide residue was found on either sample.

Table 6 and Figure 3 categorize the compounds detected by toxicity, based on the Environmental Protection Agency (EPA) toxicity classification method for pesticides. The EPA requires pesticides to be classified and labeled using signal words determined by the level of toxicity. Toxicity is based on oral, inhalation, dermal, eye, or skin effects, with categories ranging from I - IV. Pesticides in toxicity category I are considered the most toxic, and require the signal words **Danger** or **Poison** (if the classification is based on oral, inhalation, or dermal toxicity). Toxicity category IV pesticides are the least toxic, and are required to be labeled with the signal word **Caution**.

As shown in Figure 3, eight (47%) of the twenty compounds detected were toxicity category I pesticides. Six were toxicity category II pesticides, and the number of compounds was equal (3) in the other two categories. Note that this figure depicts the classification for compounds detected on both the dislodgeable residue and the glove samples. Table 6 shows the toxicity category for each compound detected.

Hand Exposure

The glove monitoring results are depicted in Table 4. The results show the total micrograms of contaminant detected on each glove, and a concentration determined by weighting the mass of pesticide detected by the time period the glove was worn (micrograms per hour [µg/hr]). Based on the results of the dislodgeable residue sampling, 10 of the 14 glove pairs (22 gloves) were analyzed for the pesticides detected on their corresponding gauze wipe sample, and in some cases for additional compounds. Glove monitors worn by an APHIS employee applying d-phenothrin in an aircraft were also analyzed.

Residue was detected on all glove samples analyzed. Fourteen different pesticides were found on the glove samples (Figure 4). Several pesticides that were detected on the gauze samples were not found on the glove monitors. Note that the analytical LODs varied considerably (e.g., the LOD for captan was 80X [800 µg] that of benomyl [10 µg]), possibly explaining why some compounds were not detected on the glove samples. The fungicide chlorothalonil and the insecticide carbofuran were detected on all glove monitors, and benomyl was detected on 9 of the 10 glove pairs. The carbofuran results, however, are suspect as one of the blank gloves showed a concentration between the LOD and LOQ of 31 µg.

In addition to compounds found on the gauze samples not found on the corresponding glove sample, some compounds not detected on the gauze wipe samples were found on the corresponding glove sample. For example, carbofuran and cypermethrin were detected on the glove monitors of a USDA-APHIS employee inspecting spices from Costa Rica (sample #106), yet neither of these compounds were detected on gauze wipe #15, which was from this commodity. Further evaluation of the data in Table 4 shows that only 26 of the 52 (50%) compounds detected on the glove samples were also measured on the corresponding dislodgeable residue sample. Possible explanations for this finding include prior hand contamination that transferred to the glove

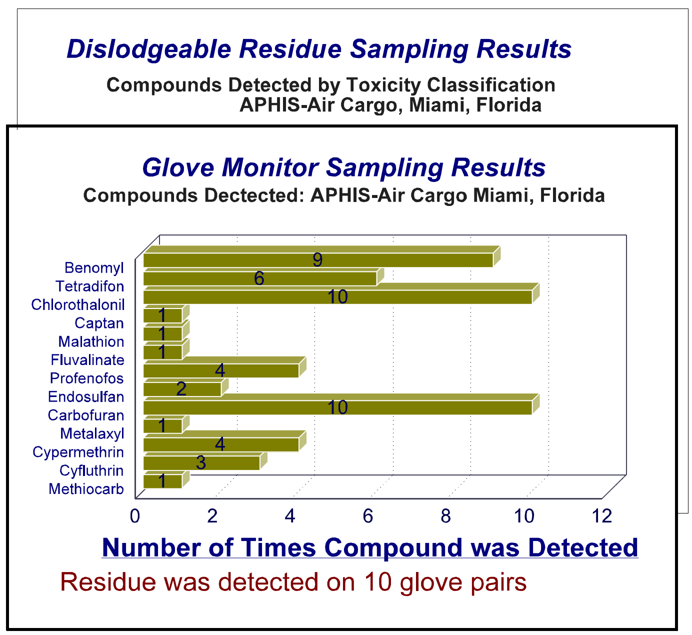

Figure 3

monitor, or that the wipe sample may not be representative of what was present on the commodity. This is likely, as a much larger volume of the commodity is handled during the inspection than is sampled with the gauze wipe.

Furthermore, some compounds not detected on **any** of the dislodgeable residue samples were found on the glove monitors. For example, profenofos was found on glove samples #114 and #115, yet this pesticide was not detected on any gauze wipe samples obtained during Cargo inspections. Note that the gauze wipe samples were not analyzed for some of the compounds detected on the glove samples. Profenofos, cyfluthrin, and cypermethrin were not included in the routine gauze analysis. However, during the additional GC/MSD analysis of certain gauze wipe samples, these compounds were detected on foliar samples collected during the concurrent PIQS project (HETA 95-353-2629). As a result, all glove samples were analyzed for these compounds.

Monitoring conducted during the aerosol application of the pesticide d-phenothrin in the cargo bay of an aircraft (sample #110) indicates that considerable hand exposure occurred during this activity. Additionally, compounds not used (carbofuran, chlorothalonil) were detected on the glove samples. This suggests that prior hand exposure occurred and the contaminants were not successfully removed from the workers' hands. The monitored inspector did not wear protective gloves during the application of d-phenothrin.

Air Sampling

Based on the results of the dislodgeable residue sampling, one of the personal air samples collected during the plant inspection process was analyzed for chlorpyrifos, diazinon, malathion, methamidophos, tetradifon, and profenofos. None of these compounds were detected on any of the air samples. Due to analytical difficulties, no results were obtained from the air sample collected during the application of d-phenothrin in the aircraft cargo bay.

Methyl Bromide Treatment

Contractor personnel are required to wear positive pressure self-contained breathing apparatus (SCBA) when removing the tarps after treatment. Colorimetric detector tubes are used to monitor the treatment area after fumigation to ensure methyl bromide concentrations are below 5 ppm. Per USDA policy, personnel conducting the monitoring are required to wear SCBAs. This monitoring is conducted after the 2 hour aeration. Introduction of the methyl bromide and tarp removal requires two persons to be present. An emergency phone and safety shower are available at the fumigation facility. Warning signs were posted on each side of the perimeter fence.

Maritime Operations

A shipment of produce from Guatemala and the Honduras had recently been unloaded at the Seaboard Marine dock. The shipment consisted of 36 semi-truck trailers, some of which were refrigerated. Two of the four inspectors monitored wore disposable latex or vinyl gloves for protection. The other two employees inspected the produce bare handed. No other PPE was used by the plant inspectors. Both APHIS and Florida Department of Agriculture personnel conducted the inspection, which took approximately 90 minutes to complete. Inspectors worked rapidly, and there was considerable handling of commodities.

Dislodgeable Residue

The results of the dislodgeable residue samples obtained from imported produce are shown in Table 3. Detectable levels of pesticide residues were found on 4 of 10 (40%) samples and six different compounds were detected. Dislodgeable pesticide residues were detected on both of the snow pea samples (Guatemala) and both cantaloupe samples (Guatemala). Conversely, no residues were found on the 3 samples of honey dew melons imported from Guatemala. The highest concentration of residue detected was the fungicide metalaxyl, found on a cantaloupe imported from Guatemala. Three of the six compounds (50%) detected were fungicides.

As with the samples collected from the Cargo inspections, the presence of visible residue was not a good indicator that a pesticide would be detected. Four of the six (67%) compounds detected are toxicity category I pesticides, the other two are classified as category III (metalaxyl) and IV (benomyl) pesticides.

Hand Exposure

Four sets of glove samples (8 gloves) were collected and analyzed from the Maritime inspection. Residue was detected on all glove pairs. Seven different pesticides were detected on the glove samples. Endosulfan compounds were detected on all glove samples, and chlorothalonil was detected on 3 of the 4 glove pairs. Carbofuran was detected on 2 of the 4 glove pairs, but the results were between the analytical LOD and LOQ. The highest concentration detected was metalaxyl (sample # 135).

As with samples collected during the Cargo inspections, there was not a good correlation between compounds detected on the dislodgeable residue samples and the corresponding glove samples. Comparing Table 5 to Table 3 shows that only 11 of the 19 (57%) compounds detected on the glove samples were also measured on the corresponding gauze sample. Some compounds found on the gauze samples were not detected on any of the glove samples (e.g., captan, aldicarb). Other compounds detected on the glove samples were not found on the gauze wipe samples (e.g., chlorothalonil). As previously noted, a large volume of commodity is handled by the inspector and the dislodgeable residue sample may not be representative. Other possible explanations include analytical sensitivity and prior hand contamination that transferred to the glove monitor.

Air Sampling

Because none of the dislodgeable residue samples from the Maritime operations indicated the presence of an organo-phosphate pesticide, the personal air samples collected during this survey were not analyzed.

Methyl Bromide Treatment

USDA-APHIS employee involvement with the Maritime fumigation station primarily entails oversight of the treatment contractors, determining the proper treatment dose and contact time, and monitoring the treatment. Because treatment activity is high (up to 20 treatments daily), an extensive system for monitoring methyl bromide concentrations inside the fumigation tarpaulins has been implemented. The tygon® and polyethylene line from each station are connected to a manifold and pump to convey the sample to the detector. The manifold, located inside the APHIS monitoring trailer, is equipped with manual valves and there is a color-coding and numbering system to enable the operator to chose the correct port to sample. A manual has been developed for operating the gas system. The gas plumbing contains both threaded and barbed fittings. The entire manifold system operates under negative pressure except for the gas lines downstream of the pump (exhaust). The exhaust is routed outside the trailer. The exhaust outlet, however, is adjacent the air intake for the trailer ventilation system. APHIS personnel have direct reading colorimetric detector tubes for monitoring methyl chloride, and SCBA available in the event of an emergency. There is no continuous methyl bromide detector inside the trailer to notify personnel in the event of a leak or entrainment in the ventilation system.

The treatment station is located within a fenced area. However, there were no warning signs posted at the perimeter fence or gate entrance.

CONCLUSIONS

An evaluation was conducted to assess imported commodities (cut flowers and produce) for a broad array of dislodgeable pesticide residues and assess the potential for skin contact and inhalation exposure during plant inspections. The results of this evaluation found that USDA-APHIS Cargo and Maritime plant inspectors are at risk for skin exposure to pesticides while handling imported commodities. Measurable quantities of pesticide residue were found on every glove pair analyzed from the Cargo and Maritime operations. Cut flowers contained considerably more detectable pesticide residue than produce. No measurable pesticides were found on any of the air samples. Because of the low volatility of most pesticides, this was not an unexpected finding. As no inhalation hazard was detected, there is no evidence that respiratory protection is necessary during plant inspections.

Because the cotton glove monitors were worn over the inspector's vinyl or latex glove (when worn), these results only provide information on the potential for exposure if protective gloves were not worn. The efficacy of the disposable gloves to prevent contact with pesticide residues was not evaluated during this project. However, the results of two previous NIOSH HHEs have demonstrated that disposable chemical-resistant gloves can be relied upon to protect a worker's hands from pesticide exposure under certain situations.[33,34]

This evaluation showed that the presence of visible residue or odor on plant material was not a good indicator that a pesticide would be detected. Many of the compounds found on the foliage and glove samples are considered to be highly toxic pesticides (EPA toxicity category 1). Some of the pesticides detected can present a significant hazard from skin contact and can be rapidly absorbed. For example, the fungicide zineb has been associated with chronic skin disease in occupationally exposed workers, possibly due to sensitization.[9] Also, as previously noted, the pesticide aldicarb is considered highly toxic by the dermal route.[14] The EPA has recommended that stringent measures be taken to prevent skin contact with such pesticides.

APHIS employees were aware of the potential for exposure to residual agricultural chemicals on imported commodities and the need to take precautions. However, some employees did not wear gloves during inspections. The decision to wear gloves during an inspection seems to be based on the presence of visible residue or unusual odor. Although these are prudent measures, pesticide contamination can still be present without odor or visible residue, and the senses should not be the sole determinant regarding precautions that should be taken.

The Air-Cargo survey indicates that dislodgable pesticide residues are more prevalent on cut flowers than other commodities routinely inspected. Based on function, fungicides were the most commonly detected type of pesticides found on the commodity samples.

Although there was some correlation, there was not a strong association between compounds detected on the dislodgeable residue samples and the corresponding glove samples. Conversely, some compounds detected on the glove samples were not found on the gauze wipe samples.

Glove monitoring conducted during the fumigation of an aircraft cargo bay indicated considerable hand exposure occurred and that measures to prevent skin contact during this activity are warranted.

Although APHIS employees do not conduct fumigations, their responsibilities for ensuring proper treatment require close contact with methyl bromide applications.

RECOMMENDATIONS

A "universal precautions" approach is recommended when handling all imported commodities during inspections. This approach entails handling all plant materials as if they were contaminated with pesticide residues. Disposable latex or vinyl gloves should be worn when handling all plants and plant products regardless of whether there is visible residue or odor. Employees should be encouraged to thoroughly wash their hands after inspecting plants and prior to consuming food or beverages. Adherence to this policy should be mandatory.

The USDA should establish regulations requiring exporters to identify shipments of off-shore material that have been treated with pesticides. Periodic testing of plant material for pesticide residue should also be conducted. Exporters should be penalized if pesticides are found on materials that have not been identified as being pesticide contaminated. The USDA should establish regulations requiring exporters to identify shipments of off-shore material that have been treated with pesticides. Periodic testing of plant material for pesticide residue should also be conducted. Exporters should be penalized if pesticides are found on materials that have not been identified as being pesticide contaminated.

Protective equipment (gloves, long sleeve shirt and pants) should be worn when cabin fumigation is conducted. Personnel conducting this task should be informed of the potential for skin exposure and the precautions that should be taken.

SWarning signs designating the Maritime treatment station as a methyl bromide use area should be placed on all sides of the perimeter fence and gate. The exhaust line from the gas-reading pump located in the APHIS fumigation monitoring trailer should be re-routed away from the air intake and above the roof level. Rigid PVC piping could be used to accomplish this. The exhaust should be labeled with warning signs.

If possible, the pump and manifold should be maintained in a separately vented area to contain and safely exhaust any releases that may occur. Only gas-tight fittings should be used for the gas plumbing.

Consideration should be given to installing a continuous methyl bromide detector in the fumigation trailer to warn occupants of any leaks. Prior to purchasing any monitor, however, the sensitivity (should be less than 1 ppm), specificity (will not react to other compounds potentially present), reaction time, calibration needs, and vendor support must be carefully evaluated.

REFERENCES

1. Bissel S, Troiano J, Marade J, Grahm E, del Valle M [1991]. Comparison of sampling methods for determination of pesticide residue on leaf surfaces. Bull Environ Contam Toxicol 46:397-403.

2. Hsu J, Schattenberg H, Garza M [1991]. Fast turnaround multiresidue screen for pesticides in produce. J. Assoc. Off. Anal. Chem. 74(5):886-892.

3. Nigg H, Albrigo L, Nordby H, Stamper J [1981]. A method for estimating leaf compartmentalization of pesticides in citrus. J Agric. Food Chem 29:750-756.

4. Iwata Y, Knaak J, Spear R, Foster R [1977]. Worker reentry into pesticide-treated crops. I. procedure for the determination of dislodgeable pesticide residues on foliage. Bull Environ Contam Toxicol 18:649-655.

5. NIOSH [1994]. Organophosphorous pesticides: method 5600. In Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

6. NIOSH [1992]. Recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

7. ACGIH [1996]. 1996 threshold limit values for chemical substances and physical agents and

biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

8. Code of Federal Regulations [1993]. 29 CFR 1910.1000. Washington, DC: U.S. Government Printing Office, Federal Register.

9. EPA [1986]. Pesticide assessment guidelines, subdivision U, applicator exposure monitoring. U.S. Environmental Protection Agency, Washington DC. EPA 540/9-87-127.

10. Mull R, McCarthy J [1986]. Guidelines for conducting mixer-loader studies. Vet Hum Toxicol 28(4):328-336.

11. Leonard J, Yeary R [1990]. Exposure of workers using hand-held equipment during urban application of pesticides to trees and ornamental shrubs. Am Ind Hyg Assoc J 51(11):605-609.

12. Brouwer R, van Maarleveld K, Ravensber L, Meuling W, de kort W, van Hemmen J [1993]. Skin contamination, airborne concentrations, and urinary metabolite excretion of propoxur during harvesting of flowers in greenhouses. Amer. J. Ind. Med. 24:593-603.

13. Fenske R, Bimbaum S, Methner M, Soto R [1989]. Methods for assessing fieldworker hand exposure to pesticides during peach harvesting. Bull. Environ. Contam. Toxicol. 43:805-813.

14. Doull J, Klaassen C, Amdur MO, eds. [1980]. Casarett and Doull's toxicology: the basic science of poisons, 2nd Ed. New York, NY: Macmillan Publishing Company, Inc.

15. EPA [1996]. Office of pesticide programs annual report for 1996. United States Environmental Protection Agency. EPA 735R96001.

16. Gallo MA, Lawryk NJ [1991]. Organic phosphorus pesticides. Chapter 16. In: Hayes WJ, Jr., Laws ER, Jr, eds. Handbook of Pesticide Toxicology. Vol. 2, Classes of pesticides. San Diego, CA: Academic Press, Inc.

17. EPA [1989], Recognition and management of pesticide poisonings. Washington, DC: U.S. Environmental Protection Agency, Health Effects Division, Office of Pesticide Programs. EPA Publication EPA-540/9-88-001.

18. ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th. ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

19. Ruth JH [1986]. Odor thresholds and irritation levels of several chemical substances: a review. Am Ind Hyg Assoc J *47*:A142-A151.

20. NIOSH [1978]. Occupational safety and health guidelines for chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 81-123.

21. 54 (12) Fed. Reg [1989]. Occupational Safety and Health Administration: air contaminants; final rule.

22. Methyl Bromide 100 [1994]. Commodity fumigant label: methyl bromide. EPA Registration # 8536-15-8853. Hendrix and Dail, Inc., Greenville, North Carolina.

23. Meth-O-Gas [1987]. Methyl bromide pesticide label and use directions. EPA Registration # 5785-11, 5785-41. Great Lakes Chemical Corporation, West Lafayette, Indiana.

24. Hine CH [1969]. Methyl bromide: a review of ten cases. J Occup Med *11*:1-10.

25. Roosels D, Van Den Oever R, Lahaye D [1981]. Dangerous concentrations of methyl bromide used as a fumigant in belgian greenhouses. Int Arch Occup Environ Health *48*:243-250.

26. Van Den Oever R, Roosels D, Lahaye D [1982]. Actual hazard of methyl bromide fumigation in soil disinfection. Br J Ind Med *39*:140-144.

27. Herzstein J, Cullen MR [1990]. Methyl bromide intoxication in four field-workers during removal of soil fumigation sheets. Am J Ind Med *17*:321-326.

28. Anger WK, Moody L, Burg J, Brightwell WS, Taylor BJ, Russo JM, et al [1986]. Neurobehavioral evaluation of soil and structural fumigators using methyl bromide and sulfuryl fluoride. Neurotoxicology *7*:137-156.

29. Alexeeff GV, Kilgore WW [1983]. Methyl bromide. Residue Rev *88*:101-153.

30. Torkelson TR [1994]. Halogenated aliphatic hydrocarbons containing chlorine, bromine, and iodine. Chapter 38. In: Clayton GD, Clayton FE, eds. Pattys industrial hygiene and toxicology. 4th. ed. Vol IIE, Toxicology, New York, NY:John Wiley and Sons, Inc. Pp4022-4029.

31. NIOSH [1984]. Current intelligence bulletin #43: Monohalomethanes (methyl chloride, methyl bromide, methyl iodide). Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-117.

32. California EPA [1996]. Review of restrictions on the use of methyl bromide: a report to the legislature. California Environmental Protection Agency, Department of Pesticide Regulation. November.

33. NIOSH [1992]. Hazard evaluation and technical assistance report: Green Circle Growers, Inc., Oberlin, OH. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. NIOSH Report No. HETA 92-0022-2327.

34. NIOSH [1994]. Hazard evaluation and technical assistance report: Florida Department of Agriculture and Consumer Services, Gainesville, Florida, Miami, Florida. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. NIOSH Report No. HETA 94-0096-2433.

HETA 96-083

DATA TABLES

Table 1
USDA Animal and Plant Inspection Service
Foliage Sampling (Gauze Wipe) Results
May 7, 1996

#	Sample Description	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
		Compounds Detected in Micrograms **- see coding key at the bottom of the table for compound identification. Blank space indicates compound not detected, X = compound was detected via GC/MS but not quantified**																		
29	Cut Chrysanthemums from Columbia (visible residue)	8.7							(130)		(21)									
30	Cut Carnations from Columbia (visible residue, wet)						170													
31	Cut Roses from Columbia (visible residue)								(180)			(250)								
32	Cut Chrysanthemums from Columbia	440					2200		340											
33	Cut Statice from Columbia						110		X								X		X	
34	Squash from Honduras (visible residue)																			
15	Basil/Spices from Costa Rica	0.36									82									
17	Cut Roses from Bolivia	130					480					(77)								
16	Cut Roses from Columbia (visible residue)																			
18	Cut Carnations from Columbia						800							11						
19	Cut Chrysanthemums from Columbia	900				0.38	3500	58	800			(61)								
20	Cut Alstroemeria from Columbia						48	160												
21	Cut Statice from Columbia						280		590		(35)									
22	Solidaster from Columbia	370				2.5	1100				45	(120)								
23	Cut Roses from Columbia	5.5		4.3			190		630											
24	Cut Chrysanthemums from Trinidad, W.I.																			
1	Cut Chrysanthemums from Costa Rica (visible residue)	4.7					170		(300)											

Table 1
USDA Animal and Plant Inspection Service
Foliage Sampling (Gauze Wipe) Results
May 7, 1996

#	Sample Description	***Compounds Detected in Micrograms*** **- see coding key at the bottom of the table for compound identification. Blank space indicates compound not detected, X = compound was detected via GC/MS but not quantified**																		
		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
2	Bird of Paradise from Costa Rica (visible residue)						(23)													
3	Scarlet Heliconia from Costa Rica (visible residue)	(0.28)													20					
9	Cut Statice from Columbia (visible residue)	28					66													
10	Cut Roses from Columbia						56													
11	Cut Gypophillia from Columbia	0.55																		
4	Cut Statice from Columbia						160		(170)											
5	Cut Gipsy Dianthus from Columbia						57													
6	Cut Alstroemeria from Columbia	68					190													
8	Cut Roses from Columbia						95													

Compound Codes:

A = Chlorothalonil B = Endosulfan I C = Endosulfan II D = Endosulfan Sulfate E = Endrin-Ketone F = Benomyl G = Carbofuran
H = Captan I = Fluvalinate J = Metalaxyl K = Aldicarb L = Tetradifon M = Chlorpyrifos N = Malathion
O = Diazinon P = Methiocarb Q = Dodemorph R = Vinclozolin S = Zineb

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

Table 2
USDA Animal and Plant Inspection Service
Foliage Sampling (Gauze Wipe) Results
May 8, 1996

#	Sample Description	***Compounds Detected in Micrograms*** **- see coding key at the bottom of the table for compound identification. Blank space indicates compound was not detected for that sample, X = compound was detected via GC/MS but not quantified**																		
		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
36	Squash from Dominican Republic																			
14	Green Beans from Guatemala																			
35	Snow Peas from Guatemala																			
40	Cut Chrysanthemums from Columbia	940	6.9	11		0.58	5400	51	940	9.9						(1.9)				
37	Cut Carnations from Columbia						450				(13)									
38	Cut Roses from Columbia	72					1000		(140)		(31)									
39	Cut Roses from Columbia											(270)								
41	Cut Chrysanthemums (Sunflower) from Columbia	35					120		(470)				X							X
70	Cut Roses from Columbia	X	(0.1)	0.26			200		X	(21)								X		X
82	Cut Statice from Columbia	11																		
81	Blackberries from Guatemala																			

Compound Codes:

A = Chlorothalonil B = Endosulfan I C = Endosulfan II D = Endosulfan Sulfate E = Endrin-Ketone F = Benomyl G = Carbofuran
H = Captan I = Fluvalinate J = Metalaxyl K = Aldicarb L = Tetradifon M = Chlorpyrifos N = Malathion
O = Diazinon P = Methiocarb Q = Dodemorph R = Vinclozolin S = Zineb

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

Table 3
USDA Animal and Plant Inspection Service : Maritime Operations
Foliage Sampling (Gauze Wipe) Results
May 9, 1996

Compounds Detected in Micrograms **- see coding key at the bottom of the table for compound identification.**
Blank space indicates compound was not detected for that sample, X = compound was detected via GC/MS but not quantified

#	Sample Description	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
76	Cantaloupe from Guatemala						100													
77	Honey Dew melons from Guatemala																			
78	Palm fronds from Guatemala (visible residue)																			
79	Snow Peas from Guatemala (visible residue)								(220)		(52)									
80	Green Onions from Guatemala																			
25	Squash from Honduras																			
26	Snow Peas from Guatemala						41	(13				(110)								
27	Cantaloupe from Guatemala (visible residue)				0.2						2200									
M-1	Honey Dew melon from Guatemala																			
28	Honey Dew melon from Guatemala																			
83	Blank	X													X					X
7	Blank																			
42	Blank																			
B-1	Blank																			
B-2	Blank																			

Compound Codes:

A = Chlorothalonil B = Endosulfan I C = Endosulfan II D = Endosulfan Sulfate E = Endrin-Ketone F = Benomyl G = Carbofuran
H = Captan I = Fluvalinate J = Metalaxyl K = Aldicarb L = Tetradifon M = Chlorpyrifos N = Malathion
O = Diazinon P = Methiocarb Q = Dodemorph R = Vinclozolin S = Zineb

() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)

Table 4
USDA Animal and Plant Inspection Service: Cargo Operations
Glove Monitoring Results
May 7-8, 1996

#	*Sample Description*	*Sampling Period (min)*	*Corresponding Foliage Sample*	*Compounds Detected*	*Concentration Detected*			
					Right		*Left*	
					µg	*µg/hr*	*µg*	*µg/hr*
107	Inspecting cut flowers (roses, chrysanthemums, carnations, statice) from Columbia at the Challenge Air Cargo Warehouse.	08:39-09:21 (42)	Gauze # 29-33	Profenofos	(4)	(5.7)	(5)	(7.1)
				Benomyl	41	59	63	90
				Chlorothalonil	12	17	50	71
				Endosulfan II	(0.11)	(0.16)	ND	NA
				Tetradifon	6.4	9.1	8.8	12.6
				Carbofuran	(10)	(7.1)	(21)	(30)
106	Inspecting spices (e.g., basil) from Costa Rica at the Challenge Air Cargo Warehouse	09:29-09:46 (17)	Gauze # 15	Carbofuran	(21)	(74)	ND	NA
				Cypermethrin	15	53	9.3	32.8
				Chlorothalonil	1.3	4.6	0.6	2.1
				Metalaxyl	(120)	(423)	ND	NA
108	Inspecting cut flowers (roses, chrysanthemums, carnations, statice) from Columbia at the ATC Warehouse.	13:21-14:10 (49)	Gauze # 16, 18-23	Chlorothalonil	390	478	370	453
				Cyfluthrin	7.8	9.6	8.8	10.8
				Benomyl	120	147	170	208
				Carbofuran	(30)	(37)	(33)	(40)
				Cypermethrin	16	20	16	20
				Fluvalinate	17	21	17	21
				Tetradifon	3.5	4.3	3.1	3.8
110	Fumigating cargo bay of aircraft with d-phenothrin	12:14-12:22 (8)	NA	d-phenothrin	6100	45750	1200	9000
				Carbofuran	(39)	(29)	ND	NA
				Chlorothalonil	ND	NA	(0.096)	(0.72)
113	Inspection of cut flowers and blackberries from Costa Rica at the Lacsa Warehouse and Distribution Center. Approximately 100 boxes inspected.	09:15-10:00 (45)	Gauze # 1-3	Chlorothalonil	20	27	(0.058)	(0.08)
				Malathion	20	27	8.2	10.9
				Tetradifon	3.0	4	2.4	3.2
				Benomyl	61	81	58	77
				Carbofuran	(21)	(28)	(14)	(19)
				Cypermethrin	4.8	6.4	4.9	6.5

Table 4
USDA Animal and Plant Inspection Service: Cargo Operations
Glove Monitoring Results
May 7-8, 1996

#	Sample Description	Sampling Period (min)	Corresponding Foliage Sample	Compounds Detected	Concentration Detected: Right µg	Right µg/hr	Left µg	Left µg/hr
101	Inspection of cut flowers from Columbia at the Fresco Warehouse. Many different brokers represented. Approximately 45 boxes of cut flowers inspected.	13:30-14:04 (34)	Gauze # 9-11	Benomyl	210	370	93	164
				Methiocarb	(93)	(164)	ND	NA
				Chlorothalonil	290	512	150	265
				Cyfluthrin	16	28	ND	NA
				Tetradifon	3.9	6.9	2.4	4.2
				Carbofuran	ND	NA	(16)	(28)
102	Inspection of cut flowers from Columbia at the Fresco Warehouse. Many different brokers represented. Approximately 45 boxes of cut flowers inspected.	13:30-14:04 (34)	Gauze # 9-11	Chlorothalonil	92	162	89	157
				Benomyl	(31)	(55)	(30)	(53)
				Endosulfan I	0.6	11	0.25	0.44
				Endosulfan II	2.6	4.6	1.2	2.1
115	Inspection of cut flowers from Columbia at the Arca Warehouse and Distribution Center. 21 boxes inspected.	10:42-11:10 (28)	Gauze # 4-6, 8	Benomyl	ND	NA	(14)	(30)
				Carbofuran	(18)	(39)	(24)	(51)
				Profenofos	(6)	(13)	(4)	(9)
				Chlorothalonil	4.7	10.1	1.5	3.2
114	Inspection of cut flowers from Columbia at the Arca Warehouse and Distribution Center. 21 boxes inspected	10:42-11:10 (28)	Gauze # 4-6, 8	Chlorothalonil	13	28	13	38
				Profenofos	(4)	(9)	(4)	(9)
				Benomyl	86	184	56	120
				Carbofuran	ND	NA	(10)	(21)
105	Inspection of cut flowers from Columbia at the ATC warehouse. Many different farms represented. 19 boxes inspected	11:10-11:30 (20)	Gauze #37-40	Profenofos	(5)	(15)	(5)	(15)
				Benomyl	470	1410	360	1080
				Carbofuran	(19)	(57)	(26)	(78)
				Chlorothalonil	0.86	2.58	8.9	36.7
				Tetradifon	ND	NA	6.2	18.6

Table 4 USDA Animal and Plant Inspection Service: Cargo Operations Glove Monitoring Results May 7-8, 1996								
#	*Sample Description*	*Sampling Period (min)*	*Corresponding Foliage Sample*	*Compounds Detected*	*Concentration Detected*			
					Right		*Left*	
					µg	*µg/hr*	*µg*	*µg/hr*
129	Inspection of cut flowers from Columbia at the Fresco Distributors Warehouse. Many different farms represented. Approximately 60 boxes inspected	14:05-14:40 (35)	Gauze # 41,70, 82	Benomyl	220	377	240	411
				Carbofuran	(13)	(22)	(31)	(53)
				Captan	ND	NA	(1000)	(1714)
				Chlorothalonil	160	274	220	377
				Cyfluthrin	(3.6)	(6.2)	ND	NA
				Cypermethrin	15	26	12	21
				Fluvalinate	11	19	8.7	14.9
				Tetradifon	6.5	11.1	5.2	8.9

Note: Sampling glove monitors were worn **over** latex/vinyl glove worn by workers
µg/hr = micrograms of contaminant per hour
() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)
ND = None Detected

Table 5
USDA Animal and Plant Inspection Service: Maritime Operations
Glove Monitoring Results
May 8, 1996

#	*Sample Description*	*Sampling Period (min)*	*Corresponding Foliage Sample*	*Compounds Detected*	*Concentration Detected*			
					Right		*Left*	
					µg	*µg/hr*	*µg*	*µg/hr*
112	Inspecting shipments of fruits and vegetables from Guatemala and the Honduras	09:23-10:20 (57)	Gauze # 76-80,25-28, M-1	Chlorothalonil	ND	NA	(0.087)	(0.091)
				Endosulfan I	0.28	0.29	0.39	0.41
				Endosulfan II	0.59	0.62	0.72	0.76
				Endosulfan Sulfate	ND	NA	(0.084)	(0.088)
133	Inspecting shipments of fruits and vegetables from Guatemala and the Honduras	09:19-10:56 (97)	Gauze # 76-80,25-28, M-1	Benomyl	(24)	(14.8)	(23)	(14.2
				Carbofuran	ND	NA	(18)	(11.1)
				Chlorothalonil	0.18	0.11	0.43	0.27
				Endosulfan I	0.33	0.20	0.69	0.42
				Endosulfan II	1.1	0.68	1.1	0.68
134	Inspecting shipments of fruits and vegetables from Guatemala and the Honduras	09:19-10:57 (98)	Gauze # 76-80,25-28, M-1	Chlorothalonil	0.25	0.15	0.16	0.1
				Endosulfan I	0.24	0.15	0.23	0.14
				Endosulfan II	0.50	0,31	0.48	0.29
				Endosulfan Sulfate	(0.11)	(0.07)	0.14	0.09
				Carbofuran	ND	NA	(23)	(14)
135	Inspecting shipments of fruits and vegetables from Guatemala and the Honduras	09:17-10:58 (101)	Gauze # 76-80,25-28, M-1	Benomyl	(21)	(12)	(15)	(9)
				Carbofuran	ND	NA	(12)	(7)
				Metalaxyl	(92)	(55)	740	440
				Endosulfan I	(0.12)	(0.06)	(0.11)	(0.07)
				Endosulfan II	0.29	0.17	0.25	0.15

Note: Sampling glove monitors were worn **over** latex/vinyl glove worn by workers
µg/hr = micrograms of contaminant per hour
() = Values in parentheses represent concentrations between the analytical level of detection (LOD) and level of quantification (LOQ)
ND = None Detected

Table 6 USDA - Animal and Plant Inspection Service Information on Compounds Detected on Imported Plants (foliage and glove samples)							
Compound Detected	Pesticide Action	EPA Toxicity Classification *	Compound Classification				
			Organophosphate	Carbamate	Pyrethroid	Organochlorine	Other[17]
Chlorpyrifos	Insecticide	II	X				
Diazinon	Insecticide/Nematicide	II or III	X				
Malathion	Insecticide	III	X				
Chlorothalonil	Fungicide	I				X	
Metalaxyl	Fungicide	III					Organic Fungicide
Captan	Fungicide	I					Thiophthalimide
Carbofuran	Insecticide/Nematicide	I		X			
Methiocarb	Insecticide/Acaricide	I		X			
Aldicarb	Insecticide/Nematicide	I		X			
Tetradifon	Acaricide	III				X	
Dodemorph**	Fungicide	II					Organic Fungicide
Benomyl	Fungicide	IV					Benzimadizole
Vinclozolin	Fungicide	IV				X	
Zineb	Fungicide	IV					Ethylene Bis Dithiocarbamate
Fluvalinate	Insecticide	I			X		
Endrin	Insecticide	I				X	
Cypermethrin	Insecticide	II			X		
Profenofos	Insecticide/Acaricide	II	X				
Cyfluthrin	Insecticide	II			X		
Endosulfan	Insecticide/Acaricide	I				X	

** Dodemorph manufacture has been discontinued. Dodemorph acetate is available Place Figures and Tables Here for Initial Review:

The EPA has established toxicity categories for pesticides based on oral, inhalation, and dermal toxicity, and eye and skin effects. The categories range from I (highly toxic) to IV (least toxic). These toxicity designations dictate the necessary hazard warnings on pesticide labels (e.g., danger, warning, caution, etc.). Classifications for the same compound may vary depending on the formulation.

Appendix A

Dislodgeable Residue and Glove Monitor Sampling

Assessing the presence of unknown pesticide residues on foliar surfaces presented a significant analytical challenge. Pesticide chemistry is complex because there are many types of pesticides in numerous chemical classes and no single analytical method is available to assess a sample for "all" potential pesticides. As such, the sampling and analytical method(s) conducive to measuring the largest number of pesticides at a reasonable sensitivity had to be determined. Methods for sampling dislodgeable pesticide residue from leaf surfaces have been previously developed and generally consist of leaf punch, whole leaf, or leaf wipe sampling.[1,2] Measuring dislodgeable residue is useful for worker exposure assessments (estimation of the amount of dislodgeable pesticide residue that could be transferred to workers) and for the establishment of re-entry intervals.[3,4,5,6] Studies investigating the relationship between dislodgeable foliar residue and dermal exposure have been conducted and in some cases transfer factors (from leaves to hands) have been calculated.[4,7]

The most widely referenced foliar sampling technique entails the collection of a known surface area of leaves using a leaf punch (Birkestrand Precision Sampler Punch) that allows the sample jar to be attached directly to a collection jar containing a surfactant.[2] Most dislodgeable foliar residue studies, however, have focused on measuring only a small number of pesticides that were known to have been applied, as opposed to the assessment of a large number of unknown contaminants. The advantage of the leaf punch method is that the area sampled is easily measured and standardized, and residue measurements can be reported in a mass of contaminant/leaf area unit. This allows for ready comparison with other samples. In general, the surface area sampled can only be approximated when using the wipe sampling method.

During a field trial conducted in February, 1995, dislodgeable residue samples were collected from ornamental plants at a greenhouse with a documented history of pesticide applications (volume, date, application method). Several classes of pesticides had recently been applied (organochlorine, organophosphate, and pyrethroid), ranging from over 1 month to a few days prior to sample collection. For each trial, samples were collected from each plant (when possible) or an adjacent plant, that consisted of the following sample set:

<u>Pre-extracted 3" X 3" cotton gauze</u>

1. One leaf wiped (both sides) using commercially available 70% isopropyl alcohol
2. 10 leaves wiped (both sides) using commercially available 70% isopropyl alcohol
3. One leaf wiped (both sides) using technical-grade 99% isopropyl alcohol
4. 10 leaves wiped (both sides) using technical-grade 99% isopropyl alcohol

<u>Leaf Tissue Sampling</u>

1. One 5 cm^2 leaf punch
2. Ten 5 cm^2 leaf punches

The leaf samples were obtained using a Birkestrand Precision Sampler Punch that allows the sample jar to be attached directly to the punch as previously described. No surfactant or solution was added to the leaf punch samples. The punch cutting area was cleaned between sample collections.

For each sample, the plant type, country of origin, presence of any visible residue or odor, and any shipping notations of pesticide applications were recorded. Samples were placed in labeled amber jars and stored in a freezer prior to shipment, and were shipped cold via overnight express to the NIOSH contract laboratory (Data Chem, Salt Lake City, UT) for analysis.

The results of this trial indicated the gauze wipe technique was more sensitive than the leaf punch method. It was not determined if this was due to removal efficiency, unequivalent surface area sampled, or analytical sensitivity (the LODs for the leaf punch samples were higher than the gauze samples). Although there did not seem to be much difference between the commercially available isopropyl alcohol (IPA) and the technical grade IPA, the use of technical grade IPA did have certain advantages. For instance, compounds that are particularly water soluble would be difficult to extract from 70% IPA, and the 99% IPA would be compatible with almost any other organic solvent used in the analysis, increasing the options available to the chemist. Additionally, this trial showed that wiping ten leaves instead of one leaf significantly improved the chance of detecting residue.

Based on this field evaluation, and the HHE objectives (detecting residue was more important than quantification), the gauze wipe technique using 3" X 3" pre-extracted polyester gauze (NuGauze®) moistened with technical grade IPA and wiping both sides of 5 leaves was determined to be the optimum method for this project. Recovery studies showed NuGauze® to be superior to cotton gauze for this technique.

Analytical Methods Summary

Dislodgeable Residue (Gauze) Sampling

All gauze wipe samples were left in their shipping bottle and desorbed with 25 ml. IPA. Each sample was then tumbled from 4 (carbamate) to 8 (organo-chlorine and organo-phosphate) hours. Aliquots from each sample were analyzed by three separate techniques. The foliage samples were analyzed for 60 separate pesticides.

1. Organochlorine pesticide screen using gas chromatography with electron capture detection.
2. Organo-phosphate pesticide screen via NIOSH method 5600 (modified) using gas chromatography with flame photometric detection.
3. Carbamate and selected pyrethroid pesticides, captan and metalaxyl using high performance liquid chromatography with ultraviolet absorbance detection (variable wavelength).

Media blanks and media spikes were prepared by the same techniques used for preparing the samples. For the media spikes, liquid standards were used to spike the gauze samples with various amounts of pesticides and the average recoveries were determined. Additional compounds were suspected to be present on some of the samples and a separate aliquot from these samples were further analyzed by gas chromatography/mass spectroscopy (GC/MS). These samples were selected on the basis of unique and relatively intense unknown peaks from the three analytical methods. This analysis was qualitative only and no LODs were calculated.

Compounds Measured on Foliage Samples: (LOD and LOQ units are micrograms per sample):

Compound	LOD	LOQ	Compound	LOD	LOQ
Aldicarb	30	120	Benomyl	10	41
Carbaryl	6	21	Carborfuran	10	45
Oxamyl	40	140	Fluvalinate*	10	42
Fluvalinate**	0.4	1.2	Bifenthrin*	20	83
Bifenthrin**	0.9	3.1	Azinphos Methyl	200	230
Bolstar	20	52	Chlorpyrifos	8	25
Coumaphos	60	160	Demeton	6	18
Diazinon	1	4.3	Dichlorvos	9	28
Dimethoate	5	16	Disulfoton	10	31
EPN	7	26	Ethoprop	6	19
Fenamiphos	90	210	Fensulfothion	30	83
Fenthon	2	5.2	Malathion	7	22
Merphos	40	72	Mevinphos	2	6.4
Monocrotophos	3	78	Naled	9	29
Parathion	4	12	Methyl Parathion	2	5.1
Phorate	10	42	Ronnel	7	22
Captan	100	430	Metalaxyl	10	42
Stirophos	2	5	TEPP	50	130

Compounds Measured on Foliage Samples: (LOD and LOQ units are micrograms per sample):					
Compound	LOD	LOQ	Compound	LOD	LOQ
TPP	100	240	Tokuthion	20	47
Trichloronate	8	25	Aldrin	0.03	0.083
α-BHC	0.03	0.083	β-BHC	0.04	0.14
δ-BHC	0.03	0.083	Lindane	0.03	0.083
α-Chlordane	0.04	0.13	γ-Chlordane	0.03	0.11
4,4'-DDD	0.03	0.083	4,4'-DDE	0.03	0.10
4,4'-DDT	0.03	0.083	Dieldrin	0.03	0.084
Endosulfan I	0.04	0.13	Endosulfan II	0.04	0.13
Endosulfan Sulfate	0.03	0.085	Endrin	0.03	0.092
Endrin Aldehyde	0.04	0.15	Heptachlor	0.03	0.083
Heptachlor Epoxide	0.04	0.13	Methoxychlor	0.03	0.10
Mirex	0.3	0.96	Chlorothalonil	0.1	0.4
Endrin Ketone	0.03	0.11	Toxaphene	NA	NA

NOTE: Toxaphene is a multi-component analyte which is identified by a specific pattern and quantified by summation of the most prominent peaks. Therefore, only one standard for Toxaphene was prepared to screen the samples and an LOD and LOQ could not be calculated.

The LODs and LOQs varied somewhat for each sample run, and there were four sample runs for each analytical technique. The above listed values are representative of one sample run.

* = HPLC/UV Analytical Method
** = GC/ECD Analytical Method.

Glove Samples

Quality control studies indicated that pre-extracted 65%/35% polyester/cotton glove monitors would provide better recoveries and gloves made of this material were used for the survey. At the laboratory, the gloves were left in their shipping bottle and desorbed with 40 ml. of technical grade IPA. The samples were then tumbled for 3 hours and refrigerated at 0-4° C until the analyses were completed. The samples were analyzed for the compounds detected on the corresponding gauze sample, and in some cases for additional compounds. Analysis, as follows, was similar to that used for the gauze samples.

1. Organochlorine pesticide screen using gas chromatography with electron capture detection.
2. Organo-phosphate pesticide screen via NIOSH method 5600 (modified) using gas chromatography with flame photometric detection.
3. Carbamate and selected pyrethroid pesticides, captan and metalaxyl using high performance liquid chromatography with ultraviolet absorbance detection (variable wavelength).
4. Dodemorph and Propargite using GC/MS via EPA method 8270 for semivolatiles.

Media samples were prepared by spiking new gloves with known concentrations and analyzing them in duplicate, along with the samples and media blanks. Desorption efficiencies were determined.

LOD/LOQs for the compounds measured on the glove samples were as follows. **Note: not all glove samples were analyzed for all compounds**:

Compound	LOD (µg/glove)	LOQ (µg/glove)
Chlorpyrifos	2	6.6
Diazinon	5	15
Malathion	2	6.6
Methamidophos	10	46
Profenofos	4	11
Aldicarb	60	200
Benomyl[1]	10	33
Captan	800	2700
Bifenthrin	20	72
Carbaryl	20	78
Oxamyl	80	280
Carbofuran	10	43
Fluvalinate[2]	200	670
Fluvalinate[3]	0.8	2.7
Metalaxyl	90	290
Methiocarb	70	230
d-Phenothrin[2]	100	390
d-Phenothrin[3]	80	260
Chlorothalonil	0.04	0.13
Endosulfan I	0.04	0.13
Endosulfan II	0.04	0.13
Endosulfan Sulfate	0.04	0.13
Endrin Ketone	0.04	0.13
Tetradifon	0.2	0.66
Cyfluthrin	2	3.8
Cypermethrin	1	2.1
Dodemorph	20	81
Propargite	30	110

Footnotes
1 = as carbendazim (breakdown product)
2= HPLC/UV analytical method
3 = GC/ECD analytical method

Appendix A - References

1. Bissel S, Troiano J, Marade J, Grahm E, del Valle M [1991]. Comparison of sampling methods for determination of pesticide residue on leaf surfaces. Bull Environ Contam Toxicol 46:397-403.

2. Iwata Y, Knaak J, Spear R, Foster R [1977]. Worker reentry into pesticide-treated crops. I. procedure for the determination of dislodgable pesticide residues on foliage. Bull Environ Contam Toxicol 18:649-655.

3. Nigg H, Albrigo L, Nordby H, Stamper J [1981]. A method for estimating leaf compartmentalization of pesticides in citrus. J Agric. Food Chem 29:750-756.

4. Brouwer R, van Maarleveld K, Ravensber L, Meuling W, de Kort W, van Hemmen J [1993]. Skin contamination, airborne concentrations, and urinary metabolite excretion of propoxur during harvesting of flowers in greenhouses. Amer. J. Ind. Med. 24:593-603.

5. Liesivuori J, Liukkonen S, Pirhonen P [1988]. Reentry intervals after pesticide application in greenhouses. Scand J Work Environ Health 14 (suppl1.)35-36.

6. Zweigh G, Gao R, Popendorf [1981]. Simultaneous dermal exposure to captan and benomyl by strawberry harvesters. J. Agricl. Food Chem. 31:1109-1113.

7. Brouwer D, Brouwer R, de Mik G, Maas C, van Hemmen J [1992]. Pesticides in the cultivation of carnations in greenhouses: Part II - relationship between foliar residues and exposures. Am. Ind. Hyg. Assoc. J. 53(9):582-587.

Appendix B

USDA HETA 96-0083
Pesticide List

Possible compounds applied to imported commodities

Pesticide	Compound Class	Reason for Selection
Aldicarb (Temik®)	Carbamate	1,2,3
Mirex	Organo-chlorine	1,2
Lindane	Organo-chlorine	1,2
Endosulfan	Organo-chlorine	1,2,3
Benomyl (Benlate®)	Benzimidazole	1
Carbaryl (Sevin®)	Carbamate	1,3
Carbofuran	Carbamate	1,2
Chlorothalonil (Daconil®)	Substituted Benzene	1,3
Oxamyl (Vydate®)	Carbamate	1,2,3
Fenamiphos	Organo-phosphate	1,2,3
Diazinon	Organo-phosphate	3
Dimethoate (Cygon®)	Organo-phosphate	3
Fluvalinate (Mavrik®)	Pyrethroid	2,3
Chlorpyrifos (Dursban®)	Organo-phosphate	3
Bifenthrin (Talstar®)	Pyrethroid	3

NOTE

1 = Pesticide was a high-volume import into a Central-American Country

Duszeln, J [1991]. Pesticide contamination and pesticide control in developing countries: costa rica, central america. In: Richardson, M, ed. Chemistry, Agriculture and the Environment. RSC.

2 = Pesticide is considered to have a high order of toxicity (EPA Toxicity Classification I).

3 = Pesticide is recommended for use in the ornamental plant industry.

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