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THE USE OF PREHARVEST INTERVALS, POSTHARVEST WASH TREATMENTS, AND PROCESSING IN THE REMOVAL OF PESTICIDES FROM APPLE FRUIT.

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THE USE OF PREHARVESTS INTERVALS, POSTHARVEST WASH TREATMENTS, AND PROCESSING IN THE REMOVAL OF PESTICIDES FROM APPLE FRUIT

By

Matthew Dell Siler

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ABSTRACT

THE USE FO PREHARVEST INTERVALS, POSTHARVEST WASH TREATMENTS, AND PROCESSING IN THE REMOVAL OF PESTICIDES FROM APPLE FRUIT

By

Matthew Dell Siler

The objective of this study was to determine the effectiveness of preharvest intervals (PHI), postharvest wash treatments, and processing on pesticide residues in raw and processed apple fruits.

Field studies conducted over a three year period, sprayed Golden Delicious apples with label rates of the pesticides captan and azinphosmethyl. Spray treatments were altered to study the effects of PHI on residue levels. Treated apples were subjected to six different postharvest wash treatments: (1) 21° C and pH 7; (2) 21° C and pH 11; (3) 43° C and pH 7; (4) 43° C and pH 11; (5) 21° C and pH 7, 500 ug/g Chlorine; (6) 21° C and pH 7, 2% Sodium Dodecyl Sulfate (SDS). This was followed by processing into four different products (peeled and unpeeled applesauce, juice, and slices).

The following postharvest wash variables were found most effective in the removal of the two pesticides: pH 11, 43° C, chlorine, SDS, and a longer wash time. The combination of postharvest wash treatments and processing resulted in high reductions of both pesticides for all products.

DEDICATED TO

My parents, Lorraine and Dell Siler, and my Grandmother, Mrs. Ethelyn Siler,

for thier love, support and guidance through the years ...

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INTRODUCTION

Consumer demand for food with good sensory quality has continued to sustain the use of pesticides and made them a key component of agricultural technology. Pesticide use provides numerous benefits in terms of increased production and product quality but can also be expected to result in residues in food (Lombardo, 1989). It is therefore necessary to confirm that fresh and processed fruits and vegetables are free of excessive pesticide residues.

Fruits and vegetables are often subjected to a number of different processing operations to clean, eliminate waste, and to make the raw materials more palatable. While these procedures may actually help reduce or remove pesticide residues, other processing methods have been specifically designed for such purposes. Washing including rinsing is, perhaps, the one unit operation common to the preparation of nearly all fruits and vegetables for processing (Geisman, 1975). While washing is a common practice among the processing industry, the specific methodologies used varies among processors. Chemical and physical aspects of wash treatments (i.e. temperature, detergents, pH, chlorine, wash time) are often manipulated to produce optimum results. Washing of the fruits and vegetables is most often followed by further physical manipulation of the items into a desired product. Commonly encountered technigues include peeling, trimming, blanching, juicing, and slicing. The net influence of processing almost always results in residue levels in processed foods well below tolerance for the raw product (Elkins, 1989).

Apple (*Malus x domestica* Borkh.) is considered to be a major agricultural product with substantial economic value. In terms of annual tonnage produced, apples are the third most important fruit corp grown in the United States (Downing, 1989). Michigan is one of the nation's most important apple producing states, with 9% of the total U.S. production in 1987-1990 (Ricks and Hull, 1992). As a result of its high economic value as well as the large number of plant diseases (apple scab, powdery mildew, and sooty blotch), insects (codling moth, apple maggot, scales, and apple aphids), and mites (spider mites) that infest apples during their growth, significant quantities of pesticides are often necessary for the protection of this crop. This leads to residues on or in the fruit at harvest. Although these residue levels are generally below establishes tolerances, consumer wariness warrants efforts to further reduce pesticide residues.

The two pesticides selected for this study were: Captan and Guthion® (azinphosmethyl). The selection of these two pesticides was based on their importance in the apple industry for control of major plant disease, insects, and mites. The pesticides were also selected for their non-carcinogenic potential as indicated by the EPA. Azinphosmethyl is a nonsystemic organophosphorus insecticide which works as a contact or ingestion poison. Captan is a broad spectrum, non-systemic fungicide. Both pesticides are widely used on both fruits, vegetables, and other field crops. Application of these pesticides before harvest is often necessary for the proctection of fruits during the preharvest period.

The objective of the present study was to determine the effectiveness of preharvest intervals (PHI), postharvest wash treatments, and processing on pesticide residues in raw and processed apple fruits.

LITERATURE REVIEW

A. Pesticide Use and Monitoring

The post-World War II introduction of synthetic organic chemicals such as DDT and 2,4-D brought in a new era of farming that promised effective management of insects and other destructive diseases and pests in a wide variety of crops (Lichtenberg and Zilberman, 1986). Since then, other chlorinated hydrocarbons along with newer, safer, and less persistent pesticides have been developed. Such pesticides include the organophosphates, carbamates, and the synthetic pyrethroids The total use of these pesticides in the U.S. has climbed dramatically, increasing from 250 million kilograms to 500 million kilograms between 1964 and 1980. Of theses pesticides, those used for agricultural purposes more than doubled, increasing from 150 million kilograms in 1964 to about 400 million kilograms in 1980 (Aspelin and Ballard, 1980).

In the U.S., an estimated third of all crops is lost to pests prior to harvest, with an additional 9% lost to pests after harvest (Pimental, 1976). The increased use of pesticides has resulted in a significant reduction in crop loss due to insects and disease. The value of harvest losses by pest, disease, and weeds is estimated worldwide to be about 35% of the potential total harvest (Shibamoto and Bjedanes, 1993). The consumers demand for food with good sensory quality has continued to sustain the use of pesticides. Pesticides have clearly become a key component of agricultural technology.

The use of pesticides in agriculture has provided numerous benefits in terms of increased production and product quality. At the same time, pesticides are toxic chemicals or in fact are poisons, and to avoid the toxic effects or to protect the health of human beings, most countries have introduced laws governing not only the use of pesticides, but also setting limits for the levels of pesticide residues which may be tolerated in foods (Maybury, 1989). The U.S. is no exception and has been regulating the use of pesticides since 1910: first by the U.S. Department of Agriculture; then by the Food and Drug Administration under the 1938 revisions to the Food, Drug, and Cosmetic Act; again by USDA under the 1947 Federal Insecticide, Fungicide and Rodenticide Act; and beginning in 1970, by the Environmental Protection Agency. Although, the EPA regulates pesticide use and sets residue tolerances, it is the FDA and USDA which monitor pesticide residues in the food supply. The USDA is responsible for meat, egg, and poultry products only.

The role of pesticides in modern society has become an emotional and contentious issue (Shibamoto and Bjedanes, 1993). Pesticide residues and microbial contaminants head the list of consumer fears concerning the food supply. The public was very alarmed by such incidents as the 1989 Alar scare, followed the same year by cyanide contaminated grapes from Chile. The use of pesticides in agriculture can be expected to result in residues in food (Lombarbo, 1989). It is therefore necessary to confirm that fresh and processed fruits and vegetables are free of excessive pesticide residues.

On August 3, 1996 a landmark pesticide food safety legislation was officially signed into law by President Clinton. This, the Food Quality Protection Act (FQPA), provides some of the most significant changes in food safety and pesticide law in decades. The act includes major revisions in the Federal Food, Drug, and Cosmetic Act (FFDCA) related to food safety, as well as to pesticide registration and use provisions in the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Key changes to the FFDCA include: Repeal of the Delaney Clause; new procedures for approving tolerances and modifying or revoking existing pesticide tolerances; added protection for infants and children; consumer information is established; and EPA has the given option to consider benefits in determining a safe tolerance. Key changes to FIFRA include: Reregistration of pesticides on a 15-year cycle; faster review of reduced-risk pesticides; incentives to develop and maintain minor uses; and a new definition of minor use. How this law will impact current practices is not fully understood. Only time can tell.

Increased public concern has led to increased monitoring of pesticide residues in fresh produce and processed foods. The National Food Processors Association (NFPA) has long been serving the food processing industry and consumers by helping to assure the safety, wholesomeness, and nutritional value of the nation's food supply (Elkins, 1989). The NFPA Protective Screen Program, introduced in 1960, was created to prevent illegal and unnecessary residues in processed foods. Since then, NFPA in cooperation with the food processing industry, has shown that residues are very infrequently encountered in processed foods and when found they are present at levels lower than in the raw agricultural product (Chin, 1991).

Since the 1960s, the FDA has also been carrying out its own pesticide monitoring program. The program has 2 principal approaches: (1) Regulatory or Commodity Monitoring, to measure residue levels in domestic and imported foods to enforce tolerances and other regulatory limits; and (2) the Total Diet Study, to determine intakes of pesticides in foods prepared for consumption (Lombardo, 1989). Regulatory Monitoring has focused on the raw agricultural commodity and annually collects and analyzes about 15,000 samples for 253 different pesticides. The Total Diet Study examines foods as eaten, covers only selected pesticides, and makes possible the determination of dietary intakes. The 1987 residue findings showed that out of 253 pesticides only 113 were detected. Less than 1% exceeded tolerances, and no residues were detected in half the samples. The 1987 Total Diet Study determined that the calculated dietary intakes were below the Acceptable Daily Intakes (ADI) established by the World Health Organization (WHO).

In 1991 the Agricultural Marketing Service of the USDA implemented the Pesticide Data Program (PDP) to collect objective, comprehensive data on pesticide residues for fresh fruits and vegetables (USDA, 1992). This program was designed to provide government agencies with an improved data base to respond more effectively to food safety issues. The primary recipient of the program's data will be the EPA, which will use the information to support its risk assessment process. The 10 most prevalently consumed fruit and vegetable commodities in the U.S. were chosen as samples. Samples were collected from six representative states, 25 other states, and 13 foreign countries. During the first six months of 1992, a total of 2,859 samples were collected and analyzed. A total of 42 different pesticides were detected in 1,664 (58%) of the samples. In general, the levels of pesticide residues detected were substantially below tolerances.

B. Pesticides Involved

The two pesticides selected for this study were: Captan, a fungicide, and Guthion®, an insecticide. The selection of these two pesticides was based on their importance in the apple industry for control of major plant disease, insects, and mites. The pesticides were also selected for their non-carcinogenic potential as indicated by the EPA.

(1) Azinphosmethyl

Guthion® is the commercial name for azinphosmethyl. The chemical name for azinphosmethyl is O,O-dimethyl S-[(4-oxo-1,2,3-benzotriazen-3(4H)-yl)methyl] phosphorodithioate.

Azinphosmethyl is a nonsystemic organophosphorus insecticide which works as a contact or ingestion poison. Azinphosmethyl was first introduced for use on cotton in 1956 in the U.S.. It has since come into widespread use on fruit as well as various field crops and many vegetables. Azinphosmethyl's wide use pattern requires it to be applied in various formulations. It is used primarily for foliage applications and is applied mainly as a spray (Chemagro Division Research Staff, 1974).

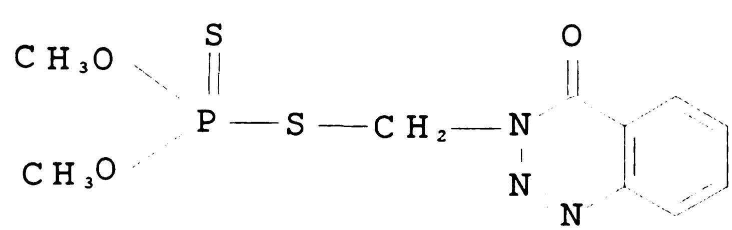


Figure 1 : Structure of Azinphosmethyl

Azinphosmethyl is also applied in combination formulations with other pesticides and many important commercial formulations have been produced. Azinphosmethyl is known to be compatible with most insecticides and fungicides, including captan (Chemagro Division Research Staff, 1974). The pesticide products based on azinphosmethyl, alone or in combination, have a broad spectrum of activity, especially against lepidopterous larvae, bugs, sawfly larvae, fleas, scale insects, and aphids (FAO, 1991).

In terms of deciduous fruits, azinphosmethyl has proved so effective against North American insects that it often has been the only insecticide applied by many fruit growers. It should also be of great interest that despite its widespread use, few insects have shown tolerances or resistance to azinphosmethyl (Chemagro Division Research Staff, 1974).

(2) Captan

Captan is the common name for (N-trichloromethylthio-4-cyclohexane-1,2-dicarboximide). It is a broad spectrum, non-systemic fungicide. Captan was first introduced in the 1950s and since has attained very wide use on fruit, vegetable, ornamental, turf, and seeds. It is recommended for more diseases on deciduous fruit than any other fungicide (Vettorazzi, 1977). As a surface fungicide it is widely used for control of scabs, blotches, rots, mildew, and other diseases on fruits, vegetables, and flowers (Wolfe *et al.*, 1976). Captan is used in general purpose pesticide mixes and approximately 600 federally registered products contain captan as an active ingredient (Gilvydis *et al.*, 1986).

Captan has also been the subject of an EPA Special Review since 1980 because of concerns over possible oncogenicity, mutagenicity, and other chronic effects (Gilvydis *et al.*, 1986).

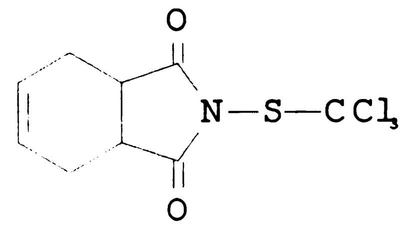


Figure 2 : Structure of Captan

Captan has also been the subject of an EPA Special Review since 1980 because of concerns over possible oncogenicity, mutagenicity, and other chronic effects (Gilvydis *et al.*, 1986).

C. Pesticide Residues in Raw Fruits and Vegetables

The importance of pesticide use and the potential risk it poses has made information on the presence of pesticide residues very important. Much of the data available regarding residues in fruit and vegetable crops is obtained through large and small scale monitoring programs and controlled field studies. Data from government pesticide monitoring programs show that detectable residues are present in raw agricultural commodities. Although most residues are within established tolerances, some are not, often because there are no established tolerances for a specific chemical on that food (Petersen *et al.*, 1996).

Residue tolerances have been established for both captan and azinphosmethyl on a great number of raw agricultural commodities in many different countries. In the U.S. these tolerances are determined by the EPA under Section 408 of the Federal Food Drug and Cosmetic Act (FFDCA). The maximum residues, from preharvest and postharvest use or combinations of such uses, in or on apples is 2.0 μg/g for azinphosmethyl and 25 μg/g for captan (Code of Federal Regulations, 1996).

A pesticide is registered to control specific pests on specific crops as long as certain conditions, such as application and timing, are met. The legal conditions for a pesticide use are on the label and it is illegal to apply a pesticide in a manner not specified on the label. Residues that exceed tolerance values generally indicate pesticide misuse (Beall *et al.*, 1991).

Residue levels in crops are dependent on a number of factors such as rate and frequency of application, nature of the plant surface, and weather conditions such as rainfall, temperature, humidity, sunlight, and wind. The pesticide and formulation in which it is applied also greatly affects the residues which are observed. The chemical makeup of the pesticide may determine if it is loosely or tightly bound to the surface of the commodity or if it will penetrate the surface and be translocated to inner tissues (Ritchey, 1986).

The preharvest interval (PHI), which is the time interval between the last spray application and harvest, has been shown to affect residue levels. The PHI employed will vary with the pesticide as well as the commodity. The pesticide manufacture will often recommend a specific PHI, as well as rates and intervals in which to apply the pesticides, in order to reduce the chance of residues on a commodity exceeding federal tolerances. The label recommended preharvest interval (PHI) for azinphosmethyl, using 50 % wettable powder (50-WP) formulation, is 7 days for apples. The label specifies that captan, using the 50 % wettable powder (50-WP) formulation, may be applied to apples up to the day of harvest (Crop Protection Reference, 1996).

Azinphosmethyl does not penetrate to any appreciable extent into the physiological processes of the plant (Chemagro Division Research Staff, 1974). The compound does, however, have an affinity for the cuticle waxes and oils which has a definite impact on the various half-life values which have been observed. The half-life for azinphosmethyl on vegetable and forage crops grown under field conditions ranges from three to five days. Azinphosmethyl persists on tree fruits somewhat longer than on field crops. The average half-life of azinphosmethyl on apples is six days.

Captan is a nonsystemic fungicide with low water solubility which results in it remaining as superficial deposits on the surface of treated crops. This allows it to be partly removed by water, especially on non-waxy crops such as strawberries (Vettorazzi, 1977).

In the 1992 PDP Report (USDA, 1992), which collected a total of 309 apple samples, 70 of the samples contained azinphosmethyl residues. The mean of the residues found was 0.1 μg/g which is only 5 % of the U.S. tolerance. Of the same 309 apple samples, 30 of the samples contained captan residues with a mean residue level of 0.15 μg/g or 0.60 % of the U.S. tolerance. The PDP Report also found that most of the pesticides detected were below tolerance levels, but a high proportion of the samples had detectable residues (Petersen *et al.*, 1996). This has been attributed to the use of much more sensitive analytical methods.

Between 1978 and 1986, Ontario-grown apples were monitored for residues of a wide range of pesticides used in their production (Frank *et al.*, 1989). A total of 305 samples were collected from both fresh market sources and from controlled atmosphere (CA) .

storage. Both captan and azinphosmethyl were among the pesticides detected and were used in production of 94.3 % and 91.2 % of the samples, respectively. Only 1.3 % of the samples had detectable azinphosmethyl residues with levels averaging 0.26 ± 0.10 µg/g with 0.45 µg/g being the highest level detected. Captan residues were detected in 45.9 % of the samples and averaged 0.089 ± 0.119 µg/g with 1.00 µg/g the highest level detected. All observed captan and azinphosmethyl residues were well below maximum residue limits (MRL) permitted under the Canadian Food and Drug Act.

Frank *et al.* (1991) studied the persistence of captan on apples, grapes, and pears in Ontario, Canada. Captan was applied at 1.7, 2.8, or 3.4 kg ha^{-1} for 1-15 applications with residues monitored over a 14-day period following the last application. Residues declined significantly in seven of nine experiments. A correlation between rainfall and captan residues was observed. The longest period required for residues to decline below 5 µg/g, the maximum residue limit permitted under the Canadian Food and Drug Act, was 5 days for grapes, 3 days for pears, and 7 days for apples.

Captan was sprayed 7 times at 7 day intervals and 4 times at 15 day intervals to examine the degradation behavior on greenhouse tomatoes (El-Zemaity, 1988). Results showed that captan sprayed at 7 day intervals was more persistent than sprayed at 15 day intervals. Captan residues at 0 and 7 days after last application were determined to be 2.73, 1.96 µg/g for the 7 day interval and 1.84, 0.53 µg/g for the 15 day interval spray program.

Rashid *et al.*(1987) looked at captan residues on Golden Delicious apples when applied at 2.4 g/l in a single treatment or as part of a standard treatment program with eight applications. Samples were taken at midseason, 56 days after single treatment application, and at harvest, 56 days following. Captan residues in the fruit at midseason were 0.02, 5.7µg/g and at harvest were 0.01, 1.2 µg/g for the single and standard treatment, respectively.

Fresh strawberries and grapes grown in Michigan and Indiana were surveyed for captan residues (Gilvydis *et al.*, 1986). Captan was applied by a number of different methods and at amounts ranging from 0.5 to 6 lb formulation/acre. Last application dates ranged from 2 days to nearly 5 months. Captan residues were found in all 28 of the strawberry samples collected, ranging from <0.01 to 1.5 µg/g. Captan residues were found in only 6 of the 15 grape samples treated with captan, ranging from <0.01 to 0.082 µg/g. Residue levels were found to be inconsistent with amount and dates of application, most likely because of variations in weather conditions, especially rainfall.

Hansen *et al.* (1978) examined the pesticide residues found on apple and peach foliage in an orchard spray program. Azinophosmethyl and captan, the two pesticides of interest, showed a 69% and 50% reduction, respectively, of residues following the tenth day of post-application. There was no evidence of a buildup of either azinphosmethyl or captan on treated foliage as the season progressed.

Azinphosmethyl residues were reported from several supervised trials with apples in both the U.S. and Europe (FAO, 1991). Azinphosmethyl (50WP) was applied at a rate of 1.12-1.68 kg ai/ha in the U.S. rials and reported residues ranged from 0.07-1.69 µg/g after a 7 day PHI.

Belanger *et al.* (1991) determined azinphosmethyl residues on apples in Canada at different plant stages. Residue analysis revealed detectable residues on the foliage until mid season. However, negligible residue levels were found on the peel and the whole fruit at harvest.

Azinphosmethyl (50WP) was applied to field-grown grapes at maximum recommended rate of pest control in Fresno County, California (Winterlin *et al.*, 1974). Azinphosmethyl residues were found on leaves at approximately 20% of their original levels 42 days after initial application. Residue levels on the fruit were 12, 14, and 4.4 μg/g after 28, 31, and 42 day PHI, respectively.

D. Pesticide Residues in Processed Fruits and Vegetables

The U.S. EPA, under Section 409 of the FFDCA, specifies tolerances for pesticide residues in processed food. Section 409 tolerances are established only when a pesticide is added indirectly or directly to a processed form of a food or concentrated to levels exceeding those of the raw agricultural commodities as a result of processing. If the residues remaining in a processed food have been removed to the extent possible in good manufacturing practices and do not exceed the tolerance on the raw product, the processed product complies with Section 408 for raw agricultural commodities.

Concerns expressed about residues in processed foods frequently reflect a lack of knowledge about food processing operations and their effect on residue levels. Processing has been interpreted as any operation performed on a food, food source, or food product from the point of harvest through consumption (Ritchey, 1981). Unit operations in processing typically include washing the raw product with fairly large volumes of water, frequently using high pressure sprays and often incorporating surfactants or other washing aids; peeling the product mechanically with knives, abrasive discs or water; blanching with hot water or steam; and in the case of canned foods, the cooking of the product at temperatures at or above that of boiling water. Thus, the chemicals which may be present are subject to not only physical removal by washing or peeling, but also acid or base hydrolysis and thermal degradation (Chin, 1991). In almost all cases the net effect of these operations is to reduce residues which may be on the raw product.

The amount of pesticide removed , if any, depends largely on the specific pesticide, the commodity, and the severity of the processing operation. Pesticide residues loosely held to the surface may be removed by washing or blanching, but residues which penetrate the surface (systemic) are more difficult to remove (Ritchey, 1981). Peeling may also remove residues confined to the surface but is often ineffective against those below the surface. Systemic pesticides are typically registered for use early in the growing season so that residual amounts at harvest are below tolerance (Beall *et al.*, 1991). The extent to which residues can be dislodged is also dependent upon the weathering of the residue on the crop. Following the label recommended use of a pesticide along with the various food processing methods available can help to achieve the desired residue levels.

The common consensus among those familiar with food processing methods is that pesticide residues decrease, often dramatically, during processing and food preparation. The NFPA has long been interested in the effect of commercial processing on pesticide residues in food. Residue data, assembled in 1988 by the NFPA, on processed products showed that of the 20,310 samples analyzed, 93% had no detectable residues (Chin, 1991). NFPA continues to collect data from the food industry in order to develop a sound database on pesticide residues in processed foods.

The FDA Total Diet Study determines the intake of pesticides in processed foods or table-ready foods. The study helps to determine dietary intakes of pesticides and then compares these intakes with acceptable daily intakes (ADIs), as established by the WHO, to identify trends. ADI refers to the level of daily exposure to a pesticide which, over a 70 year human life span, will have no negative effect. According to the 1987 Total Diet Study report, the dietary intakes calculated were well below the established ADIs and by a significant amount in most cases (Lombardo, 1989). The FDA continues to update this program to reflect more recent food consumption trends and to continue providing information necessary for the reassessment of pesticide uses and tolerances.

Pesticide residue data in foods are continually criticized for having too few samples, covering too few pesticides, or having inadequate quality assurance documentation. However, when taken as a whole, all of the databases consistently demonstrate that pesticide residues are infrequently encountered in processed foods (Chin, 1991).

E. Common Pathways of Pesticide Residue Degradation

The degradation of pesticides can be classified as physical, chemical, and biological with a combination of these factors influencing their breakdown over time (Coats, 1991). The relative importance of these factors is highly dependent on a pesticide's use pattern, physical properties, and chemical structure as well as the nature of the treated plant including physical characteristics of its surface, rate of growth, and factors causing erosion of surface deposits. The degradation mechanisms affecting a pesticide in the field, when applied to a crop for pest control, may differ from those affecting it during postharvest treatment of the crop, as well as during processing. The following discussion of the degradation of captan and azinphosmethyl will focus on the physical and chemical pathways.

(1) Physical

The degradation or disappearance of a pesticide through physical means is of particular importance to a pesticide in the field and may include wind, rain, heat, and light (photolysis). Such environmental forces can have a significant effect on a pesticide, the sum of which has been termed "weathering".

Frank *et al.* (1987) studied the effect of rainfall on the disappearance of captan from tomatoes by comparing field grown tomatoes to greenhouse grown. Captan residues declined significantly faster in the field and was directly correlated to rainfall. Captan residue study by Frank *et al.* (1985) showed similar results.

The effects of sunlight on the degradation of azinphosmethyl were examined by Liang and Lichtenstein (1976). Azinophosmethyl was applied to corn and bean leaves. The control, exposed to darkness, was compared to samples exposed to sunlight for 8 hours. Results showed an 88% and 94% recovery of azinphosmethyl in the controls and an 86% and 72% recovery in the light samples, respectively. The leaves exposed to darkness showed no degradation products while those exposed to sunlight indicted the appearance of N-methylbenzazimide on the corn leaves and N-methylbenzazimide sulfide, benzazimide, and the oxygen analogue of azinphosmethyl on both corn and bean leaves. Liang and Lichtenstein (1972) also showed that azinphosmethyl in aqueous solutions formed organosoluble and water-soluble breakdown products in the presence of UV light and to a lesser extent sunlight. The organosoluble products were identified as benzazimide, anthranilic acid, methyl benzazimide sulfide, and N-methyl benzazimide, whereas the water-soluble products remained unidentified.

Climatic conditions were shown to have a considerable influence on disappearance rate of azinphosmethyl in or on oranges. Florida experiments (Chemagro Division Research Staff, 1974) showed a half-life of 46 days for oranges exposed to an average rainfall of 10 to 15 inches compared to a half-life of 340 to 400 days under the arid conditions prevailing in California and Arizona (Gunther *et al.*, 1963). Gunther (1963) indicated these results agreed with those reported by Williams in 1961 who demonstrated a significant loss of azinphosmethyl from apple foliage with as little as 0.13 inch of rain.

The effect of wind and rain on emulsion sprays of selected organophosphate pesticides (malathion, toxaphene, phosdrin, methyl parathion) was reported in 1958 by Hightower and Martin using cotton plants (Ebling, 1963). Artificial wind was applied at 5 mph for 24 hours with 1/2 inch of artificial rain applied in three minutes. The percent reduction resulting from wind ranged from 10% for malathion to 73% for phosdrin, respectively. The percent reduction resulting from rain ranged from 25% for toxaphene to 76% for malathion.

Work reported by Decker in 1950 and 1958, on deciduous fruits and forage crops found, with other factors being equal, there is a definite correlation between the vapor tensions of pesticides and the rates of the residue losses (Ebling, 1963). A majority of the loss of more volatile compounds occurred in the course of their passage through the air from the spray nozzle to the plant, as well as on the plant surface.

(2) Chemical

Pesticides may undergo a number of chemical transformations to include: hydrolysis and other nucleophilic reactions, oxidation, isomerization, reduction, and free radical reactions (Goring *et al.*, 1975). Chemical oxidation and hydrolysis, two of the more commonly observed chemical degradation pathways will be discussed further.

Chemical degradation of azinphosmethyl is assumed to occur primarily by hydrolysis, but oxidation is also possible (Eto, 1974). Hydrolysis has been shown to be an important mechanism of organophosphate degradation in both soil and aqueous environments (Freed *et al.*, 1979). The hydrolysis of azinphosmethyl in solution may proceed under acid, neutral, and alkaline pH, but is generally more persistent under alkaline conditions (Faust & Gomma, 1972). It was observed to have its greatest stability under acidic conditions with an increasing rate of hydrolysis at higher pH. At pH 1.0, 3.0, 5.0, 7.0, and 9.0, the $t_{1/2}$ values for azinphosmethyl were 24, 9, 8.9, 4.8, and 0.6 hours, respectively. Laing and Lichtenstein (1972) reported azinphosmethyl to be relatively stable under neutral and acidic conditions but at pH 11, 97% of the pesticide was converted to degradation products such as anthranilic acid, benzazimide and 3 unidentified compounds.

Oxidation of azinphosmethyl dislodgeable residues on southern California citrus foliage was reported by Gunther *et al.* (1977). Azinphosmethyl-oxon levels never exceeded 1.0% of the azinphosmethyl present. The oxon formed was more stable, but dissipated rapidly following rainfall. Degradation of azinphosmethyl through oxidation was not found to be of significance during the relatively wet and humid summer months normally experienced in the temperate eastern United States. Azinphosmethyl can be converted to analogous phosphorothiolate by oxidizing agents (Zweig, 1964).

Wolf *et al.* (1976) reported on the susceptibility of captan to hydrolysis in water, having a maximum half-life of 710 minutes in water. The hydrolysis of captan was pH independent over the pH range 2-6 and pH dependent from pH 6 to 9. At pH 6,7 and 8.25, the half-life of captan was 250, 175, and 10 minutes, respectively. The products of the reaction were identified as sulfur, chloride, and 4-cyclohexene-1,2-dicarboximide. Aizawa (1982) similarly indicates the formation of 4-cylclohexene-1,2-dicarboximide from captan which is easily hydrolyzed via very unstable intermediates. Frank *et al.* (1983) reported a half-life of less than one hour for captan at a pH of 8.5 in 22° C water and 13 hours at 5° C. At pH 5.5 the half-life was 13 hours at 22° C and 208 hours at 5° C.

Literature indicates that captan undergoes reactions of a hydrolytic nature or with cellular thiols resulting in N-S bond cleavage and the release of tetrahydrophtalimide (THPI), tetrahydrophthalamic acid, and o-aminotetrahydrophthalimide. Epoxides of captan and tetrahydrophthalimide are possible alteration products which may form under conditions of weathering or degradative metabolism (Buyanovsky *et al.*, 1988). The fate of captan residues on Golden Delicious apples during normal processing procedures was reported (FAO, 1991). Captan was converted to THPI during cooking in the production of apple sauce or warm juice. In the preparation of cold apple juice, captan and THPI partitioned into the pomace, with only minor residues remaining in the juice. Some of the captan residue was converted to THPI during the production of dried apples. Captan and THPI residue levels, measured in raw apples during a supervised field trial (FAO, 1991) showed levels of 0.45, 0.87, and 1.5 μg/g for captan and < 0.05 μg/g for THPI following 28, 21, and 14 day PHI, respectively.

F. Effect of Processing on the Degradation and Removal of Pesticide Residues

Fruits and vegetables are often subjected to a number of different processing operations to clean, eliminate waste, and to make the raw materials more palatable. While these procedures may actually help reduce or remove pesticide residues, other processing methods have been specifically designed for such purposes. It is important to note that the effectiveness of various processing operations in the removal of residues is dependent on numerous vectors which include: the nature of the commodity being processed; the pesticide used and its chemical properties, formulation applied, method of application, rate of application; and the interaction of the pesticide with the commodity in terms of contact time (Geisman, 1975). The net influence of processing almost always results in residue levels in processed foods well below the tolerance for the raw product (Elkins, 1989).

Washing including rinsing is, perhaps, the one unit operation common to the preparation of nearly all fruits and vegetables for processing (Geisman, 1975). While washing is a common practice among the processing industry, the specific methodologies used vary from processor to processor. To help increase the effectiveness of a wash treatment, physical and chemical aspects of the wash are manipulated to produce optimum results. The following list of the physical and chemical aspects were employed during the present study to examine their effectiveness in the removal of captan and azinphosmethyl from apples: temperature, pH, chlorine, and detergent (sodium dodecyl sulfate). Data pertaining to these processing methods was readily available in some cases and limited in others.

(1) Temperature

Studies by Koivistoinen *et al.* (1965) showed the loss of captan in various preservation processes depended chiefly on whether or not the process included a heating phase. Boiling, steaming, autoclaving, or pasteurization generally resulted in a 98% to 100% loss in captan residues. In the preparation of apple juice, 88% of captan was removed during a mechanical pressing step with nearly complete removal being achieved during pasteurization of the juice. A 90% loss of captan was observed in string beans blanched for 2 minutes at 80° to 90° C.

The effect of temperature on both azinphosmethyl and captan were examined by Easter and DeJonge (1985). The study evaluated the launderability of fabrics contaminated with the two pesticides. The wash treatment compared the effect of three different wash temperatures and found an increase in temperature resulted in an increase in removal of both pesticides.

Elkins *et al.* (1972) examined the ability of thermal processing to degrade or remove pesticides from spinach and apricots. The selected products were fortified with 15 pesticides, including captan and azinphosmethyl, and subjected to processing temperatures ordinarily encountered in canning. Sample analysis showed that thermal processing degraded captan almost completely. A 93% and 97% decrease in captan residues was observed as a result of thermal processing in spinach and apricot samples, respectively. Similar results were found for azinphosmethyl with a 100% and 61% loss in spinach and apricot samples, respectively. The observed captan and azinphosmethyl results were found to be in agreement with those of Klayder (1963) and Carlin *et al.*(1966) who determined that canning, with the usual heat processing, largely destroys the pesticides on raw produce (captan) and green beans (azinphosmethyl), respectively.

Faust and Gomma (1972) studied the effects of temperature on the degradation of azinphosmethyl, and showed the compound to be less stable as temperature increased. Liange and Lichtenstein (1972) similarly found that rapid degradation of azinphosmethyl occurred above 37° C.

(2) Detergents

A 1967 report from the National Canners Association indicated that the use of detergents improved the removal of various residues by washing procedures in potatoes, tomatoes, and spinach (Liska and Stadelman, 1969). Fruits and vegetables are often subjected to several immersion or spray washing operations followed by a detergent to aid in cleaning. Several such detergents have been accepted as washing aids in produce destined for canning.

A detergent was shown to significantly increase the removal of parathion from spinach and broccoli (Elkins, 1989). Water washing reduced parathion residues by 9% and 0% while detergent washing reduced residues by 24% and 33% in spinach and broccoli, respectively. Similar results were determined in the 1960's by the National Canners

Association (Chin, 1991). Parathion residues were unsuccessfully removed from spinach by a water wash. The incorporation of a detergent in the wash water increased the removal of parathion from spinach by nearly three-fold over that removed by water alone. Frank *et al.* (1983) studied the removal of captan from treated apples and found that while thorough rinsing and wiping of apples removed 94% of captan residues the addition of a detergent did not increase residue removal.

(3) pH

A number of studies have examined the effects of pH on both captan and azinphosmethyl in solution. Faust and Gomma (1972) indicated that azinphosmethyl was less stable under basic than acidic conditions, the half-lives of azinphosmethyl in buffered solutions at pH 1,3,5,6,7, and 9 maintained at 21° C were 24, 9, 8.9, 7.5, 4.8, and 0.6 hours, respectively. Ong *et al.* (1996) found similar results which showed azinphosmethyl to be stable in pH 4.5 and 7.0 solutions at 21° C and 44° C, with 96-100% (21° C) and 93-96% (44° C) residual pesticide remaining after 31 minutes. Azinphosmethyl was found to be less stable at pH 10.7 which decreased further with an increase in temperature and time.

Captan was reported to undergo degradation in water with a maximum half-life of half a day (Wolfe *et al.*, 1976). The reaction was reported to be pH independent over a pH range of 2-6 and pH dependent from pH 6 to 9. The half life of captan was 250, 175, and 10 minutes at pH 6, 7, and 8.5, respectively. Similar results were reported by Ong *et al.* (1996) which indicated captan to be completely unstable in a pH 10.7 solution at ambient temperature and 0 minutes. In pH 4.5 and 7.0 solutions, 47% and 42% of captan remained for approximately 31 minutes at ambient temperature, respectively. Captan stability decreased with increasing temperature (44° C).

(4) Chlorine

Chlorine and several of its derivatives are used extensively to disinfect municipal water supplies, process and preserve foods, and sterilize equipment (Braude and Wade, 1983). The use of chlorine in the oxidation of organic compounds has led to the investigation of its capacity to degrade organic pesticides (Gomma and Faust, 1972). A limited amount of data exists on the effects of chlorine on the pesticides azinphosmethyl and captan.

Suzumoto *et al.* (1983) reported on the degradation effects of chlorine on 13 different pesticides in water, one of which was captan. The results showed that all 13 pesticides were easily degraded by chlorine at concentrations of 1 ppm. It was also shown that those pesticides containing sulfur were degraded more easily. Captan at 0.04 ppm was degraded only 5% after 24 hours in a 1 ppm chlorine solution.

Apples sprayed with captan and azinphosmethyl were dipped in a 50 and 500 μg/g chlorine wash at ambient temperature for 15 minutes with constant agitation (Ong *et al.*, 1996). The apples were then analyzed for pesticides in the whole fruit and in applesauce. The chlorine wash reduced captan and azinphosmethyl levels by 66% and 75% in the 50 μg/g solution and 77% and 83% in the 500 μg/g solution, respectively, when compared to residues found on unwashed fruit. Processing the apples into sauce further reduced residue levels with degradation averaging 100% for captan and 98% for azinphosmethyl in both chlorine solutions. Ong *et al.* (1996) also looked at the effects of chlorine on captan and azinphosmethyl in solution. Results indicated that captan and azinphosmethyl were rapidly degraded in 50 and 500 μg/g solutions of chlorine at low pH (4.5), but degradation decreased at higher pH (10.7). It was determined that an increase in pH decreased the percent HOCl, and consequently its reactivity with the pesticides. Both chlorination levels decreased azinphosmethyl and captan by 80-100% after only 6 minutes. Elevated temperatures further increased the degradation of the two pesticides in the chlorinated water. The 500 μg/g chlorine treatment proved the most effective in the degradation of both pesticides.

MATERIALS AND METHODS

A. Orchard Study

(1) Orchard Applications

The experiment was conducted in a block of 23-year-old Golden Delicious cultivar trees on M7a rootstock located on the Botany Research Field Laboratory at Michigan State University, East Lansing, Michigan, each year of the three year study (1993 - 95). The study required harvesting fruit with 7 day, 14 day, and 21 day preharvest intervals (PHI) along with a Control. The study plot was divided into 4 rows of trees, each representing one of the four samples, with one buffer row located between individual samples. Refer to the Field Plot diagram in Appendix 1. Maintenance pesticides were applied throughout the growing season to provide the necessary insect, mite, and disease control. A final spray application of the test pesticides, at their recommend label rates (Guthion® 50W - 1.0 lb. ai/A, Captan 50W - 3.0 lb. ai/A), was made to give the appropriate PHI's. Application of the final spray was altered so that all samples could be harvested on the same date. All pesticides were applied as a foliar spray with an FMC airblast sprayer at 80 gallons/acre and 300 psi. For the final application, the test pesticides were tank mixed and applied as a single application. Control samples did not receive a final application. Refer to Tables 1-3 for records of the 1993-95 spray applications.

Table 1: 1993 Spray Schedule for Golden Delicious Apples

Date Applied	Product and Formulation	Rate (lb AI/A)	Purpose of Application	Plots Applied
			Maintenance Spray Schedule	
5/6/93	Rubigan 1EC	0.1	apple scab	7 day PHI
	Polyram 80W	2.4	apple scab	all
	Nova 40W	0.15	apple scab	14 & 21 day PHI
	Asana 0.66XL	0.04	leaf miner	all
5/13/93	Rubigan 1EC	0.1	apple scab	7 day PHI
	Polyram 80W	2.4	apple scab	all
	Nova 40W	0.15	apple scab	14 & 21 day PHI
5/26/93	Rubigan 1EC	0.07	apple scab	7 day PHI
	Polyram 80W	2.4	apple scab	all
	Nova 40W	0.11	apple scab	14 & 21 day PHI
5/28/96	Guthion 50W	1.0	curculio, aphids	all
6/7/93	Guthion 50W	1.0	aphids, budmoth	all
6/11/93	Polyram 80W	2.4	apple scab	all
	Guthion 50W	1.0	aphids, budmoth	all
6/21/93	Captan 50w	1.5	apple scab	all
7/2/93	Polyram 80W	2.4	apple scab	all
	Guthion 50W	1.0	coddlingmoth, leafroller	all
7/13/93	Omite GE	1.9	european red mite	all
	Lorsban 50W	1.0	coddlingmoth, applemaggot	all
	Polyram 80W	2.4	apple scab	all
8/3/96	Guthion 50W	1.0	coddlingmoth, applemaggot	all
	Captan 50W	1.5	apple scab	all
	Omite GE	1.9	european red mite	all
			Final Spray - Application of Test Pesticides	
9/20/93	Guthion 50W	1.0	treatment spray	21 day PHI
	Carzol 92SP	1.1	treatment spray	21 day PHI
	Captan 50W	3.0	treatment spray	21 day PHI
9/27/93	Guthion 50W	1.0	treatment spray	14 day PHI
	Carzol 92SP	1.1	treatment spray	14 day PHI
	Captan 50W	3.0	treatment spray	14 day PHI
10/4/93	Guthion 50W	1.0	treatment spray	7 day PHI
	Carzol 92SP	1.1	treatment spray	7 day PHI
	Captan 50W	3.0	treatment spray	7 day PHI

Harvest Date: October 11, 1993

Table 2: 1994 Spray Schedule for Golden Delicious Apples

Date Applied	Product and Formulation	Rate (lb AI/A)	Purpose of Application	Plots Applied
			Maintenance Spray Schedule	
4/30/94	Spray Oil GE	2% / 1.6 gal	mite and insect control	all
	Nova 40W	0.15	apple scab	14 & 21 day PHI
	Rubigan 1EC	0.1	apple scab	7 day PHI
	Polyram 80DF	2.4	apple scab	all
5/4/94	Asana XL 0.66EC	0.04	leaf miner	all
5/10/94	Nova 40W	0.11	apple scab	14 & 21 day PHI
	Rubigan 1EC	0.07	apple scab	7 day PHI
	Polyram 80DF	2.4	apple scab	all
5/12/94	Streptomycin 17%	2 x .17	fireblight	all
5/18/94	Streptomycin 17%	2 x .17	fireblight	all
5/19/94	Nova 40W	0.15	apple scab	14 & 21 day PHI
	Rubigan 1EC	0.1	apple scab	7 day PHI
	Polyram 80DF	2.4	apple scab	all
	Guthion 50W	0.75	curculio, aphids	all
5/23/94	Mycoshield 17%	0.68	fireblight	all
5/27/94	Nova 40W	0.15	apple scab	14 & 21 day PHI
	Rubigan 1EC	0.1	apple scab	7 day PHI
	Polyram 80DF	2.4	apple scab	all
	Guthion 50W	0.75	curculio, aphids	all
6/9/94	Guthion 50W	0.75	aphids, budmoth	all
	Captan 50W	6 x 1.5	apple scab	all
6/16/94	Sevin 80W	4.8	insects, fruit thinning	all
	Captan 50W	6 x 1.5	apple scab	all
6/23/94	Guthion 50W	0.75	aphids, budmoth	all
	Captan 50W	6 x 1.5	apple scab	all
7/11/94	Guthion 50W	0.75	coddlingmoth, apple magot	all
	Captan 50W	6 x 1.5	apple scab	all
7/28/94	Guthion 50W	0.75	coddlingmoth, apple magot	all
	Captan 50W	6 x 1.5	apple scab	all
8/17/94	Guthion 50W	0.75	coddlingmoth, apple magot	all
	Captan 50W	6 x 1.5	apple scab	all
			Final Spray - Application of Test Pesticides	
9/19/94	Guthion 50W	1.0	treatment spray	21 day PHI
	Carzol 92SP	1.1	treatment spray	21 day PHI
	Captan 50W	3.0	treatment spray	21 day PHI
9/26/94	Guthion 50W	1.0	treatment spray	14 day PHI
	Carzol 92SP	1.1	treatment spray	14 day PHI
	Captan 50W	3.0	treatment spray	14 day PHI
10/3/94	Guthion 50W	1.0	treatment spray	7 day PHI
	Carzol 92SP	1.1	treatment spray	7 day PHI
	Captan 50W	3.0	treatment spray	7 day PHI

Harvest Date: October 10, 1994

Table 3: Spray Schedule for Golden Delicious Apples

Date Applied	Product and Formulation	Rate (lb AI/A)	Purpose of Application	Plots Applied
			Maintenance Spray Schedule	
4/28/95	Nova 40W	0.15	apple scab	14 & 21 day PHI
	Rubigan 1EC	0.1	apple scab	7 day PHI
	Polyram 80DF	2.4	apple scab	all
5/5/95	Nova 40W	0.11	apple scab	14 & 21 day PHI
	Rubigan 1EC	0.07	apple scab	7 day PHI
	Polyram 80DF	2.4	apple scab	all
5/12/95	Asana 0.66XL	0.04	leaf miner	all
5/17/95	Streptomycin 17%	0.26	fireblight	all
5/26/95	Nova 40W	0.15	apple scab	14 & 21 day PHI
	Rubigan 1EC	0.1	apple scab	7 day PHI
	Polyram 80DF	2.4	apple scab	all
	Guthion 50W	0.5	curculio, aphids	all
6/1/95	Sevin 80W	3	fruit thinning	all
6/2/95	NAA (20ppm)	0.01	fruit thinning	all
6/9/95	Captan 50W	1.5	apple scab	all
	Lorsban 50W	1.0	aphids, budmoth	all
6/25/96	Captan 50W	1.5	apple scab	all
	Guthion 50W	0.5	curculio, budmoth	all
7/9/95	Captan 50W	1.5	apple scab	all
	Guthion 50W	0.5	coddlingmoth	all
7/19/95	Omite 30W	1.5	mites	all
7/31/95	Captan 50W	1.5	apple scab	all
	Guthion 50W	0.5	coddlingmoth, applemaggot	all
8/18/95	Captan 50W	1.5	apple scab	all
	Guthion 50W	0.5	applemaggot	all
			Final Spray - Application of Test Pesticides	
9/18/95	Guthion 50W	1.0	treatment spray	21 day PHI
	Carzol 92SP	1.1	treatment spray	21 day PHI
	Captan 50W	3.0	treatment spray	21 day PHI
9/25/95	Guthion 50W	1.0	treatment spray	14 day PHI
	Carzol 92SP	1.1	treatment spray	14 day PHI
	Captan 50W	3.0	treatment spray	14 day PHI
10/2/95	Guthion 50W	1.0	treatment spray	7 day PHI
	Carzol 92SP	1.1	treatment spray	7 day PHI
	Captan 50W	3.0	treatment spray	7 day PHI

Harvest Date: October 9, 1995

(2) Sampling and Harvesting

Apples were hand picked at optimum maturity, coinciding with the appropriate PHI's, from all regions of the tree except fruit within one foot of the ground was excluded. Harvest began about 9:00 AM and took approximately two hours to complete. Gloves were worn during harvest and changed between each treatment to prevent cross contamination. All four samples were collected on the same day with the Controls collected first followed by 21 PHI, 14 PHI, and 7 PHI samples. Approximately 10-12 crates(50 -60 lb./crate) of fruit were collected from each of the four sample rows. Immediately following harvest, the samples were transported to a designated refrigeration cubicle (2° C) for storage at the MSU Food Science and Human Nutrition building until post harvest treatment and processing. Individual treatments and controls were separated by sheets of plastic to prevent cross contamination during storage. Samples for 1993-95 were harvested on October 11, 10, and 9, respectively. Sample processing for 1993 took place October 20, 21, 26, 28 of 1993. Similarily, processing took place October 18-21,1994 and October 19-22, 1995.

(3) Fruit Post Harvest Treatments

All post harvest treatment and processing were conducted at the Fruit and Vegetable Processing Laboratory, Department of Food Science and Human Nutrition, Michigan State University, East Lansing, Michigan. The Golden Delicous apple samples were subjected to a series of post harvest wash treatments and two wash times. Each of the treated samples were processed into four different products. Post harvest treatment and processing was done over a four consecutive day period. One sample type was treated and processed each day starting with Control and followed by 21 PHI, 14 PHI, and 7 PHI. All samples were prepared in triplicate except for the Controls where only one replicate was prepared for analysis.

Three reps of 8 apples each were removed from all 4 sample types prior to postharvest treatment and processing. The apples were placed in plastic bags and immediately frozen for analysis and to serve as the unwashed, unprocessed controls for each treatment.

a. Post Harvest Wash Preparation

The Golden Delicious apples were subjected to six different wash treatments to determine their effectiveness on removal and degradation of the test pesticides. The six wash treatments were: (1) 21°C and pH 7; (2) 21°C and pH 11; (3) 43°C and pH 7; (4) 43°C and pH 11; (5) 21°C and pH 7, 500 µg/g Chlorine; (6) 21°C and pH 7, 2% Sodium Dodecyl Sulfate (SDS). Five minute and 15 minute wash times were employed to study the effects of wash duration.

All wash treatments were prepared in 20 liter volumes to allow for complete submersion of the apple samples. Tap water at 21°C was used to prepare Treatments #1. Tap water for Treatment #2 was placed in a steam heated vessel and brought to 43° C.

Treatments #2 and #4 were prepared using deionized water. The treatments were both brought to pH 11 with the addition of 1.00 N NaOH solution (Columbus Chemical Industries, Inc.). A calibrated pH meter, model 601A (Corning Glass Works, Medfield, MA), was used to determine the pH of the wash treatments. Treatment #4 was placed in a steam heated vessel and brought to 43° C while Treatment #3 remained at 21°C.

Chlorox Bleach, which contains 5.25% NaOCl by weight, was added to 21°C and pH 7 deionized water to provide a 500 µg/g solution of chlorine for Treatment #5.

Treatment #6, 2% SDS solution, was prepared by adding 400 g of Electrophoretic Grade SDS (Boehringer Mannheim Co.) to 19.6 L of 21°C and pH 7 tap water.

b. Post Harvest Wash Treatment

Apple samples for each of the six post harvest washes (PHW) were divided in half and placed in separate mesh bags. The use of mesh bags allowed samples to be easily removed after the 5 minute wash time had expired. Each onion bag contained 3.4 to 3.9 Kg of apples.

Once the wash treatments were prepared, two bags of apples were placed in each of the six PHW. The apples were kept submerged , without agitation, during the duration of the wash. After 5 minutes one bag of fruit was removed from each of the six PHW. The second bag remained submerged an additional 10 minutes before removing. When samples were removed from the wash treatments they were rinsed with tap water prior to processing. Table 4 shows the samples prepared during the PHW treatments and the sample identification assigned to each.

Table 4: Postharvest Wash Treatment Samples

A1	B1	C1	D1	E1	F1
A2	B2	C2	D2	E2	F2
A3	B3	C3	D3	E3	F3
A4	B4	C4	D4	E4	F4
A5	B5	C5	D5	E5	F5
A6	B6	C6	D6	E6	F6

Sample I.D.

A = 7 day PHI, 5 minute wash time	D = 7 day PHI, 15 minute wash time
B = 14 day PHI, 5 minute wash time	E = 14 day PHI, 15 minute wash time
C = 21 day PHI, 5 minute wash time	F = 21 day PHI, 15 minute wash time

1-6 = Wash Treatments #1 through #6

(4) Fruit Processing

Each PHW treated sample listed in Table 4 was divided into four parts to be processed as: juice; peeled, frozen slices; sauce from unpeeled, uncored apples (Gerber Process); and sauce from peeled, cored apples. The two types of sauce represent products currently being manufactured and were expected to differ in residue level. The following weights of apples were required during processing to ensure sufficient product was available for residue analysis: 1.33-1.44 Kg, peeled sauce; 0.95-1.0 Kg, unpeeled sauce; 0.55-0.66 Kg, juice; 0.66-0.77 Kg, slices. The apples were processed using the following Standard Operating Procedures developed by the Food Science and Human Nutrition Department, Michigan State University, East Lansing, Michigan:

a. Apple Slices

Weighed apple samples were peeled and cored on a Leader apple peeler. The peeled and cored fruit was sliced with a Sunkist slicer. The apple samples were transferred into ziplock bags, weighed, labeled and immediately placed in -20° C storage to await residue analysis.

b. Apple Juice, 1993 Method

Weighed apple samples were macerated in a Hobart Food Chopper (Hobart MFG. Co., Troy, OH). The macerated apple tissue was placed on a nylon press cloth and pressed with a hydraulic press to express the juice. The juice volume was measured, poured into labeled 12 oz french square glass bottles, and placed immediately in -20° C storage to await residue analysis.

c. Apple Juice, 1994 & 1995 Method

Weighed apple samples were sliced with a Sunkist slicer. The apple slices were put through an Acme Juicerator. The grinder/centrifuge basket of the Acme Juicerator was lined with one layer of Kimwipe tissue. The apple slices were introduced into the juicerator through the opening in the top and automatically ground, juiced, and filtered. The volume of juice was measured, placed in labeled 12 oz french square glass jars, and immediately placed in -20° C storage to await residue analysis.

d. Apple Sauce, Peeled and Unpeeled

Weighed samples of apples intended for peeled sauce were peeled and cored with a Leader apple peeler. The peeled and cored samples were sliced with a Sunkist slicer. Weighed samples of unpeeled, uncored apples were sliced with the Sunkist slicer to be used for unpeeled sauce. Apple slices were placed in a single layer on a stainless steel tray for steaming in a Dixie blancher. Each tray of apple slices was steamed for 10 minutes to adequately soften the fruit and inactivate enzymes. After steaming, the fruit was cooled in air for 1 to 2 minutes before grinding and finishing in a Langsencamp pilot plant finisher with a 0.033-0.045 inch screen to remove coarse fibers, seeds, stems, and peel particles. The applesauce samples were placed in ziplock bags, labeled, weighed, and immediately placed in -20° C storage to await residue analysis.

B. Sample Extraction and Cleanup

(1) Reagents

All organic solvents used for preparaton of pesticide stock solutons, sample extraction, and cleanup were distilled-in-glass grade. Acetone and methylene chloride were obtained from Mallinckrodt, Co. (Paris, KY) and hexane and acetonitrile were obtained from EM Science, Inc. (Gibbstown, NJ).

(2) Chemicals

Azinophosmethyl and captan standards were obtained from AccuStandard, Inc. (New Haven, CT). The stock solutions and working standards of azinphosmethyl and captan were prepared in hexane and stored in a freezer. Reagent grade anhydrous sodium sulfate was used during sample extraction.

(3) Glassware

All glassware was thoroughly washed with detergent and warm water then rinsed with distilled water. The glassware was then rinsed once with acetone before being placed in an oven overnight before use.

(4) Extraction and Cleanup

Both azinophosmethyl and captan were extracted from the raw and processed apple samples with a modificaiton of the method described by Liang and Lichtenstein (1976). A 50 g sample size was used for all sample extractions. Applesauce was blended with 100 ml of acetone for 3 minutes using a Pro 200 hand held homogenizer. (Both apple slices and raw apple samples were macerated with a Hobart food chopper before they could be blended with acetone. Apple juice samples did not require the blending and filtering step and were added directly to the 500 ml separatory funnel with acetone.) The sample was filtered under vacuum through a ceramic buchner funnel containing Whatman #1 filter paper. The filter cake was rinsed twice with 10 ml of acetone. The filtrate was transferred to a 500 ml separatory funnel and extracted twice with 100 mL and 50 ml of methylene chloride. The methylene chloride extracts were collected through a glass funnel containing a glass wool plug and anhydrous sodium sulfate into a 250 ml round bottom flask. The extract was evaporated to dryness with a roto-vap evaporator. The dried sample was redissolved with 50 ml of hexane and poured through a glass funnel containing a glass wool plug and anhydrous sodium sulfate into a 250 ml separatory funnel. The round bottom flask was rinsed with an additional 50 mL of hexane and transferred to the separatory funnel. The hexane was partitioned with 3 x 25 ml portions of acetonitrile. The acetonitrile extracts were combined in a turbo-vap tube and evaporated to dryness. The residue was redissolved in 5 ml of hexane, transferred to a 4 dram glass vial, and placed in the freezer to await GC analysis.

(5) Gas Chromatographic Analysis

a. Azinophosmethyl

Azinphosmethyl residues were detected and quantified using a Hewlett Packard Series II 5890 gas chromatograph equipped with a Nitrogen Phosphorus Detector (NPD). The GC was equipped with a DB-5 fused silica capillary column (30 m x 0.25 mm i.d.) with a 0.25 micron film thickness (J.W. Scientific, Folsom, CA). The oven temperature was programmed isothermally at 230° C, while the injector and detector temperatures were both set at 250°C. Helium and nitrogen were used as the GC carrier gas and makeup gas, respectively. Hydrogen and air were used as the detector gases. The injection volume was 3 µl and samples were injected with a HP 7673 automatic sampler linked to the GC. Integration was carried out with HP Chemstation software interfaced to the GC.

b. Captan

Captan residues were detected and quantified using a Hewlett Packard Series II 5890 gas chromatograph equipped with a Ni^{63} Electron Capture Detector (ECD). The GC was equipped with a DB-5 fused capillary (60 m x 0.25 mm i.d.) with a 0.25 micron film thickness (J.W. Scientific, Folsom, CA). The oven temperature was programmed isothermally at 180° C, while the injector and detector temperatures were 220° C and 275° C, respectively. Helium and nitrogen were used as the GC carrier gas and makeup gas, respectively. The injection volume was 2 µl and samples were injected with a HP 7673 automatic sampler linked to the GC. Integration was carried out with HP Chemstation software interfaced to the GC.

(6) Calculation of Pesticide Residue Concentration

Pesticide residue concentrations were calculated by comparing the integrated area of the identified pesticide peak found in the sample to a standard curve of that pesticide. Both captan and azinphosmethyl standards, for GC use, were prepared in hexane at concentrations in the range of 0.05 µg/g to 4.0 µg/g for azinphosmethyl and 0.05 µg/g to 2.0 µg/g for Captan. Using Microsoft Excel (Microsoft Corporation, Redmond, WA) software, a linear regression standard curve of each pesticide was obtained by plotting the standard concentration against its integrated peak area. Appendix 2 and 3 show examples of the standard curves for azinphosmethyl and captan, respectively. The concentration of each pesticide residue was calculated as µg/g using the following formula:

$$\frac{\text{Conc. of pesticide in sample extract based on std. curve } (\mu g/g) \times \text{Vol. final extract } (5\text{ ml})}{\text{Weight of sample analyzed } (50\text{ g})}$$

(7) Method Recovery Study

Recovery studies for azinphosmethyl and captan were carried out in triplicate using the above desribed analytical methods. The recovery samples were prepared by adding a known amount (spike) of each pesticide to a 50 g sample of apple (juice, sauce, slice) and taking each sample through the entire analytical method. Recovery study samples were spiked at a level of 0.2 and 2.0 µg/g for both captan and azinphosmethyl.

(8) Method Detection Limit Study

Method Detection Limit (MDL) studies were carried out for both captan and guthion in apple samples (sauce, juice, slices). MDL was accomplished by spiking known amounts of each pesticides into 50g samples at a range of concentrations (µg/g) and determining the minimum level at which each pesticide

could be detected in a particular sample type. Postive detection required a peak response height 3 times the baseline noise height. MDL samples were done in triplicate and taken through the entire analytical method.

(9) Statistical Analysis

Means and standard deviations for all samples were calculated using Microsoft Excel 5.0. All sample determinations were made in duplicate except method recovery and method detection limit samples which were done in triplicate. Systat 7.0 was used to calculate significant differences between treatment means using a paired sample t test. Statistical outliers in the data were determined and eliminated using the test proposed by Grubbs (1969).

RESULTS AND DISCUSSION

A. Chromatographic Analysis

(1) Azinphosmethyl

The pesticide azinphosmethyl was detected using gas chromatography linked to a nitrogen phosphorus detector (NPD). The compound appeared as a single peak with a retention time of 8.9 minutes. Figure 3 shows a typical chromatogram of an azinphosmethyl standard while Figure 4 illustrates the chromatogram of azinphosmethyl detected in an actual sample. A typical standard curve for azinphosmethyl can be found in Appendix 2 and is representative of those used to calculate azinphosmethyl concentrations in sample extracts. Regression analysis was utilized to determine standard curve linearity, with a correlation coefficient (R^2) of >0.9 being the criteria for acceptance.

Recovery study samples for azinphosmethyl were spiked at a level of 0.2 and 2.0 μg/g. Table 5 gives the percent recoveries obtained for azinphosmethyl in apple samples (juice, sauce, slice). Control samples originally produced during each year of the study were found to contain residues of azinphosmethyl. Thus the apple samples used for the recovery studies were commercial apple products obtained through the Michigan State University stores. Only one type of applesauce was obtained to represent both unpeeled and peeled applesauce. The method detection limit (MDL) for azinphosmethyl was determined to be 0.02 μg/g in all sample types. Similarly, the percent recoveries at MDL

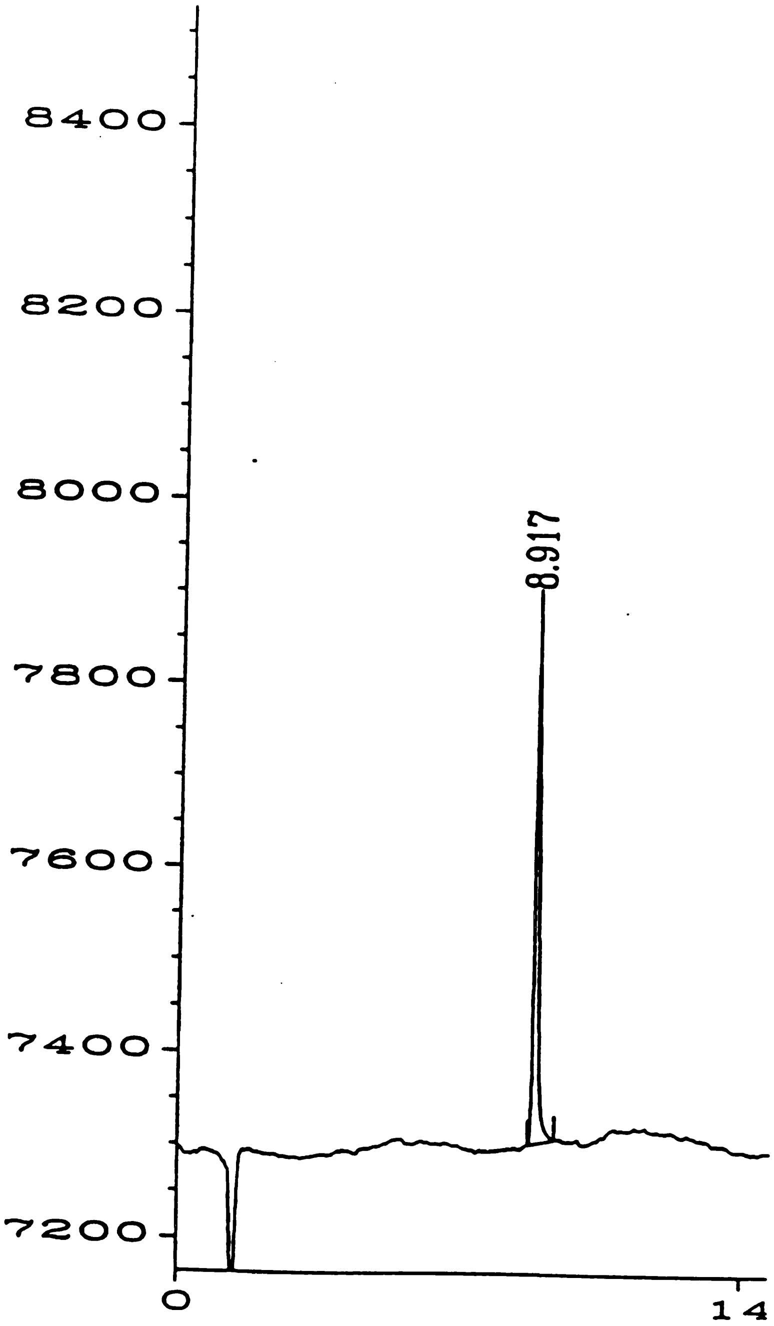


Figure 3: GC Chromatogram of an Azinphosmethyl Standard
1) 1.0 ppm standard
2) Rt=8.917 minutes

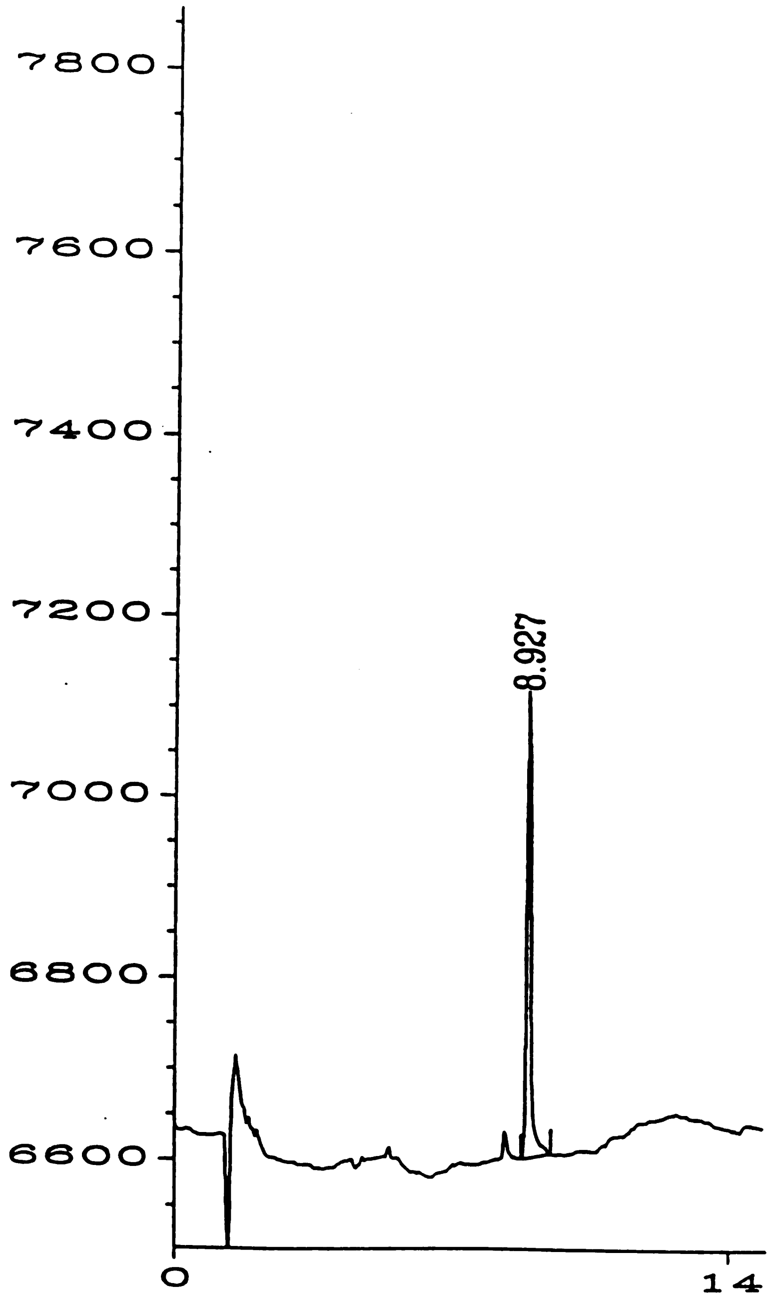


Figure 4: GC Chromatogram of an Azinphosmethyl Sample
1) 1993 Apple Juice, 7 day PHI, 43°C and pH 7, 5 minute wash time
2) Rt=8.927 minutes

are listed in Table 5. High recoveries for azinphosmethyl, listed in Table 5, were obtained for all three products but were highest in applesauce and apple juice. Recoveries greater than 100% represent both analytical error and matrix enhancment of the residues. Recoveries appeared to decline for all sample types when spiked at a lower level. The lower recoveries may be a result of matrix affects or extraction efficiency. Samples which contain low levels initially, are more likely to show these discrepancies. Apple slices had lower recoveries overall. This slight decline in recovery may be a direct result of the more involved extraction process required for apple slices, which required one more step in the extraction process than applesauce and two more than apple juice.

Table 5: Azinphosmethyl and Captan Recovery Study

Sample Type	* Azinphosmethyl			* Captan		
	(MDL) 0.02 ug/g	0.2 ug/g	2.0 ug/g	(MDL) 0.02 ug/g	0.2 ug/g	2.0 ug/g
Sauce	90.5 +/- 6.3%	96.7 +/- 5.8%	102 +/- 2.9%	85.2 +/- 8.5%	95.0 +/- 5.0%	95.0 +/- 5.0%
Slice	87.1 +/- 7.6%	95.0 +/- 5.0%	96.7 +/- 2.9%	87.0 +/- 6.0%	98.3 +/- 2.9%	98.3 +/- 7.6%
Juice	92.9 +/- 4.7%	93.3 +/- 2.9%	102 +/- 2.9%	90.3 +/- 5.0%	98.3 +/- 5.8%	100 +/- 5.0%

* Each value represents a 3 rep average

(2) Captan

The pesticide captan was detected using gas chromatography linked to an electron capture detector (ECD). The compound appeared as a single peak with a retention time of 9.2 minutes. Figure 5 shows a typical chromatogram of a captan standard while Figure 6 illustrates the chromatogram of captan detected in an actual sample. A typical standard curve for captan can be found in Appendix 3 and is representative of those used to calculate captan concentrations in sample extracts. Regression analysis was utilized to

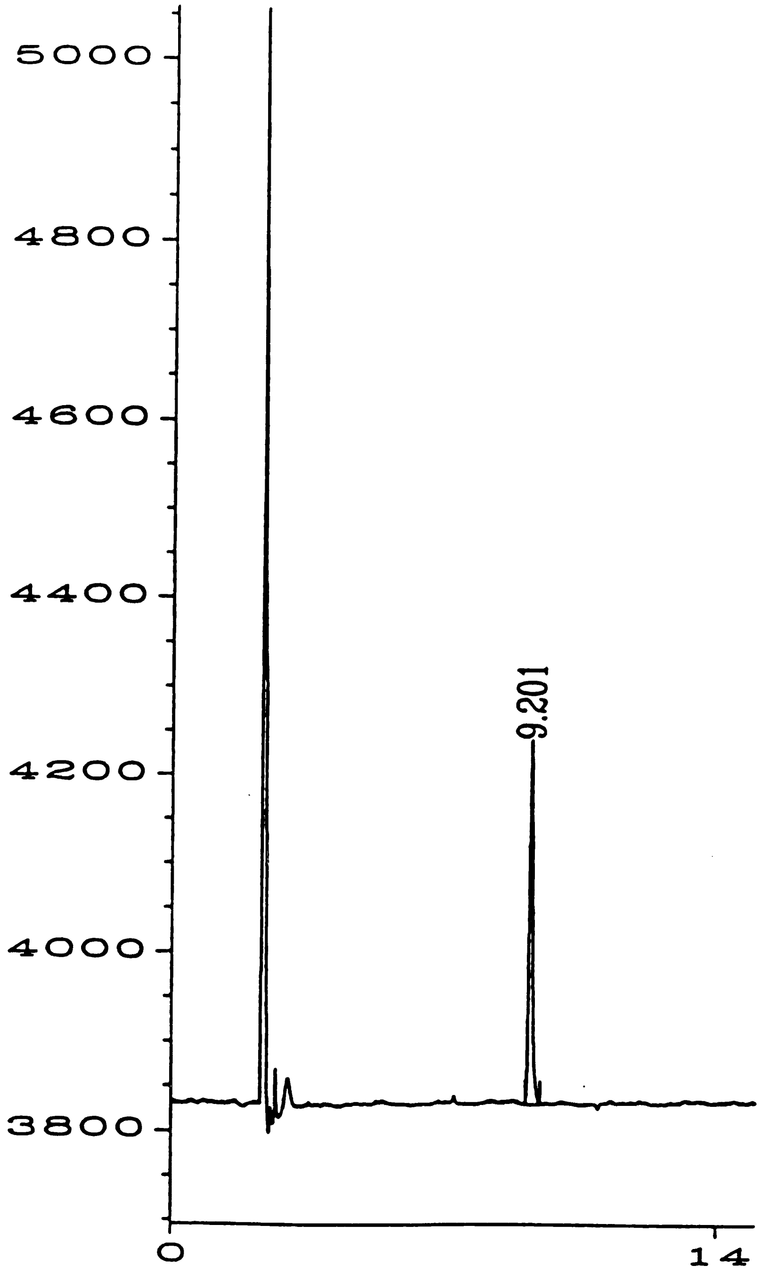


Figure 5: GC Chromatogram of a Captan Sample
1) 0.8 ppm standard
2) Rt=9.201 minutes

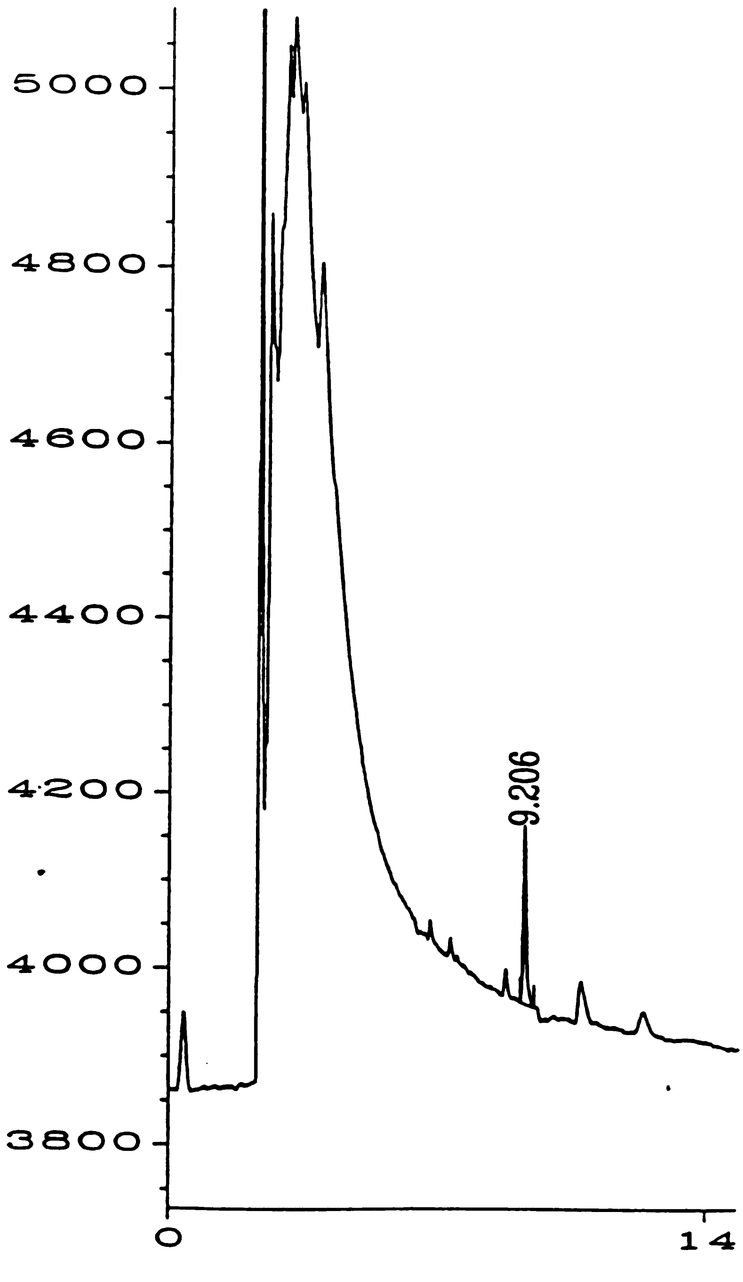


Figure 6: GC Chromatogram of a Captan Sample
1) 1995 Apple Slice, 14 day PHI, 21°C and pH 7, 15 minute wash time
2) Rt=9.206 minutes

determine standard curve linearity, with a correlation coefficient (R^2) of >0.9 being the criteria for acceptance.

Recovery study samples for captan were spiked at a level of 0.2 and 2.0 μg/g. Table 5 gives the percent recoveries obtained for captan in apple samples (juice, sauce, slice). Control samples originally produced during each year of the study were found to contain residues of captan. Thus, the apple samples used for the recovery studies were commercial apple products obtained through the Michigan State University stores. Only one type of applesauce was obtained to represent both unpeeled and peeled applesauce. The method detection limit (MDL) for captan was determined to be 0.02 μg/g in all sample types. The percent recoveries at MDL are listed in Table 5. Similarily, high recoveries were also obtained for captan in all sample types. Recoveries again declined in all sample types when spiked at a lower level. The lower recoveries most likely resulted from the same factors which affected azinphosmethyl.

B. Pesticide Residues in Unprocessed Apples

During all three years (1993-95) of the study, Golden delicious apple trees were sprayed with the test pesticides, Captan and Azinphosmethyl, at their recommended label rates. Final spray applications were altered to obtain apples with preharvest intervals (PHI) of 7, 14, and 21 days so that all PHI treatments could be harvested on the same date at optimum maturity.

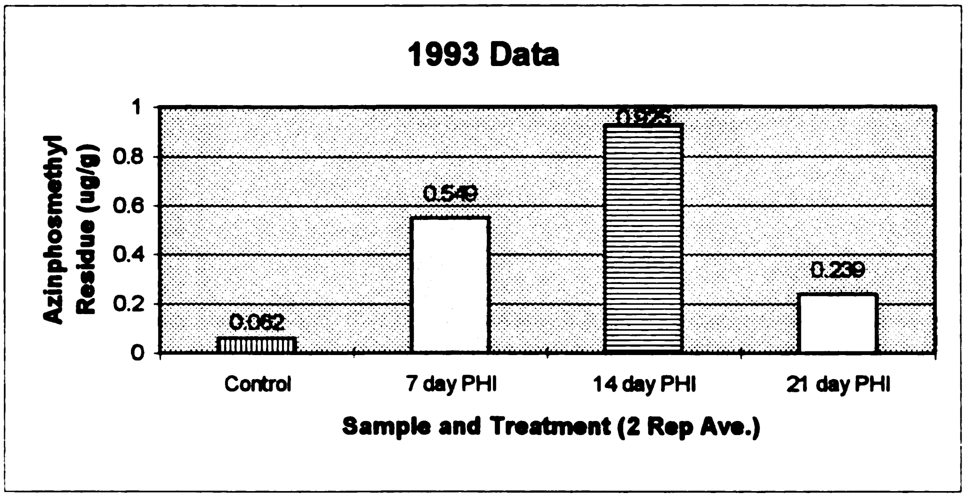
(1) Preharvest Interval Study

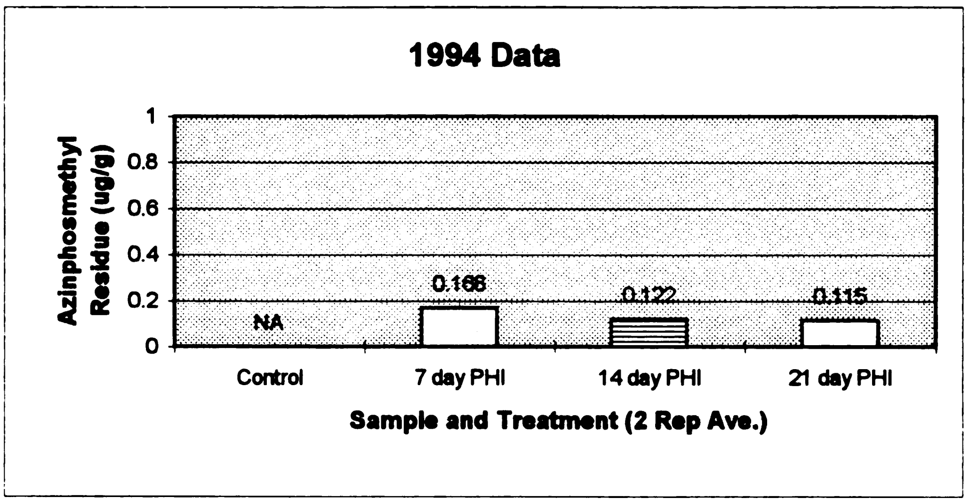
PHI represents the time interval between the last spray application and harvest. Previous studies indicate that longer PHI's help to lower pesticide residue levels. El-Zamity (1988) and Rashid et.al. (1987) both reported lower residue levels for captan, with an increase in PHI, on tomatoes and apples, respectively. Similar studies by El-Hadide (1993) and Belanger et.al. (1991) found residue levels to decrease with an increase in PHI when looking at azinphosmethyl on apples. Pesticide manufacturers often recommend a specific PHI in combination with a particular crop and pesticide. Such recommendations help to reduce the chance of residues exceeding federal tolerances. According to the 1996 Crop Protection Reference, the recommended PHI for azinphosmethyl (50-WP formulation) is 7 days for apple while captan (50-WP formulation) may be applied up to the day of harvest.

Residue analysis of azinphosmethyl in raw apple samples at 7, 14, and 21 day PHI, indicated patterns not consistent with data from previous studies. Figure 7 shows the average residue levels during 1993-1995. As indicated by previous studies, residue levels can be expected to decrease with an increase in PHI. Only during the 1994 season did residue levels follow the expected pattern. As for 1993 and 1995 seasons, the largest residue levels showed up during the 14 day PHI for both years, followed by the 7 day and 21 day PHI, respectively.

Residue analysis for captan , Figure 8, indicated similar findings. The 1994 season follows the pattern of decreasing residue with an increase in PHI. As for 1993 and 1995 data, we see a pattern very similar to that observed for azinphosmethyl.

The cause of the residue patterns in Figure 7 and 8 for 1993 and 1995 data years is unknown. As indicated, the residue patterns observed for the two pesticides were very similar during all three years of the study. Most likely those factors which affected the patterns noted in one pesticide came into play for the other pesticide. Factors which may





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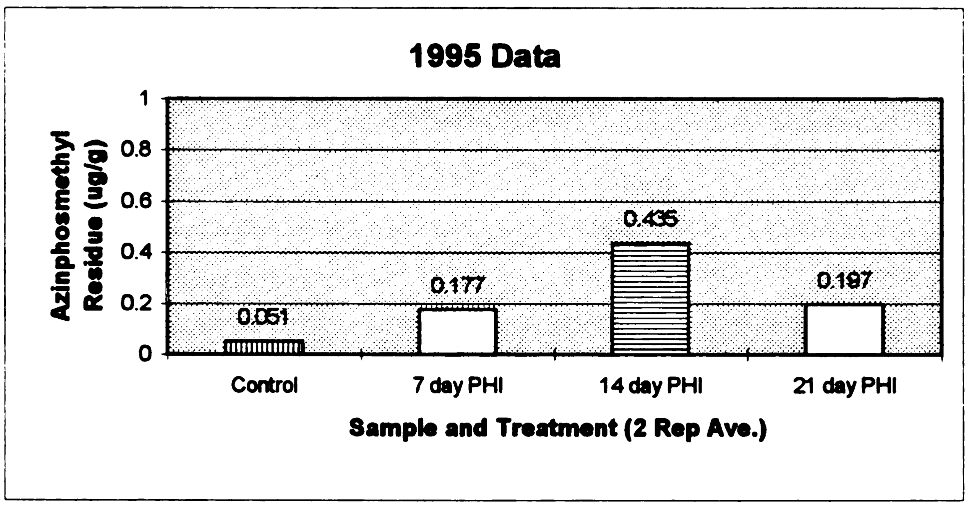
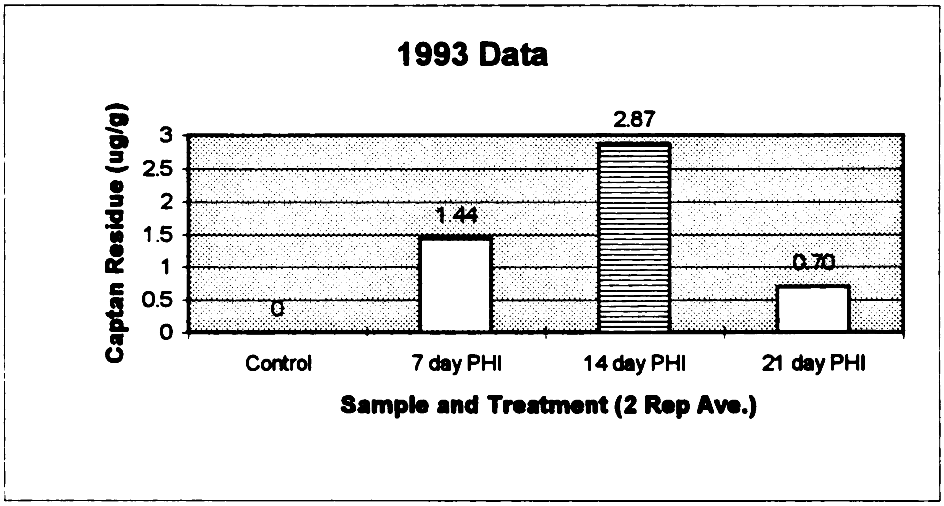
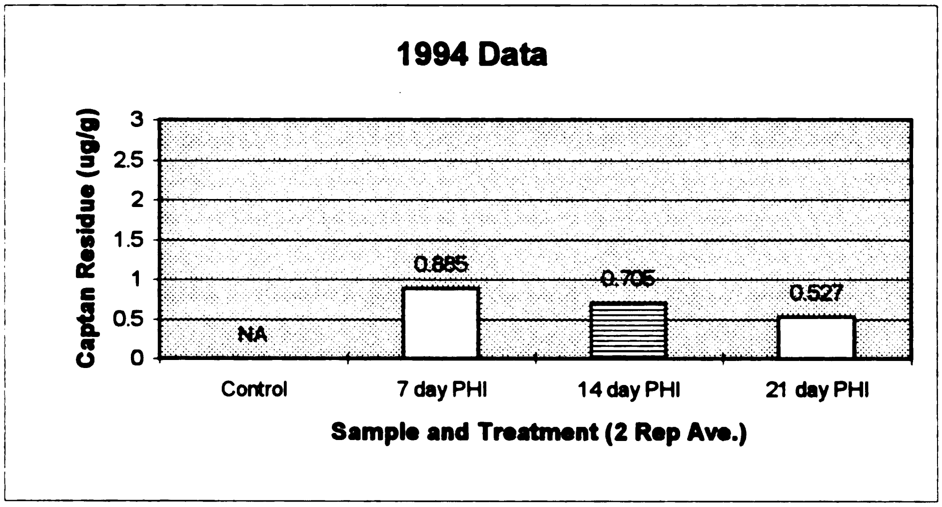


Figure 7: Azinphosmethyl Residues in Raw Apple





* NA = Not Analyzed

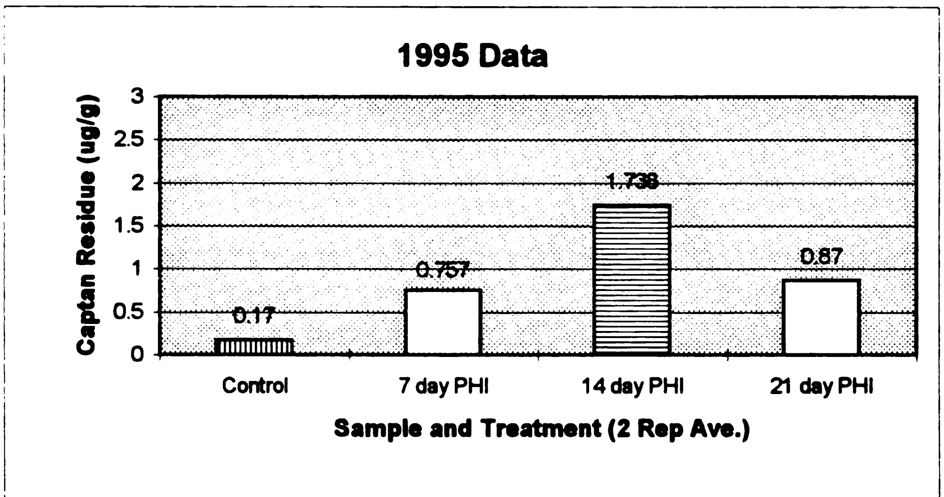


Figure 8: Captan Residues in Raw Apple

have contributed to these unexpected results include the effects of weather during or after the time of spray, the spray program itself, or any combination of these factors.

We can speculate on the potential of spray drift to be a factor. Numerous reports show that in virtually all pesticide applications, a fraction of released material drifts away from the target site and settles downwind of the application (Salyani et.al., 1991). A study by Salyani et.al. (1991), which included air blast sprayers, similar to that used in this project, indicated the potential for drift up to 195 m downwind. Referring to Appendix 1, the field plot diagram, only one buffer row exists between each treatment. Further, the 14 day PHI sample row is located directly between the 7 day and the 21 day PHI sample rows which would have the potential of collecting drift from both of the adjacent row of trees. The close proximity of the three treatments, particularly the location of the 14 day PHI samples, make spray drift a potential problem. This may help to explain why the 14 day PHI samples, during the 1993 and 1995 spray season, contained the highest residue levels for both pesticides. Unfortunately, this does not explain why 1994 residue levels followed the expected residue trend in respects to PHI.

Information regarding weather conditions during the 1993-95 growing seasons was collected by field staff at the Botany Research Field Laboratory, Michigan State University and entered into a Residue Study Field Report for this particular study. The weather data collected included: precipitation records prior to the application of the final spray program and extending through harvest; as well as conditions observed during the final spray applications themselves, which included wind, temperature, and other general observations. The only weather condition which showed a potential for disrupting the spray treatment or which could have resulted in the erroneous results observed in the PHI data, was the that of rain. Rain is one of the weather conditions that can significantly affect the environmental fate of foliar-applied pesticides (Willis *et al.*, 1994).

According to the Residue Study Field Report for 1994, 0.72 inches of rain followed the 14 day PHI final spray application. The amount of elapsed time between pesticide foliar application and initial rainfall can dramatically affect pesticide persistence, efficacy, and runoff losses (Willis *et al.*, 1994). It is possible that the rain may have affected this particular application. If so, this may help to explain why the 14 day PHI residues, in 1994 raw apples, were not higher than the 7 day and 21 day PHI residue as observed during 1993 and 1995. This supports previous speculations regarding spray drift, which is being considered as the cause of the residue patterns observed in 1993 and 1995 raw apple data, Figures 7 and 8. Previous studies by Northover *et al.* (1986), Smith and MacHardy (1984), Gunther *et al.* (1963), and Willis *et al.* (1994) indicate both pesticides to be susceptible to losses during rainfall.

Table 6. Azinphosmethyl and Captan Residues in Raw Apples

Data Year	* Azinphosmethyl (ug/g)	* Captan (ug/g)
1993	0.57+/- 0.34	1.67 +/- 1.1
1994	0.14 +/- 0.03	0.71 +/- 0.18
1995	0.27 +/- 0.14	1.12 +/- 0.54

* These values represent the average residue for 7, 14, and 21 day PHI treatments in raw apples

Due to the results indicated above, the effects of PHI on processed apple products will not be discussed. It was determined that the best results could be obtained by averaging the 7, 14, and 21 day PHI for each year, which will serve as a comparison between the raw apple residues and processed apple residues. Table 6 lists the averaged values for both captan and azinphosmethyl residues in the raw apple during all three years of the study.

(2) Residue Levels in Raw Apples

Referring to Figures 7 and 8, the overall residue levels fluctuated from year to year for both pesticides and with a striking similarity. Residue levels were at their highest in 1993 and lowest in 1994 for both pesticides even though the same spray schedule was used during all three years of the study. The method of application, the PHI employed, stage of apple development at harvest, and dates of application and harvest varied little from year to year. It is conceivable that the same factors which affected the PHI data may have come into play here as well.

Despite the variance in residue levels between study years, both azinphosmethyl and captan levels were well below the tolerances levels determined by the EPA under section 408 of the FFDCA. The maximum residues from preharvest and postharvest use or combination of such uses, in or on apples is 2.0 μg/g for azinphosmethyl and 25 μg/g for captan (Code of Federal Regulations, 1996). The highest value observed for azinphosmethyl in raw apples was 0.925 μg/g which is over 50% lower than the maximum allowable residue. The highest value observed for captan was 2.873 μg/g and is 88.5% lower than the maximum allowable residue for captan. The highest residues for both pesticides were found in 1993 raw apples with a PHI of 14 days. The lowest residues noted for azinphosmethyl and captan in raw apples were 0.115 μg/g and 0.527 μg/g, respectively. Both of these low values were observed in 1994 raw apple data for 21 day PHI and represent 5.75% and 2.11% of the maximum allowable residues for azinphosmethyl and captan, respectively.

These data did not give consistent results from year to year in terms of residue levels. It may however, indicate that those factors affecting pesticide residues in the field can not be counted on to give repeat performances from year to year.

(3) Product Yield

During all three years of the study, with the exception of apple juice, the processing methods employed were the same. Table 7 lists yield data for all three years of the study. Apple juice prepared during 1993 was processed using a different method than during 1994-95. Due to this change in procedure apple juice yield in 1993 was lower than 1994 and 1995. Yield data can be expected to vary from year to year. This may be a result of a number of factors including: apple size, apple shape, and the efficiency of the processing method. Average apple size can vary between years and is affected by the individual growing season. Although a majority of apples have uniform shape, those apples altering from that mold may not be peeled or cored with the same efficiency. This may result in portions of peel and core not being removed or the removal of the apple flesh. These factors were readily observed during the processing phase. Applesauce yields are lower than the other processed fractions because of the number of unit operations neccessary to produce this product and declines with each of the following processing steps: peeling and coring (peeled applesauce only), slicing, blanching, and finishing.

Table 7: Yield Data for 1993-1995

Product	Sampling Year	Raw Apple Wt (Kg)	Product Wt (Kg)	Yield
Unpeeled Applesauce				
	1993	0.82 +/- 0.16	0.33 +/- 0.09	0.41 +/- 0.04
	1994	1.00 +/- 0.07	0.40 +/- 0.01	0.40 +/- 0.03
	1995	0.88 +/- 0.12	0.39 +/- 0.09	0.44 +/- 0.05
Peeled Applesauce				
	1993	1.61 +/- 0.25	0.37 +/- 0.07	0.23 +/- 0.02
	1994	1.42 +/- 0.05	0.39 +/- 0.06	0.27 +/- 0.02
	1995	1.44 +/- 0.07	0.44 +/- 0.08	0.31 +/- 0.02
Apple Slice				
	1993	0.58 +/- 0.09	0.40 +/- 0.18	0.69 +/-0.02
	1994	0.74 +/- 0.12	0.54 +/- 0.09	0.73 +/- 0.02
	1995	0.80 +/- 0.12	0.62 +/- 0.09	0.77 +/- 0.01
Product	**Sampling Year**	**Raw Apple Wt (Kg)**	**Product Vol (ml)**	**Yield (ml/Kg)**
Apple Juice				
	1993	1.59 +/- 0.27	643 +/- 133	404 +/- 64
	1994	0.57 +/- 0.06	408 +/- 65	710 +/- 71
	1995	0.62 +/- 0.07	396 +/- 38	640 +/- 46

C. Azinphosmethyl Residue Study

The following sections will discuss the residue studies which were set up to examine the effects of individual postharvest wash treatments and their ability to reduce or eliminate azinphosmethyl residue in finished apple products. The raw data pertaining to azinphosmethyl residues in peeled applesauce, unpeeled applesauce, apple juice, and apple slices is contained in Appendices 4, 5, 6, and 7, respectively. These data are illustrated in the Figures 9 - 44. Only those findings which were calculated to be statistically significant are discussed.

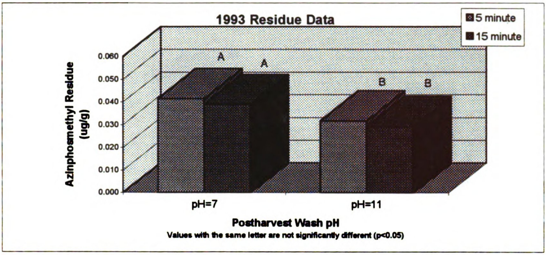
(1) Postharvest Wash Treatment Variables

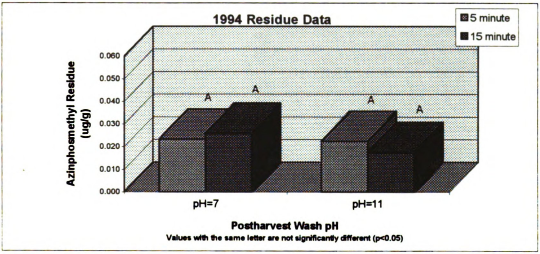
Postharvest wash treatment variables were examined to determine their effect on the removal or degradation of azinphosmethyl surface residues on raw apples. Residue levels were examined only after processing of the postharvest wash treated apples into applesauce (peeled and unpeeled), apple juice, and apple slices. Thus, the residues encountered in the following sections will reflect the effect of postharvest wash treatments and processing.

a. Effect of Postharvest Wash pH at 21°C

Figures 9-12 compare a pH 7 wash to a pH 11 wash, both at 21°C. Figure 9, peeled applesauce, showed a reduction in azinphosmethyl residue in the pH 11 wash over the pH 7 wash during the 1993 data year. This was observed for both the 5 minute and the 15 minute wash treatments.

Figure 10, unpeeled applesauce, shows the pH 11 wash for 5 minutes to be more effective than a pH 7 wash during 1993. The 15 minute wash was found to be more





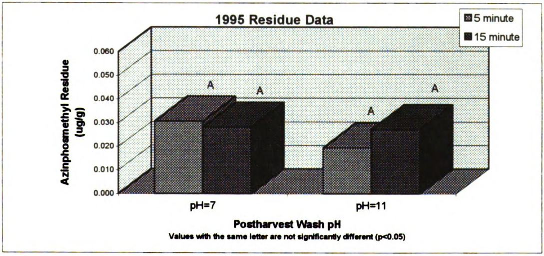


Figure 9: Effect of Postharvest Wash pH on the Removal of Azinphosmethyl at 21°C in Peeled Applesauce

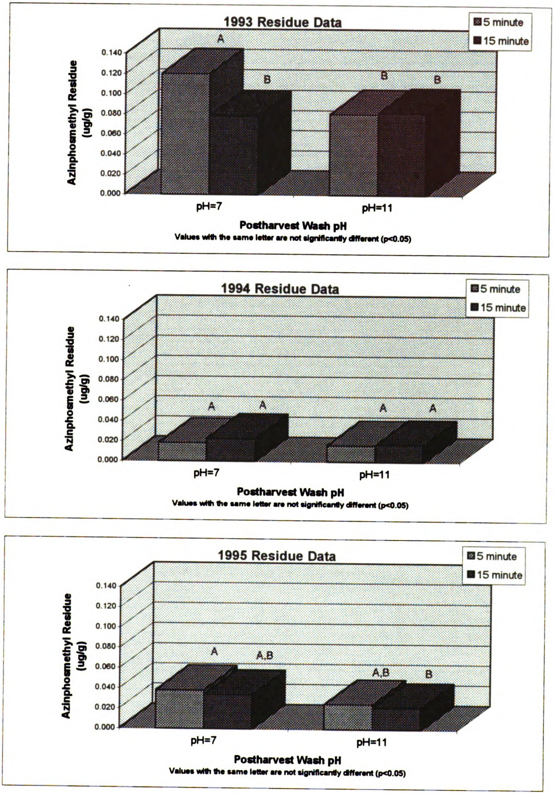
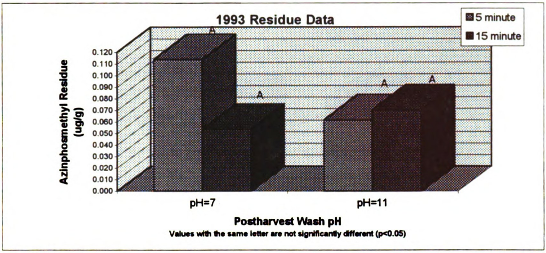
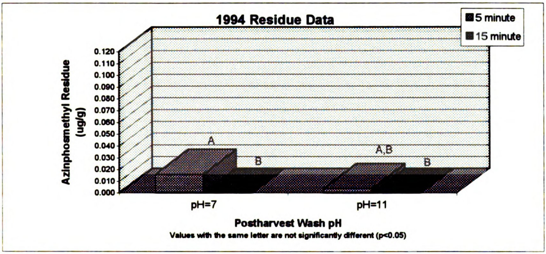


Figure 10: Effect of Postharvest Wash pH on the Removal of Azinphosmethyl at 21°C in Unpeeled Applesauce





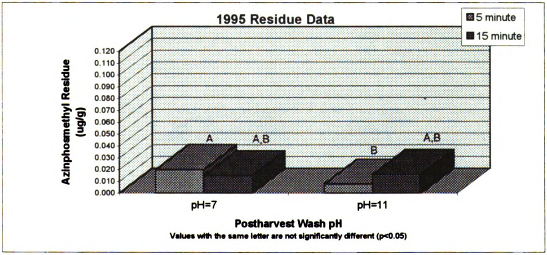


Figure 11: Effect of Postharvest Wash pH on the Removal of Azinphosmethyl at 21°C in Apple Juice

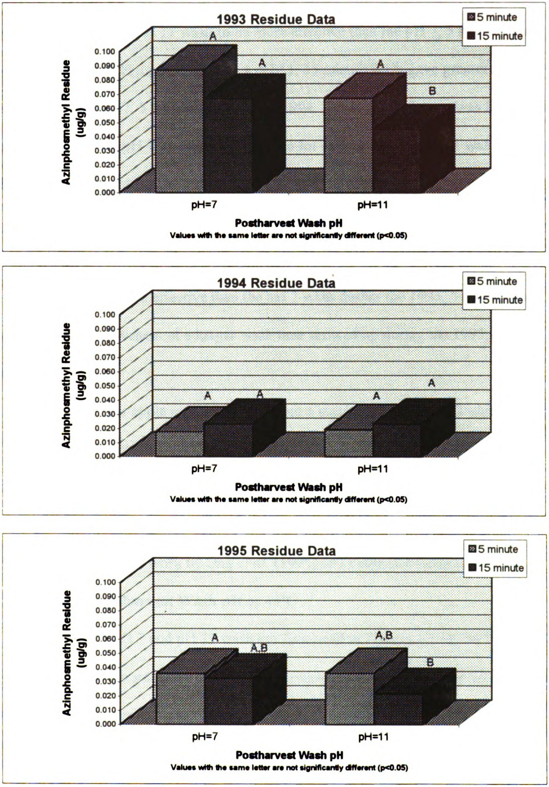


Figure 12: Effect of Postharvest Wash pH on the Removal of Azinphosmethyl at 21°C in Apple Slices

effective in residue removal than the 5 minute wash at pH 7 in 1993. Data for 1995 showed the 15 minute, pH 11 wash to be more effective than the pH 7, 5 minute wash.

Apple juice data, Figure 11, showed a pH 11, 15 minute wash gave greater residue removal than the pH 7, 5 minute wash during 1994. A longer wash time was found to be more effective in the pH 7 wash for 1994. Data for 1995 indicated pH 11 was more effective than pH 7 during the 5 minute wash.

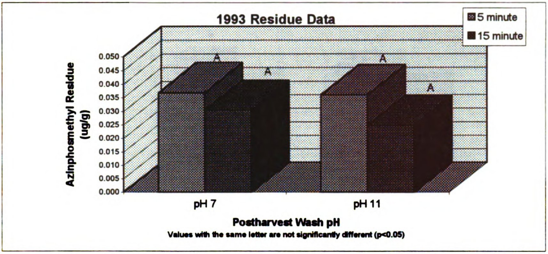
In apple slices, Figure 12, the pH 11, 15 minute wash was found to be more capable of removing residues over pH 7, 5 minute wash as observed during 1993 and 1995. The pH 11 wash was found more effective than the pH 7 wash during the 1993, 5 minute wash. The increased effectiveness of a longer wash time showed up during the 1993, pH 11 wash.

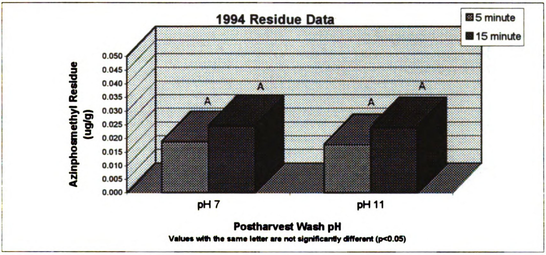
In each of the four apple products, there were a number of instances in which the pH 11 wash and a 15 minute wash time were observed to be statistically more effective in reducing azinphosmethyl residues than the pH 7 wash for 5 minutes. These observations are in agreement with various studies on the behavior of azinphosmethyl in aqueous solutions which includes work by Ong *et al.* (1995) and Faust and Gomma (1972).

b. Effect of Postharvest Wash pH at 43°C

The effects of a pH 7 and pH 11 wash are illustrated in Figures 13-16. In Figure 13, peeled applesauce, no statistical differences between treatments was observed during all three years. No determinations could be made concerning pH or wash time variables.

Figure 14, unpeeled applesauce, indicated the pH 11, 15 minute wash to be more effective at reducing azinphosmethyl residues when compared to the pH 7, 5 minute wash in the1995 data.





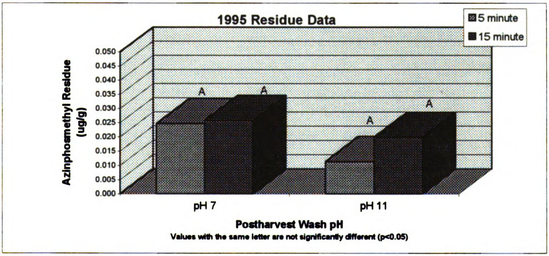
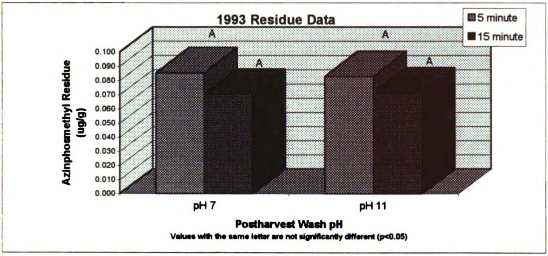
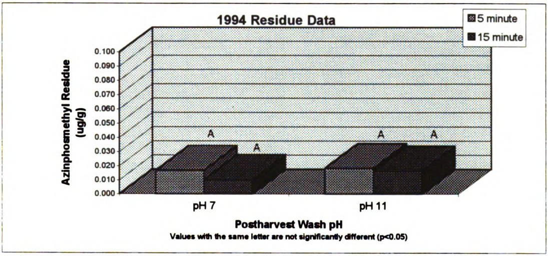


Figure 13: Effect of Postharvest Wash pH on the Removal of Azinphosmethyl at 43°C in Peeled Applesauce





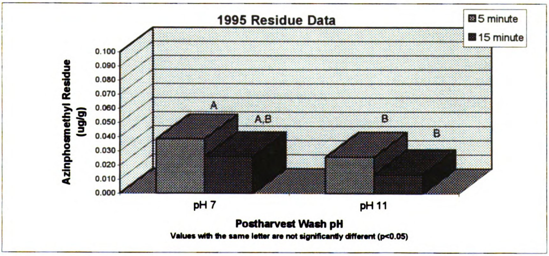
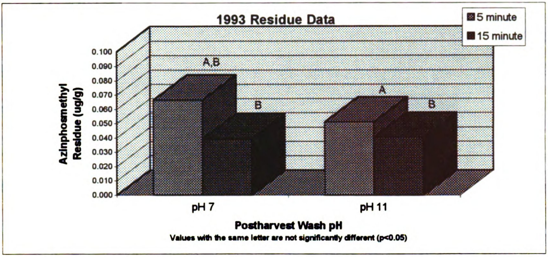
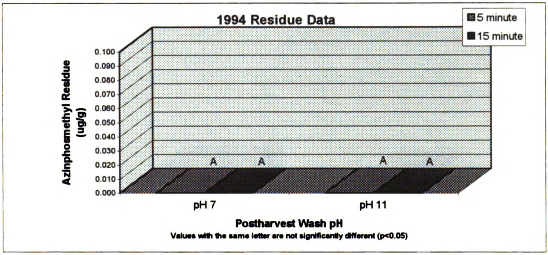


Figure 14: Effect of Postharvest Wash pH on the Removal of Azinphosmethyl at 43°C in Unpeeled Applesauce





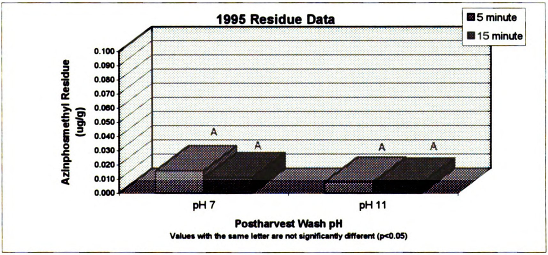
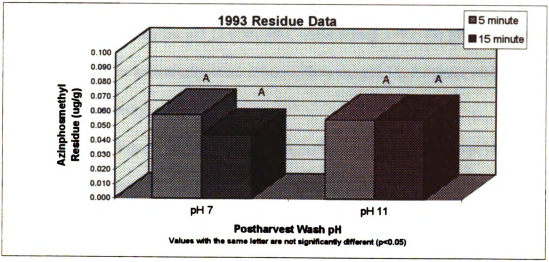
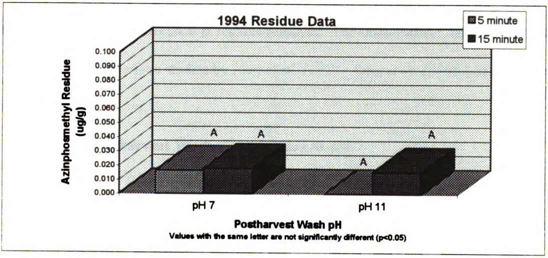


Figure 15: Effect of Postharvest Wash pH on the Removal of Azinphosmethyl at 43°C in Apple Juice





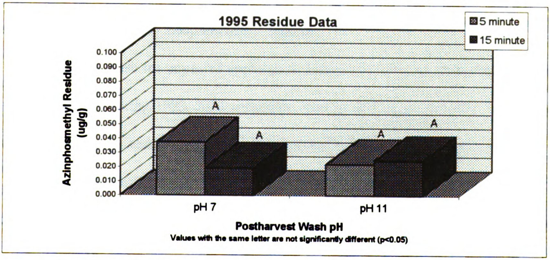


Figure 16: Effect of Postharvest Wash pH on the Removal of Azinphosmethyl at 43°C in Apple Slices

Data for 1993 apple juice, Figure 15, showed the 15 minute wash to be more effective over 5 minute wash during the pH 11 treatment. Also during 1993, the pH 7, 15 minute wash was shown to be statistically more effective than the pH 11, 5 minute wash, at removing azinphosmethyl residues.

Apple slice data, Figure 16, showed the same lack of statistical distinction between treatments as that observed in Figure 13. No determinations as to the effectiveness of the wash treatment variables could be made.

Data from unpeeled applesauce and apple juice indicated a longer wash time and the pH 11 wash to be more effective at residue removal. The observations, though minor, are in agreement with previous studies by Flint *et al.* (1970), Ong *et al.* (1995), and Faust and Gomma (1972).

c. Effect of Postharvest Wash Temperature at pH 7

The effects of 21° C and 43°C wash temperature at pH 7 are illustrated in Figures 17-20. From Figure 17, peeled applesauce, only one statistically significant observation was made. Data for 1993, 15 minute wash samples showed a higher temperature (43°C) to be more effective in removing azinphosmethyl residues.

The 15 minute wash for unpeeled applesauce, Figure 18, removed more residues than the 5 minute wash during 1993, 21°C treatment. During 1993 and 1995, the 43°C wash was more effective at residue removal when compare to the 21°C, 5 minute wash.

Figure 19, apple juice, displayed the longer wash time as being more adequate at reducing residues in the 1994, 21°C wash. Residue levels were found to be significantly lower in 43°C, 15 minute wash when compared to the 21°C, 5 and 15 minute wash for

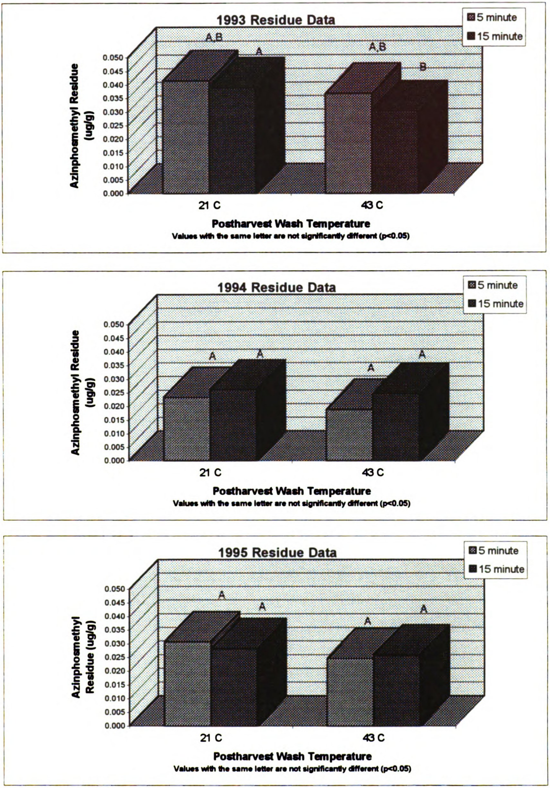
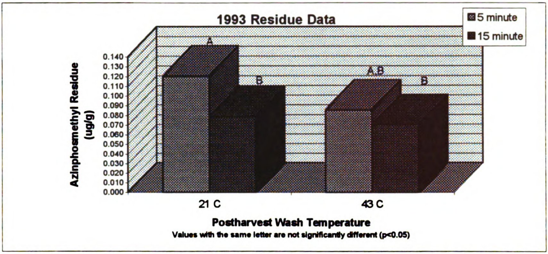
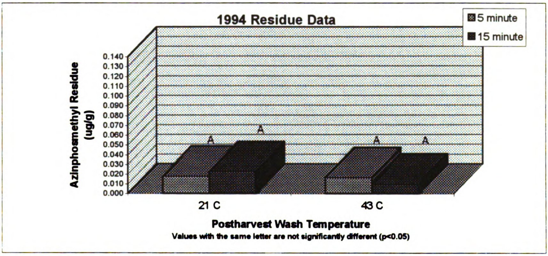


Figure 17: Effect of Postharvest Wash Temperature on the Removal of Azinphosmethyl at pH 7 in Peeled Applesauce





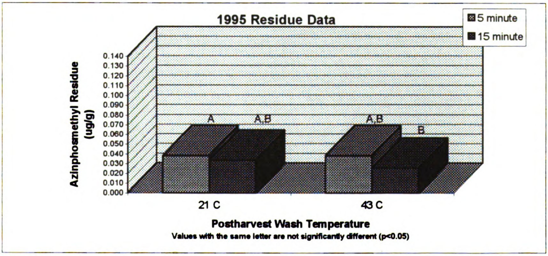


Figure 18: Effect of Postharvest Wash Temperature on the Removal of Azinphosmethyl at pH 7 in Unpeeled Applesauce

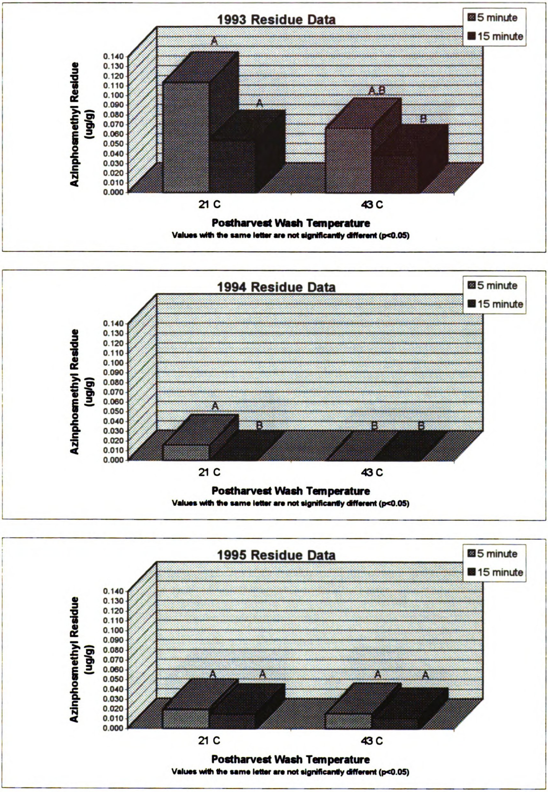
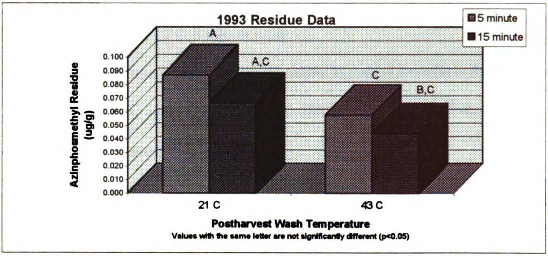
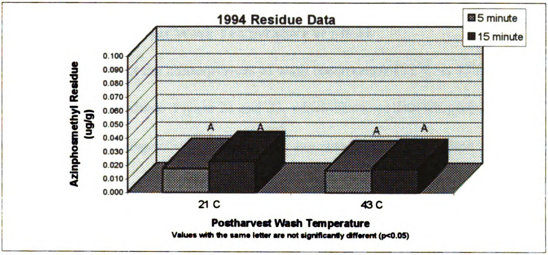


Figure 19: Effect of Postharvest Wash Temperature on the Removal of Azinphosmethyl at pH 7 in Apple Juice





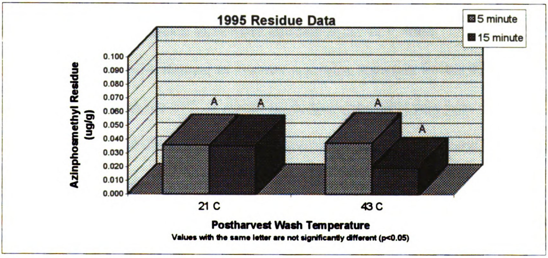


Figure 20: Effect of Postharvest Wash Temperature on the Removal of Azinphosmethyl at pH 7 in Apple Slices

1993. Data for 1994 showed residues from the 43°C, 5 and 15 minute wash to be lower than that observed for the 21°C, 5 minute wash.

The higher temperature wash was more successful in residue removal in the 5 minute wash treatment for 1993 apple slices, Figure 20. Data for 1994 and 1995 showed no statistical differences between wash treatments.

Observations relating to the increased capacity of a 43°C wash to remove azinphosmethyl were noted for all four products. The increased effect of wash time on reducing residues was observed only once with any statistical significance.

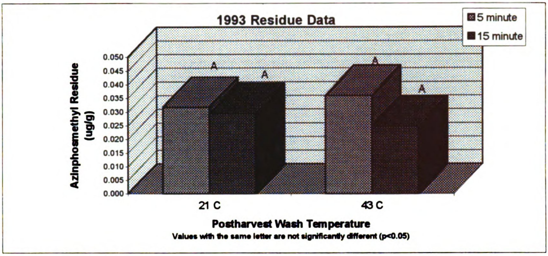
d. Effect of Postharvest Wash Temperature at pH 11

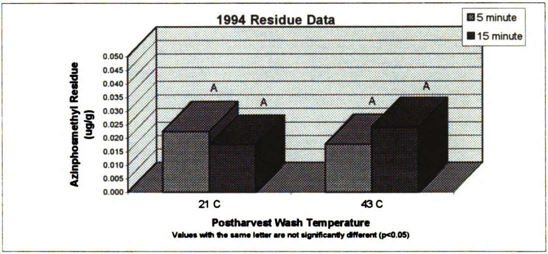
Figures 21-24 depict the consequences of wash temperature (21°C vs 43°C) at pH 11, on azinphosmethyl residues. Figure 21 and 22, which illustrate data for peeled and unpeeled applesauce, respectively, did not offer any statistical differentiation between wash treatment means.

Figure 23, 1993 apple juice, showed the 43°C, 15 minute wash to be statistically more effective in reducing azinphosmethyl residues compard to the 21°C, 5 and 15 minute wash. A longer wash time was shown to be more effective in the 43°C wash.

Apple slices, Figure 24, showed an increase in residue reduction for the 43°C, 5 minute wash when compared to the 21°C, 5 minute wash during the 1994 data year. Data for 1993 exhibited a longer wash time to be more effective in the 21°C wash and also found the 43°C, 5 minute wash to increase residue reduction over the 21°C, 15 minute wash.

Apple juice and apple slices revealed the increased effectiveness of a longer wash time and a higher wash temperature at removing azinphosmethyl residues. These observations are in agreement with data by Liang and Lichtenstein (1972) and Ong *et al.* (1995).





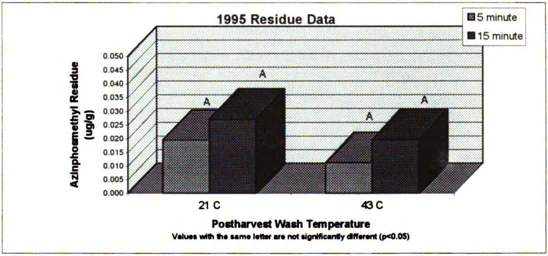
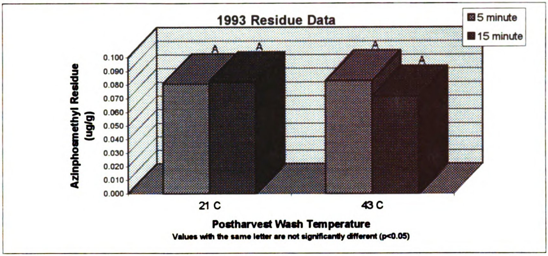
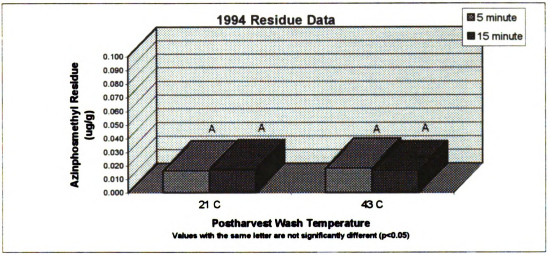


Figure 21: Effect of Postharvest Wash Temperature on the Removal of Azinphosmethyl at pH 11 in Peeled Applesauce





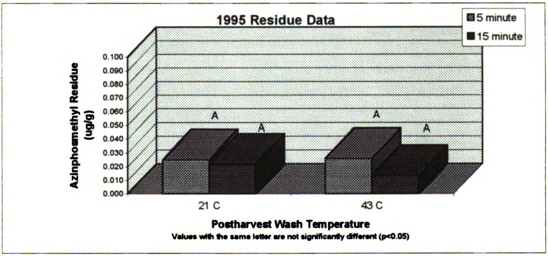
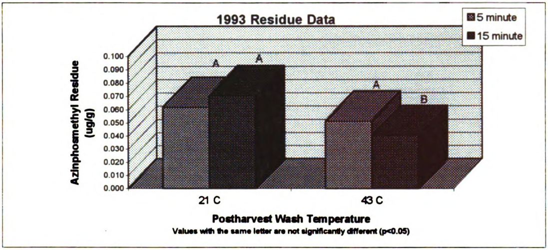
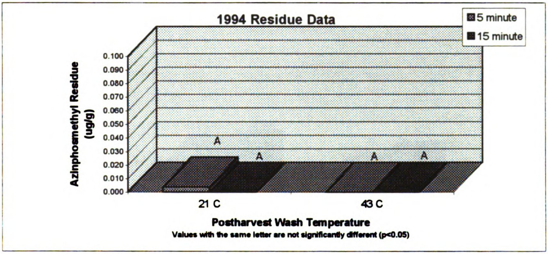


Figure 22: Effect of Postharvest Wash Temperature on the Removal of Azinphosmethyl at pH 11 in Unpeeled Applesauce





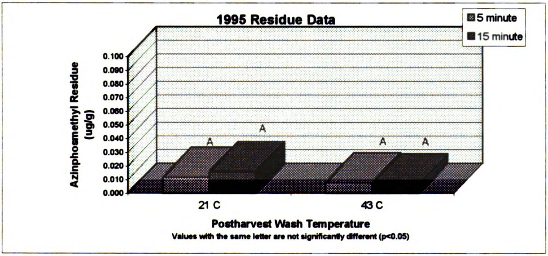
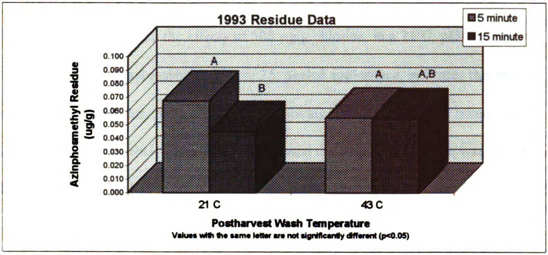
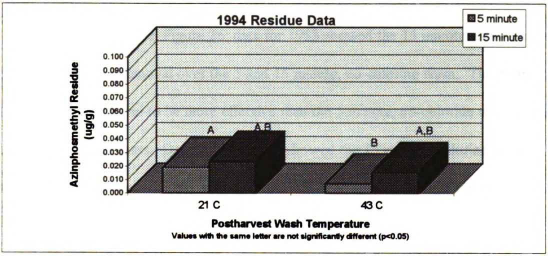


Figure 23: Effect of Postharvest Wash Temperature on the Removal of Azinphosmethyl at pH 11 in Apple Juice





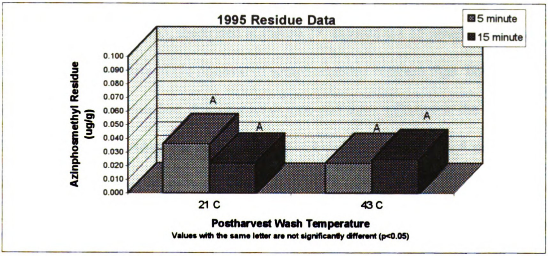


Figure 24: Effect of Postharvest Wash Temperature on the Removal of Azinphosmethyl at pH 11 in Apple Slices

e. Effect of 500 μg/g Chlorine in Postharvest Wash

Figures 25-28, illustrate the effects of 500 μg/g chlorine, in a 21°C, pH 7 postharvest wash, on azinphosmethyl residues. Figure 25, peeled applesauce, indicates that the 5 minute chlorine wash was more effective in removing residues than the 5 minute, no-chlorine wash during 1993. Data for 1995 showed the 5 minute, chlorine wash to be more effective than the 5 and 15 minute, no-chlorine wash. Data for 1995 also showed the 5 minute, chlorine wash as being more effective in residue removal than the 15 minute, chlorine wash.

In unpeeled applesauce, Figure 26, data for 1993 showed the 15 minute, chlorine wash as increasing residue removal over the 5 and 15 minute, no-chlorine wash. The 5 minute, chlorine wash was found to be more effective than the 5 minute, no-chlorine wash during 1993 and 1995 data years. Data for 1995 also showed the 15 minute, chlorine wash to be more effective than the 5 minute, no-chlorine wash. The increased effectiveness of a longer wash time was exhibited during 1993 in both the chlorine and no-chlorine wash treatments.

Apple juice data for 1993, illustrated in Figure 27, showed the 15 minute, chlorine wash to be more adequate in the removal of azinphosmethyl residues than both the 5 and 15 minute, no-chlorine washes. A longer wash time was more effective in the 1993, chlorine wash and also observed in the 1994, no-chlorine wash. Both the 5 and 15 minute, chlorine washed showed lower residue levels compared to the 5 minute, no-chlorine wash.

No determinations could be made statistically, concerning wash time or chlorine effects for 1994 or 1995 data in apple slices, Figure 28. Data for 1993 did show the 5 and 15

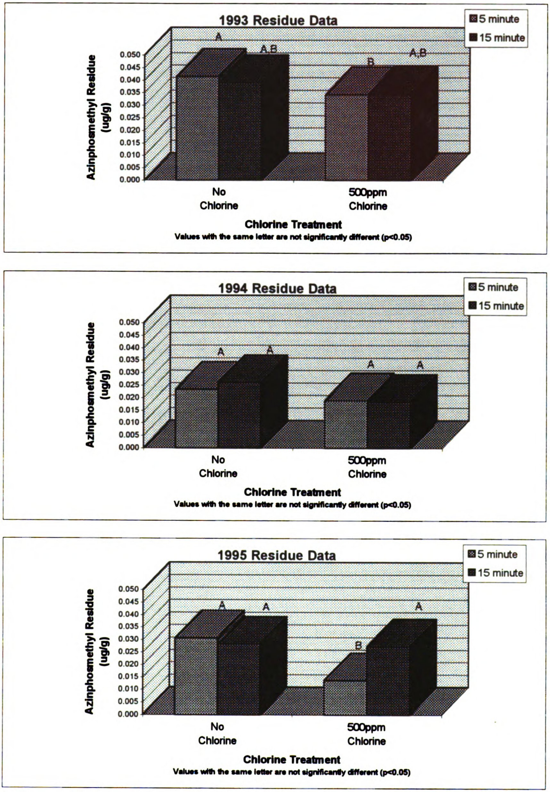
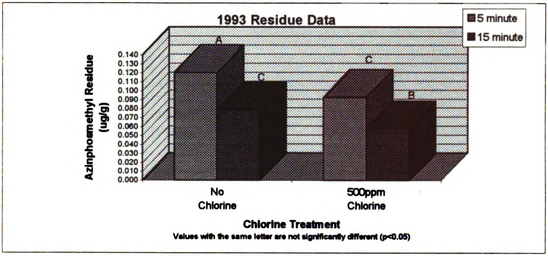
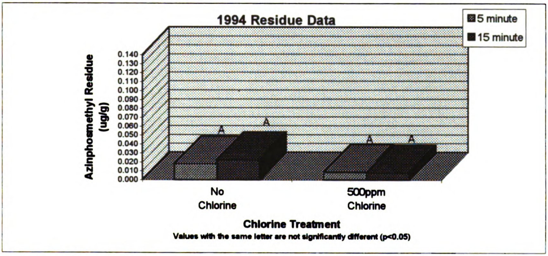


Figure 25: Effect of 500 ppm Chlorine on the Removal of Azinphosmethyl at 21°C and pH 7 in Peeled Applesauce





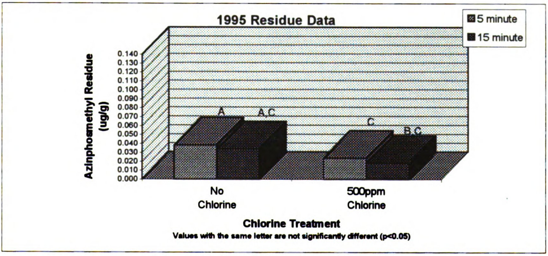
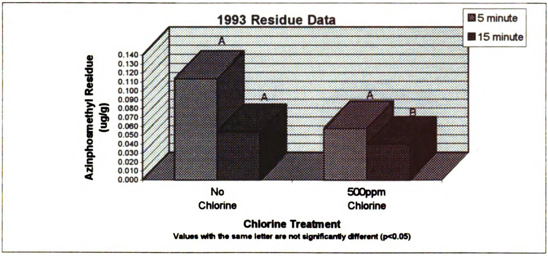
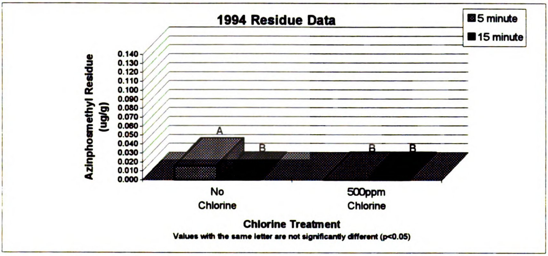


Figure 26: Effect of 500 ppm Chlorine on the Removal of Azinphosmethyl at 21°C and pH 7 in Unpeeled Applesauce





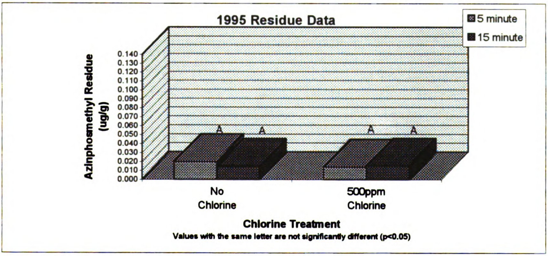
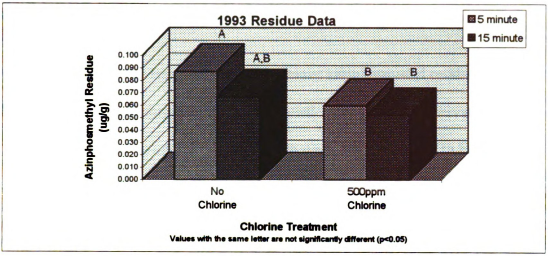
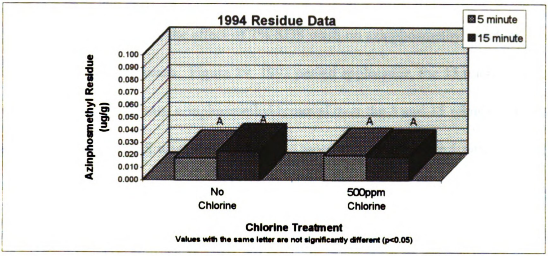


Figure 27: Effect of 500 ppm Chlorine on the Removal of Azinphosmethyl at 21°C and pH 7 in Apple Juice





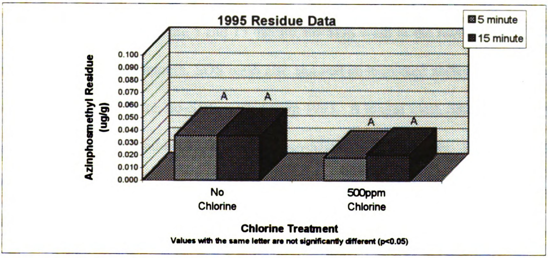


Figure 28: Effect of 500 ppm Chlorine on the Removal of Azinphosmethyl at 21°C and pH 7 in Apple Slices

minute, chlorine washes to be more effective in residue removal when compared to the 5 minute, no-chlorine wash.

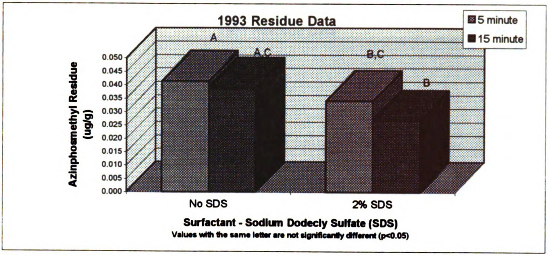
Chlorine exhibited an increased ability to remove azinphosmethyl residues in comparison to the no-chlorine wash. These statistically significant observations occurred at least once in all four products. An increase in wash time was found to be advantageous in residue removal in both the chlorine and no-chlorine washes for unpeeled applesauce and apple juice.

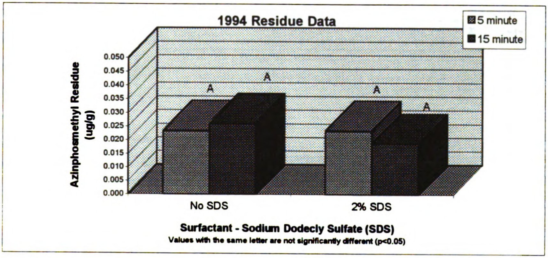
f. Effect of 2% SDS in Postharvest Wash

Figures 29-32, illustrate the effect of 2% SDS wash on azinphosmethyl residues, in a 21°C, pH 7 postharvest wash. Figure 29, 1993 peeled applesauce, the 15 minute, SDS wash was shown to increase azinphosmethyl removal over the 5 and 15 minute, no-SDS wash. The 5 minute SDS wash was found to be more effective that the 5 minute, no-SDS wash. No statistical distinctions could be made between wash treatments in the 1994 and 1995 data.

Data for 1993 unpeeled applesauce, Figure 30, indicated the 15 minute, SDS wash to be more effective than both the 5 and 15 minute, no-SDS wash in the removal of azinphosmethyl. The 5 minute, SDS wash also showed an increased ability to remove residues over the 5 minute, no-SDS wash during 1993. A longer wash time was shown to significantly decrease residues during both the no-SDS and SDS washes. In the data for 1995 samples, the 15 minute, SDS wash was more effective than the 5 minute, no-SDS wash.

Figure 31, apple juice, showed the 15 minute, SDS wash to be more advantageous when it came to removing azinphosmethyl residues in comparison to the 5 minute,





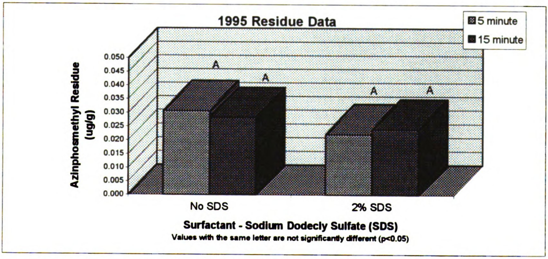


Figure 29: Effect of 2% SDS on the Removal of Azinphosmethyl at 21°C and pH 7 in Peeled Applesauce

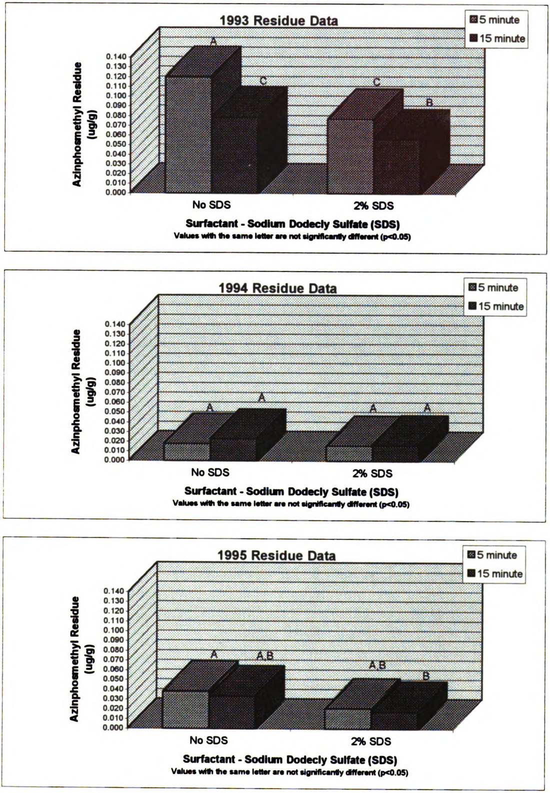
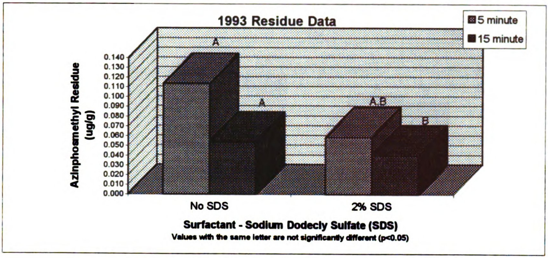
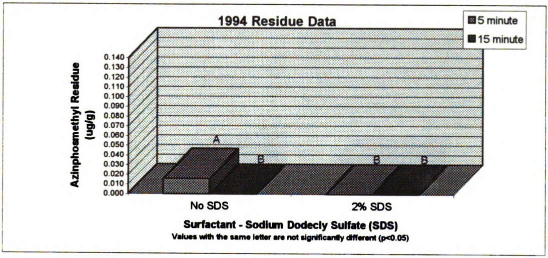


Figure 30: Effect of 2% SDS on the Removal of Azinphosmethyl at 21°C and pH 7 in Unpeeled Applesauce





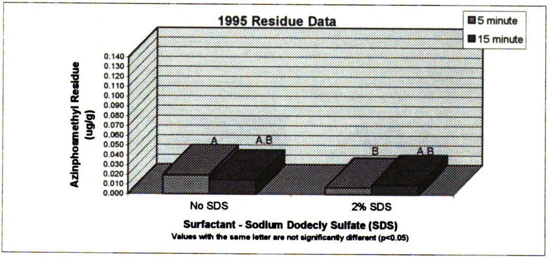
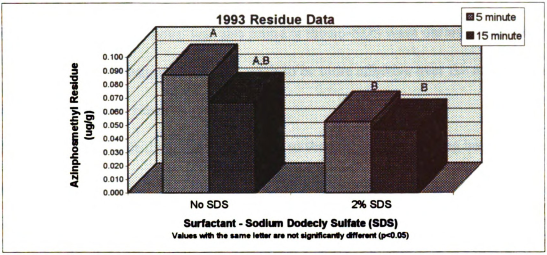
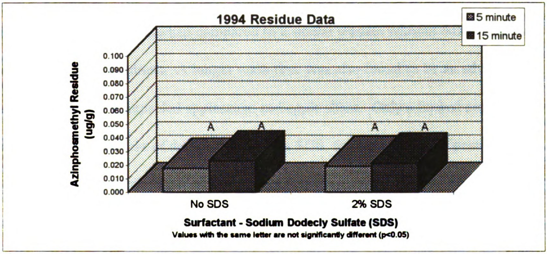


Figure 31: Effect of 2% SDS on the Removal of Azinphosmethyl at 21°C and pH 7 in Apple Juice





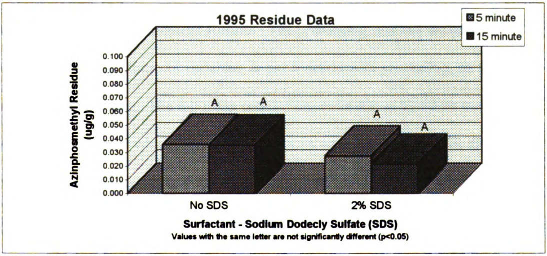


Figure 32: Effect of 2% SDS on the Removal of Azinphosmethyl at 21°C and pH 7 in Apple Slices

no-SDS wash. This was observed during 1993 and 1994. The ability of a longer wash time to increase residue removal was also found in the no-SDS wash during 1994. Data for 1994 and 1995 both showed the SDS wash to be more effective over the no-SDS wash during a 5 minute wash time.

Results for apple slice data, Figure 32, point to the SDS wash as having better residue removal ability over the no-SDS wash for the 1993, 5 minute treatment. As for the remaining data, no statistical differences were observed among the treatments.

The conclusions drawn from the results above, indicate 2% SDS did aid in the removal of azinphosmethyl residues when compared to a similar washes without SDS. This was observed in all four products. A longer wash time was also found to be an advantage in removing residues for unpeeled applesauce and apple slices. Only a limited amount of literature exists on the use of detergents, such as SDS, for the removal of pesticide residues. Although no studies directly targeted azinphosmethyl or SDS, similar work by Chin (1991) and Elkins (1989) did report the successful removal of the pesticide, parathion, from spinach and broccoli with the use of detergents in wash water.

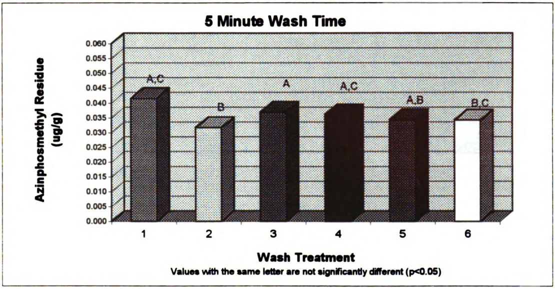
Postharvest Wash Treatment Results. The preceeding sections illustrated the effectiveness of wash treatment variables, in combination with processing, on reducing azinphosmethyl residues. The following conclusions were drawn based on the statistically significant observations which were made. A pH 11 wash was shown to be more effective over a pH 7 wash. This was true for both 21°C and 43°C wash temperatures. A 43°C wash temperature was found to be more effective over a 21°C wash, which was true for both the a pH 7 and pH 11 wash. The addition of chlorine (500 µg/g) and SDS (2%)

were both shown to be more effective in removing residue in comparison to plane water washes. As for wash time, a longer wash was shown to increase the effectiveness of the wash variables, as well as the individual wash. These findings are in agreement with previous studies.

The conclusions drawn from the preceeding sections were not found to be true for all the products or during each data year. No patterns were found which would point to a relationship between wash treatment effectiveness and product type. It was however noted that most of the statistically significant observations were found to have occured in data from 1993. Upon closer examination of Figures 9-32, 1993 data shows the highest overall residue levels, followed by 1995 and 1994 data, respectively. Referring back to Figure 7 and Table 6, this is the same pattern which was observed in the raw apple residue data prior to processing. Wheather the higher residue levels observed for 1993 increased wash treatment effectiveness is not known. The wash treatments which appeared to have the most significant effect or those which showed the most statistically significant observations were the chlorine and SDS wash treatments.

(2) Comparison of Postharvest Wash Treatments

Figures 33-44 illustrate the average azinphosmethyl residues observed in each of the six wash treatments so that they may be compared as to their relative effectiveness in relation to one another. Upon review of these figures, residue levels between the various wash treatments were not found to differ to any great extent. Among the four products, only a small number of cases were observed in which wash treatments differed statistically but with no patterns being observed in which to base any conclusions concerning a more



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

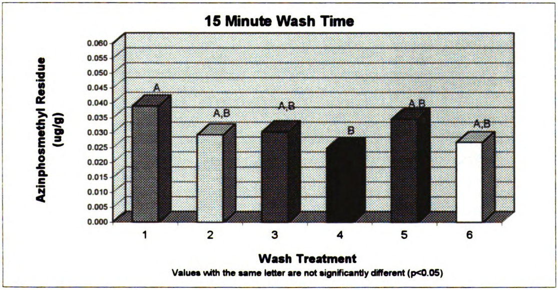
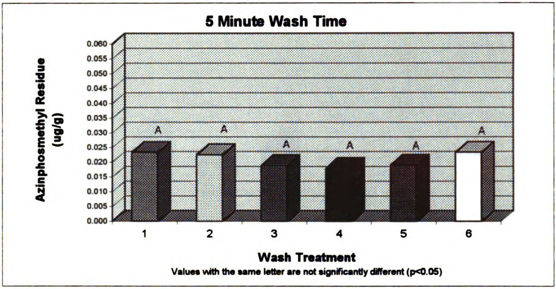


Figure 33: Comparison of Postharvest Wash Treatments - Azinphosmethyl Residue in Peeled Applesauce, 1993 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

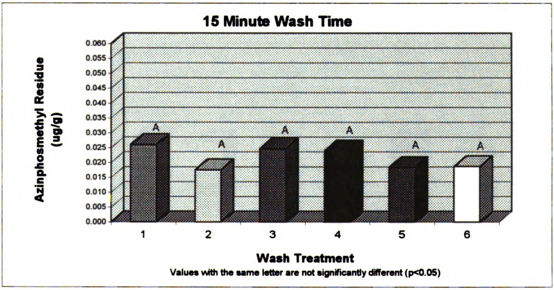
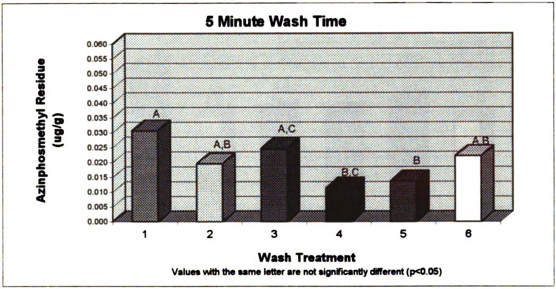


Figure 34: Comparison of Postharvest Wash Treatments - Azinphosmethyl Residue in Peeled Applesauce, 1994 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

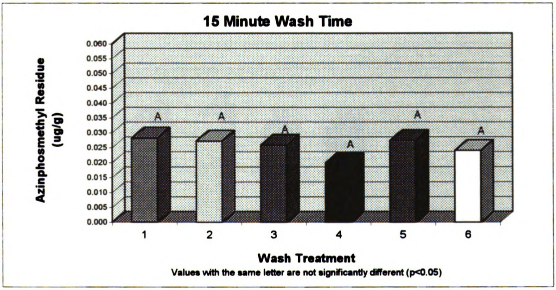
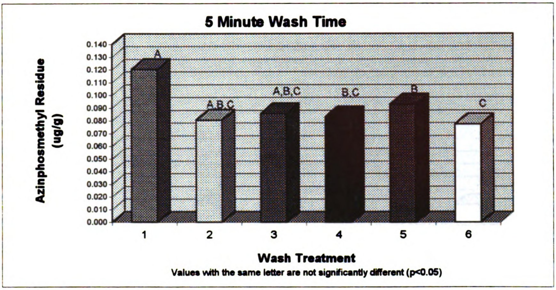


Figure 35: Comparison of Postharvest Wash Treatments - Azinphosmethyl Residue in Peeled Applesauce, 1995 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

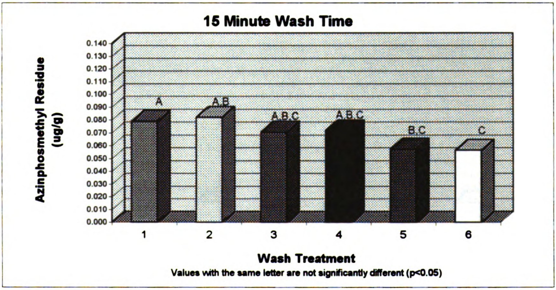
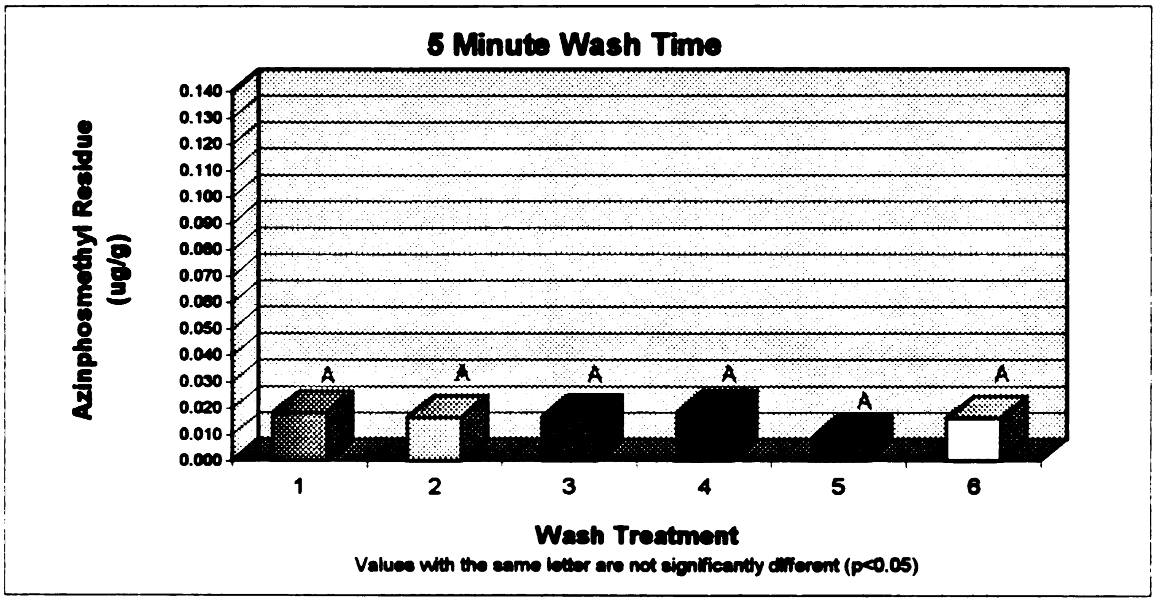


Figure 36: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Unpeeled Applesauce, 1993 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

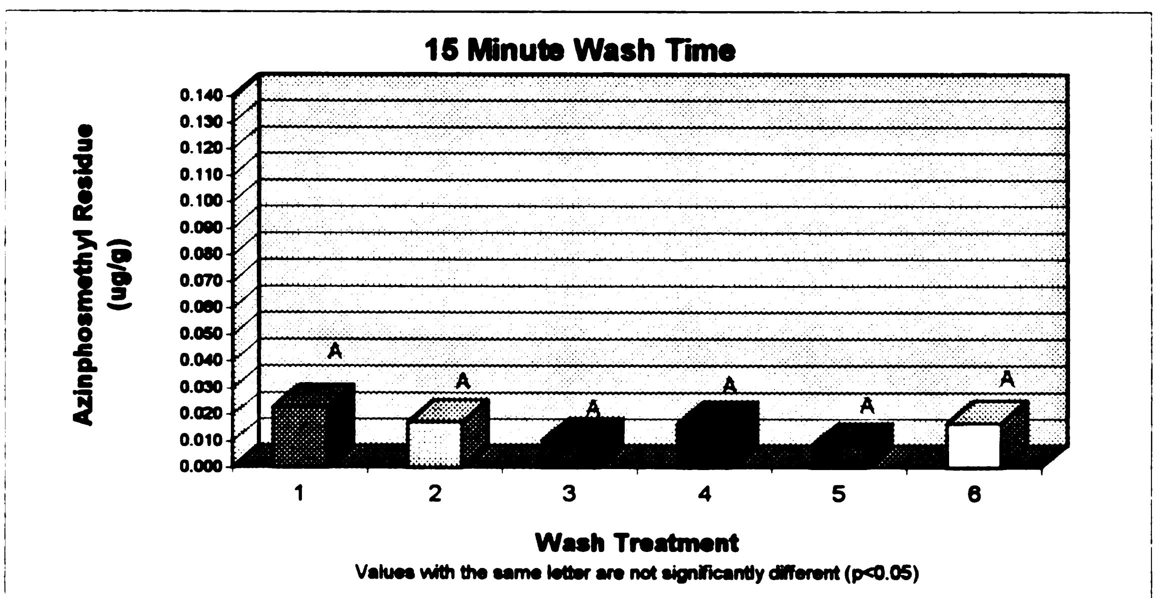
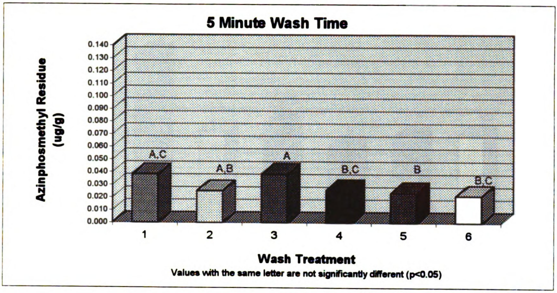


Figure 37: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Unpeeled Applesauce, 1994 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

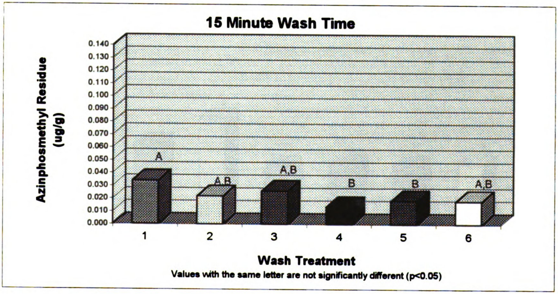
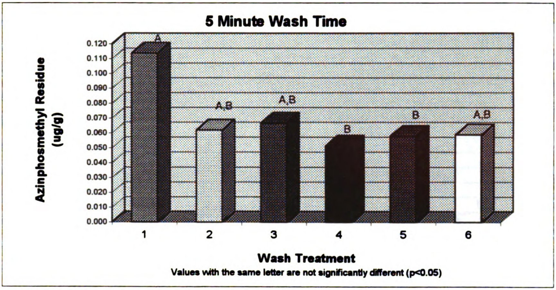


Figure 38: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Unpeeled Applesauce, 1995 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

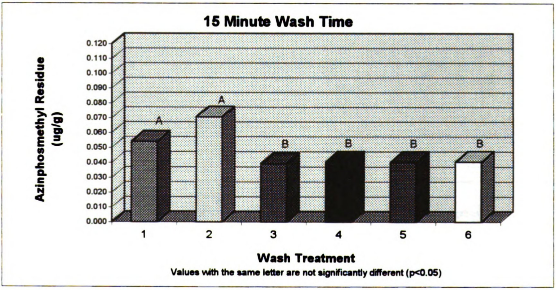
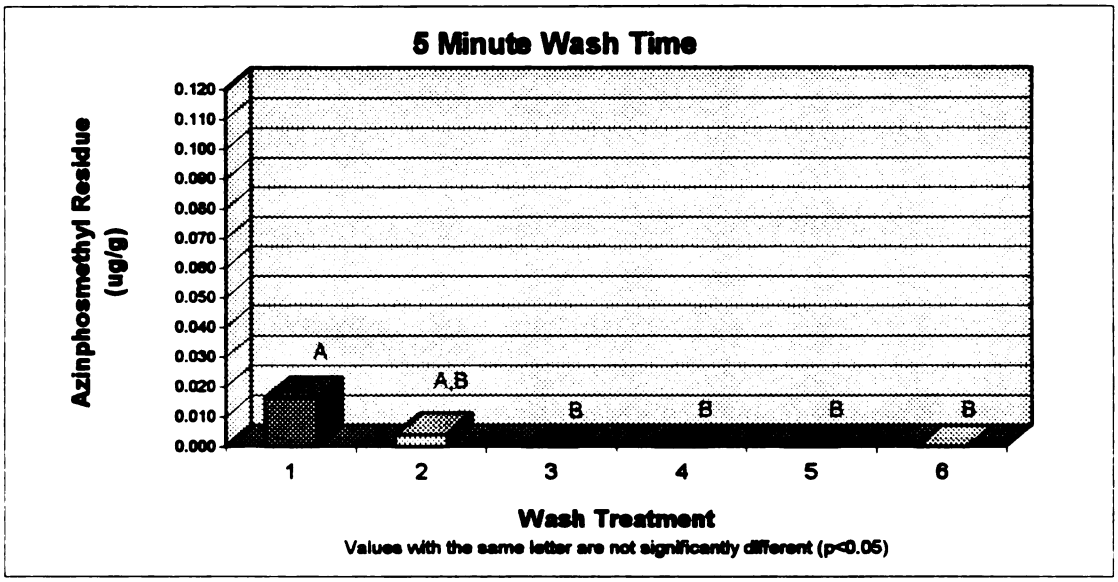


Figure 39: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Apple Juice, 1993 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

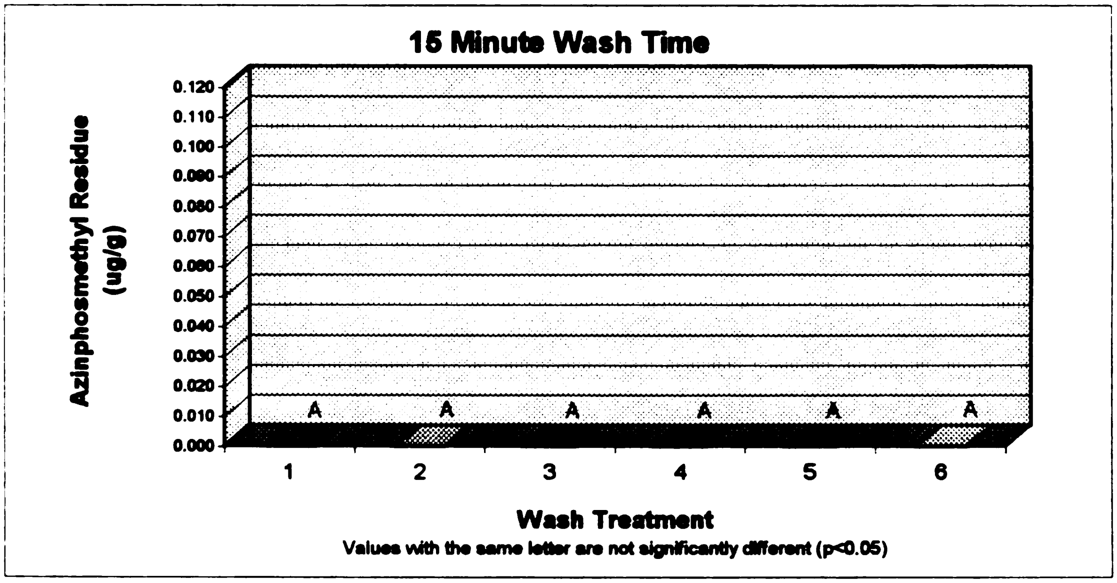
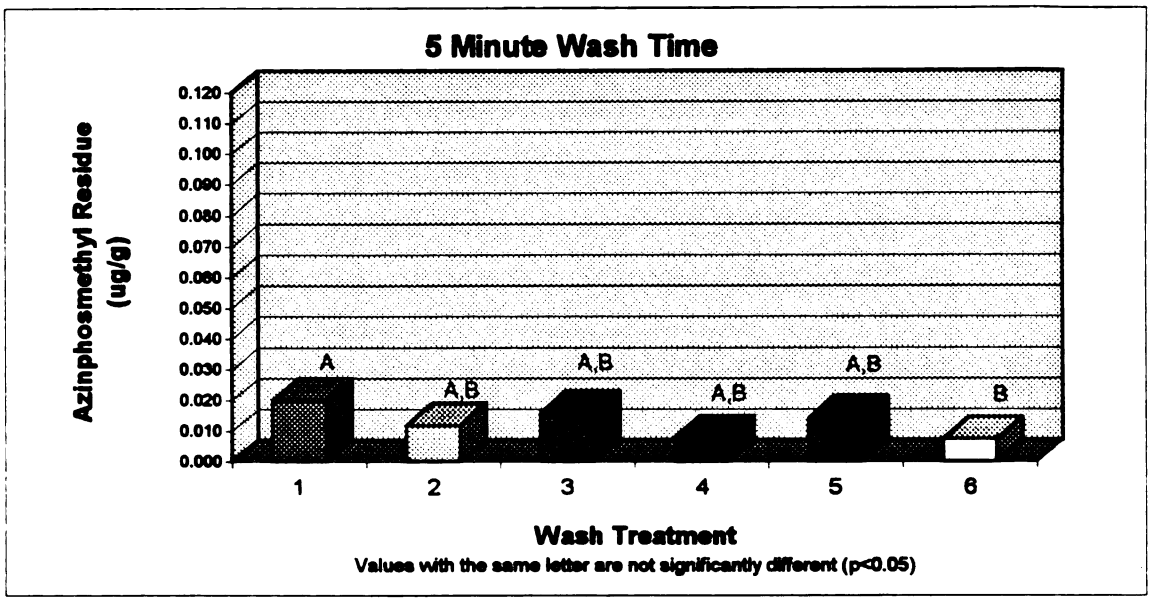


Figure 40: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Apple Juice, 1994 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

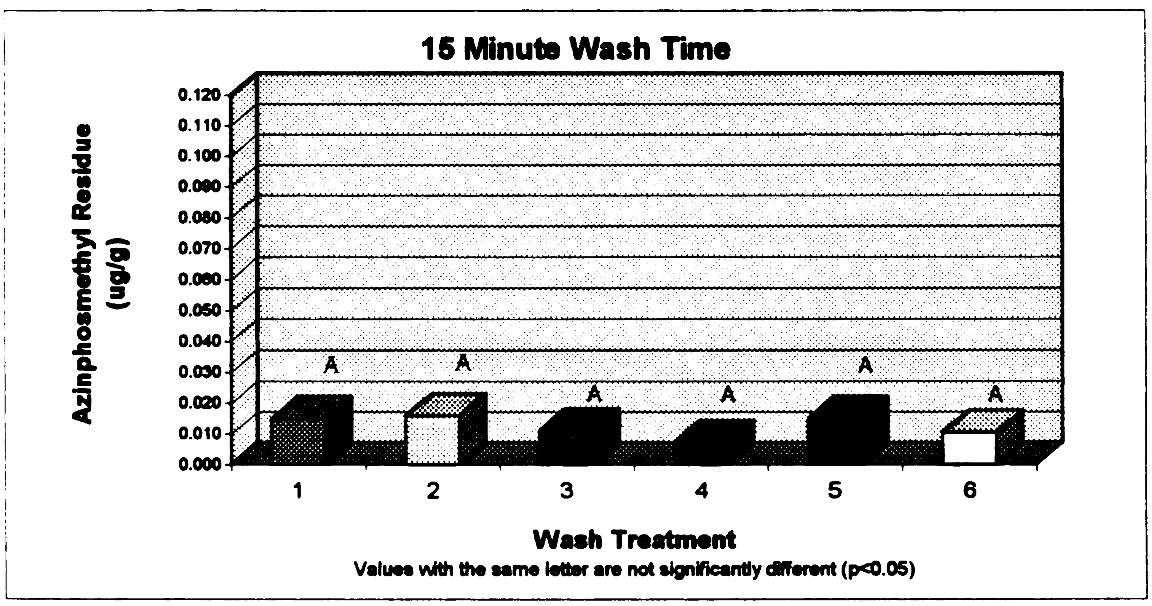
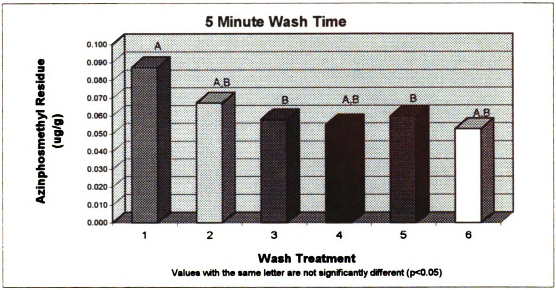


Figure 41: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Apple Juice, 1995 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

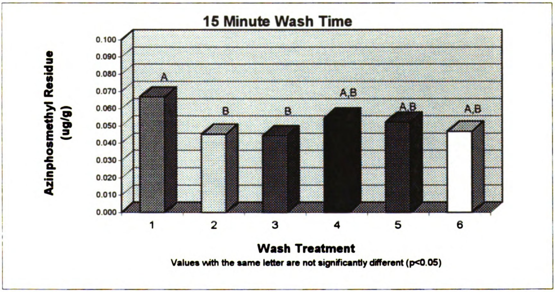
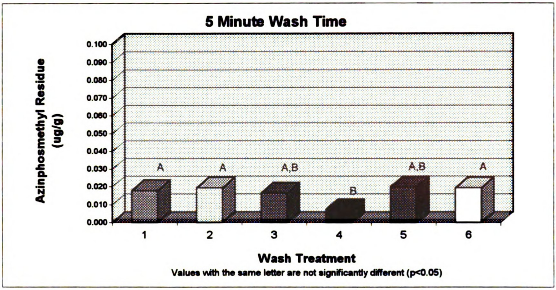


Figure 42: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Apple Slices, 1993 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

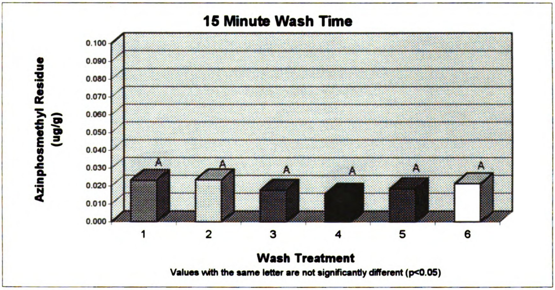
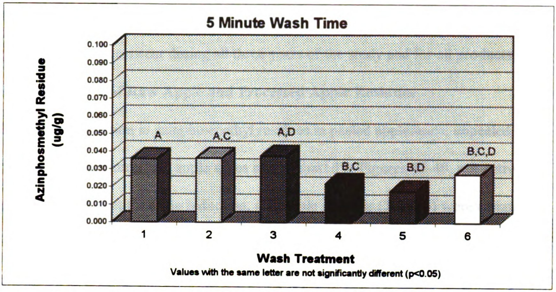


Figure 43: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Apple Slices, 1994 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

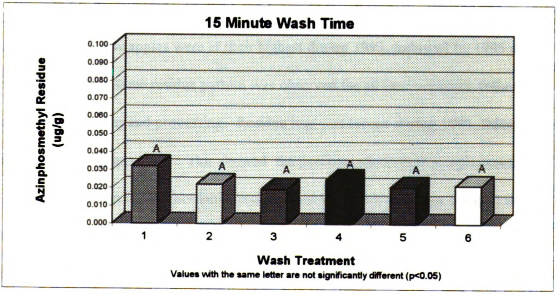


Figure 44: Comparison of Postharvest Wash Treatments Azinphosmethyl Residue in Apple Slices, 1995 Data

effective wash treatment(s). It was determined that none of the wash treatments showed a great deal of effectiveness over another in the removal of azinphosmethyl residues. This was found to be consistent during all three years of the study and for all products.

(3) Comparison of Raw Apple and Processed Apple Residues

The percent reduction in azinphosmethyl residues in peeled applesauce, unpeeled applesauce, apple juice, and apple slices are illustrated in Figures 45-48, respectively. To determine the percent residue reduction, raw apple residues (Table 6) were compared to residues found in each of the four apple products. For each apple product, the residues determined in the postharvest wash samples (Appendices 4-7) were averaged to yield values for both the 5 and 15 minute wash treatments for each year of the study. These average residue levels and those obtained for raw apples are listed in Table 8 and compared on a one to one basis to obtain a percent reduction in azinphosmethyl residues resulting from postharvest washing and processing.

From Table 8, similar observations can be made for all four apple products. The residue levels in raw apples were at their highest during 1993, followed by 1995 and 1994, respectively. This same residue pattern was observed for all four products, following postharvest washing and processing. Residue loss was lowest during 1993, followed by 1995 and 1994, respectively. This showed the percent reduction in azinphosmethyl to decrease in relation to a higher initial residue level in all four products. Despite the varying degrees of residue reduction observed between years, the high residue losses resulting from the combination of postharvest wash treatments and processing are very significant. Peeled applesauce indicated losses from 93.7-96.5% over the three year study.

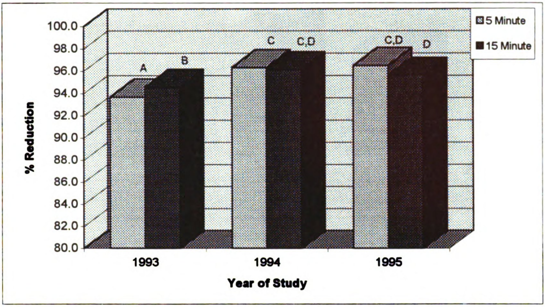


Figure 45: Percent Reduction of Azinphosmethyl Residues in Peeled Applesauce

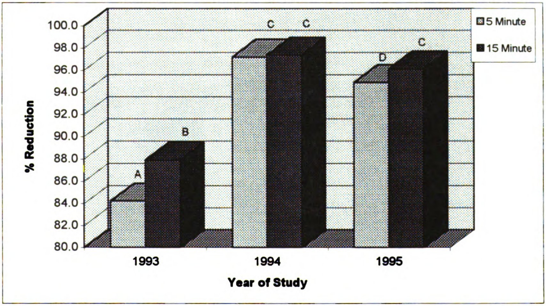


Figure 46: Percent Reduction of Azinphosmethyl Residues in Unpeeled Applesauce

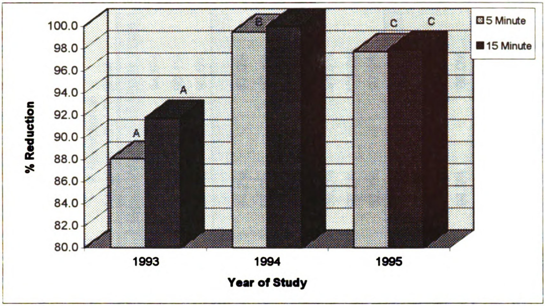


Figure 47: Percent Reduction of Azinphosmethyl Residues in Apple Juice

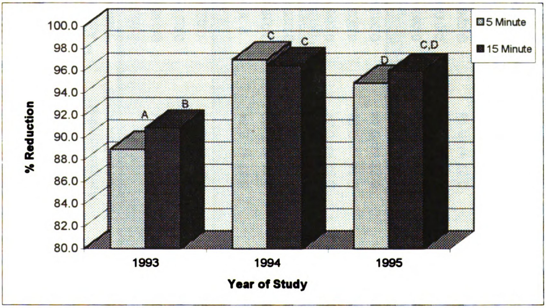


Figure 48: Percent Reduction of Azinphosmethyl Residues in Apple Slices

Table 8: Percent Reduction in Azinphosmethyl Residues Following Postharvest Washing and Processing

Year / Product	* Azinphosmethyl Residue in Raw Apple	** Azinphosmethyl Residue in Postharvest Washed and Processed Apples (ug/g)		% Reduction in Azinphosmethyl Residue	
Peeled Applesauce		5 Minute Wash	15 Minute Wash	5 Minute Wash	15 Minute Wash
1993	0.57 +/- 0.34	0.036 +/- 0.002	0.031 +/- 0.005	93.7%	94.6%
1994	0.14 +/- 0.03	0.021 +/- 0.003	0.022 +/- 0.002	96.3%	96.1%
1995	0.27 +/- 0.14	0.02 +/- 0.004	0.025 +/- 0.002	96.5%	95.6%
Unpeeled Applesauce					
1993	0.57 +/- 0.34	0.09 +/- 0.01	0.069 +/- 0.009	84.2%	87.9%
1994	0.14 +/- 0.03	0.016 +/- 0.003	0.015 +/- 0.001	97.2%	97.4%
1995	0.27 +/- 0.14	0.029 +/- 0.004	0.022 +/- 0.002	94.9%	96.1%
Apple Juice					
1993	0.57 +/- 0.34	0.068 +/- 0.022	0.047 +/- 0.006	88.1%	91.8%
1994	0.14 +/- 0.03	0.003 +/- 0.006	0.0 +/- 0.0	99.5%	100.0%
1995	0.27 +/- 0.14	0.013 +/- 0.001	0.012 +/- 0.003	97.7%	97.9%
Apple Slices					
1993	0.57 +/- 0.34	0.063 +/- 0.008	0.052 +/- 0.006	88.9%	90.9%
1994	0.14 +/- 0.03	0.017 +/- 0.002	0.020 +/- 0.003	97.0%	96.5%
1995	0.27 +/- 0.14	0.029 +/- 0.006	0.023 +/- 0.002	94.9%	96.0%

* Values obtained from Table 6

** Each values represent an azinphosmethyl residue mean for the six postharvest wash treatment samples (Appendices 4-7)

Note: A 50 gram sample size was used for both the raw and processed apple samples.

Unpeeled applesauce, apple juice, and apple slices showed similarly high residue reduction, 84.2-97.4%, 88.1-100%, and 88.9-97.0%, respectively. These findings are in agreement with previous studies by El-Hadidi (1993), Ong *et al.* (1995), Gunther *et al.* (1963), and Carlin *et al.* (1966) on the ability of washing and processing to significantly reduce azinphosmethyl residues in apples as well as other fruits and vegetables.

Figures 45 and 48, peeled applesauce and apple slices, respectively, both showed a longer wash time to significantly increase residue reduction in 1993 samples. Unpeeled applesauce, Figure 46, showed a significant reduction in residue, due to a longer wash time, during 1993 and 1995. Apple juice, Figure 47, did not indicate wash time to be a statistically significant factor in the reduction of azinphosmethyl residues.

(4) Comparison of Residue Levels between Products

Figure 49 compares the different residue levels found among the four apple products. The mean residue levels for the six postharvest wash treatments (Tables 4-7) were combined to give an average azinphosmethyl residue observed for each of the four apple products. The differences observed in the residue levels between products is a direct result of the different processing methods used.

Figure 49 shows the residue patterns among the four products differs from year to year. Residue levels were the highest during 1993 and also showed the most dramatic differences in residue levels between products. During 1993, peeled applesauce showed the lowest residues and unpeeled applesauce the highest. The differences in residues observed between the two applesauces is a result of peeling. Azinphosmethyl is a surface applied pesticide which is known to have an affinity for the cuticle waxes found on the

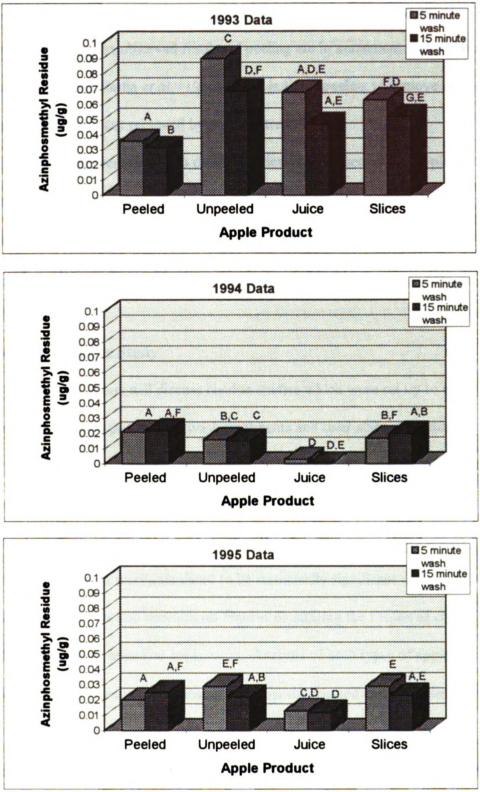


Figure 49: Comparison of Azinphosmethyl Residues in Apple Products

surface of an apple. When removing the peel you are also removing any residue which may bound to it. The observed results of peeling are in agreement with studies by El-Hadidi (1993) and Carlin *et al.* (1966) which indicate peeling to remove considerable amounts of residue not removed by washing treatments.

Residue levels were shown to differ significantly between peeled applesauce and apple slices. The processing of both samples involved peeling but only applesauce involved heat processing (blanching). The differences observed among these products is likely a result of the degradative effects of heat on azinphosmethyl residues.

D. Captan Residue Study

The following sections will discuss residue studies which were set up to examine the effects of individual postharvest wash treatments and their ability to reduce or eliminate captan residues from finished apple products. The raw data pertaining to captan residues in peeled applesauce, unpeeled applesauce, apple juice, and apple slices is contained in Appendices 8, 9, 10, and 11, respectively. This data is illustrated in Figures 50-67. Only those findings which were calculated to be statistically significant will be discussed.

The following section contains no Figures illustrating the results of captan residue studies in peeled or unpeeled applesauce. Analysis of both types of applesauce samples indicated captan residues to be absent or below the method detection limit of 0.02 μg/g. The presence of captan residues in both apple juice and apple slices points to the processing step of blanching as being responsible for the lack of residues in applesauce. In the preparation of applesauce, apples are sliced and then blanched for a period of ten minutes before they are passed through a finisher and made into sauce. It has been concluded that the thermal processing step of blanching is responsible for the absence of captan residues. A number of previous publications are in agreement and indicate captans instability in the presence of heat. Work by Klayder (1963), Elkins *et al.* (1972), and Koivistoinen *et al.* (1965) indicate heat processing, such as canning, cooking, or blanching, are responsible for 90-100% losses of captan residues in fruits and vegetables.

(1) Effect of Postharvest Wash Treatment Variables

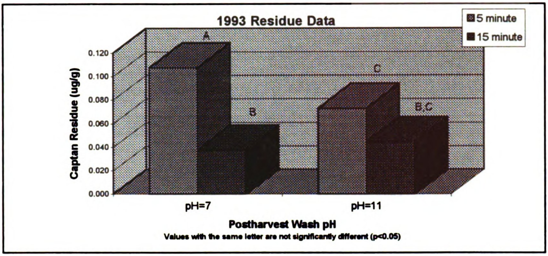
Postharvest wash treatment variables are examined for their effect on the removal or degradation of captan surface residues on raw apples. Residue levels were examined only after processing of the

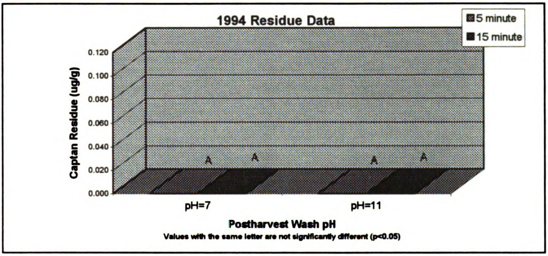
postharvest wash treated apples into applesauce (peeled and unpeeled), apple juice, and apple slices. Thus, the residues encountered in the following sections will reflect the effect of postharvest wash treatments and processing.

a. Effect of Postharvest Wash pH at 21°C

Figure 50 and 51 illustrate the effect of wash pH on Captan residues in a 21°C postharvest wash. Data for 1993 apple juice, Figure 50, showed pH 11, 5 minute wash to be more effective in removing captan compared to the pH 7, 5 minute treatment. The pH 11, 5 minute wash was found to be more effective over the pH 7, 15 minute wash. Also for 1993, a longer wash time indicated higher residue removal during the pH 7 wash. Data for 1994 and 1995 did not show any statistical differentiation in sample means.

Apple slice data, Figure 51, exhibited pH11 to be more capable of captan removal over the pH 7 wash. This was observed for 1993 and 1995 data during the 15 minute wash. A





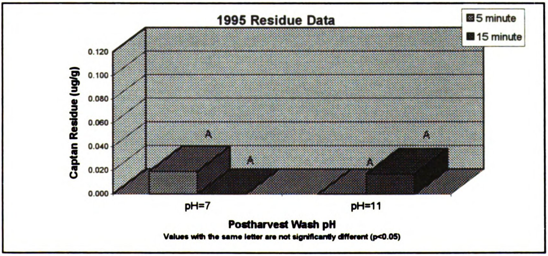


Figure 50: Effect of Postharvest Wash pH on the Removal of Captan at 21°C in Apple Juice

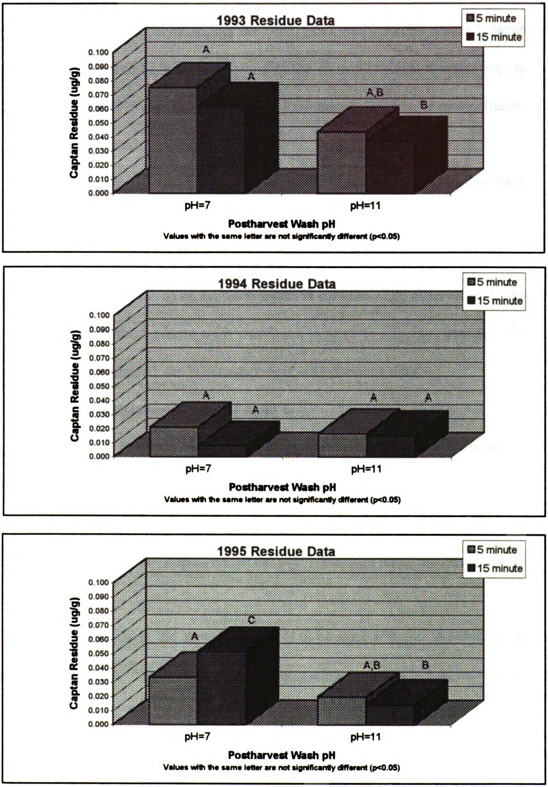


Figure 51: Effect of Postharvest Wash pH on the Removal of Captan at 21°C in Apple Slices

longer wash time also appeared to be more effective in the 1993, pH 11 wash. The opposite however was observed during the 1995, pH 7 wash. In this case, a 5 minute wash time was found to be more effective, over the 15 minute wash, at removing captan residues. Data for 1995 also showed the pH 11, 15 minute wash to be more effective than the pH 7, 5 minute wash.

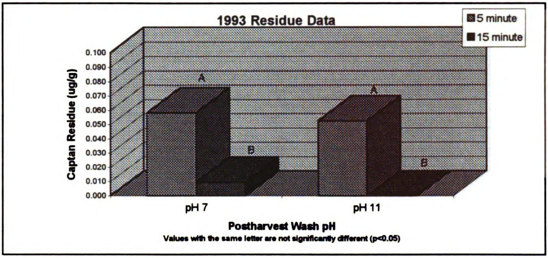
In both apple juice and apple slice studies, the pH 11 wash proved to be statistically more effective in reducing captan residues. A longer wash time was also found to be more effective for both products. This data is in agreement with previous studies by Ong *et al.* (1995) and Wolf *et al.* (1976) on captan residues in solution. The observation (Figure 51, 1995 data) in which the 5 minute wash was found to be more effective, over the 15 minute wash, can not be explained and is not agreement with previous data.

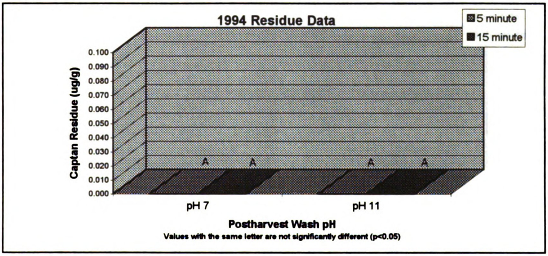
b. Effect of Postharvest Wash pH at 43°C

Figure 52 and 53 illustrate the effect of pH on captan residues in a 43°C wash. Apple juice data, Figure 52, indicated a longer wash time as more capable of removing captan residues in both the pH 7 and pH 11 treatments during 1993. The pH 11, 15 minute wash was also shown to be more effective than the pH 7, 5 minute wash, as observed in the 1993 data.

Figure 53, apple slices, did show a higher pH to be more effective in reducing captan residues during 1995. This was found when comparing the pH 11, 15 minute wash to the pH 7, 5 minute wash. No other statistically significant findings were made.

These observations showed the increased effectiveness of the pH 11 wash and a longer wash time. This data is in agreement with previous studies by Ong *et al.* (1995) and Wolfe *et al.* (1976).





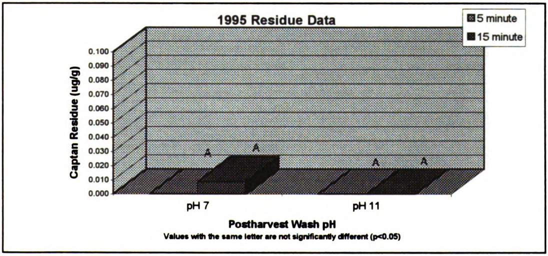
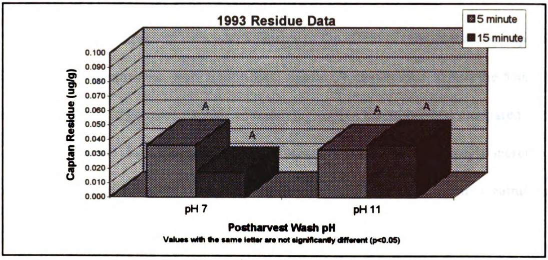
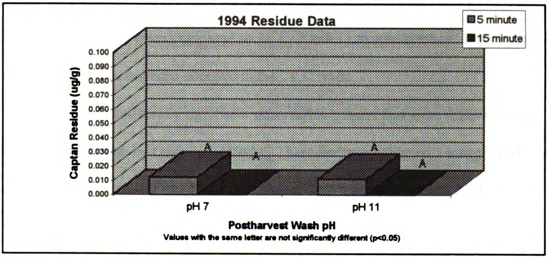


Figure 52: Effect of Postharvest Wash pH on the Removal of Captan at 43°C in Apple Juice





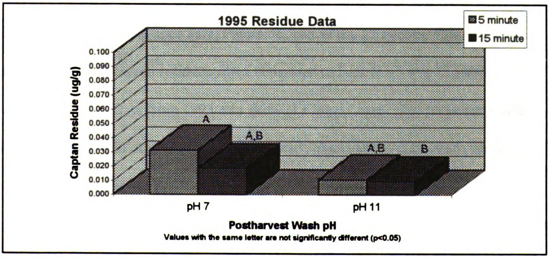


Figure 53: Effect of Postharvest Wash pH on the Removal of Captan at 43°C in Apple Slices

c. Effect of Postharvest Wash Temperature at pH 7

Figure 54 and 55 represent data which illustrates the effect of temperature on captan residues in pH 7 postharvest wash treatments. Figure 54, apple juice, shows the 5 and 15 minute, 43°C wash to be more capable of removing captan residues when compared to the 5 minute, 21°C wash for 1993 samples. A 15 minute wash time was shown to increase captan removal over a 5 minute wash in both the 21°C and 43°C temperature treatments. Data for 1994 and 1995 displayed no further information on wash treatment variables.

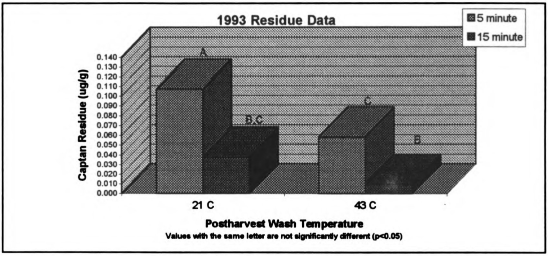
Apple slice data for 1993, Figure 55, showed the 43°C, 15 minute wash to further reduce captan residues when compared to 21°C, 5 and 15 minute washes. Data from 1995 a longer wash time to be more effective in the 21°C wash.

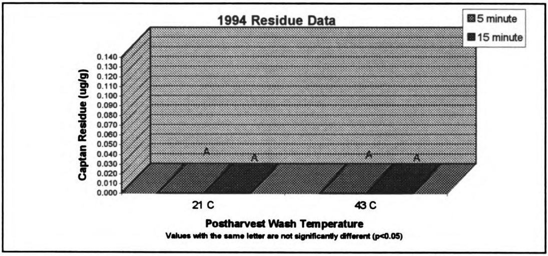
Despite the few statistically significant observations, those that were made did agree with previous research by Ong *et al.* (1995). These findings indicated a longer wash time, as well as a higher temperature, increased the removal of captan residues at pH 7.

d. Effect of Postharvest Wash Temperature at pH 11

Figures 56 and 57 illustrate the effect of 21°C and 43°C wash temperature on captan residues at pH 11. Apple juice data, Figure 56, shows the 15 minute, 43°C wash to significantly reduce captan residues when compared to both the 5 and 15 minute, 21°C wash during 1993. Data from 1993 also showed a longer wash time to be more effective in the 43°C wash. No other statistically significant observations were made for apple juice or for apple slices, Figure 57.

The statistically significant observations made are in agreement with previous studies by Ong *et al.* (1995). A longer wash time and a higher wash temperature were more beneficial to the removal of captan residues at pH 11.





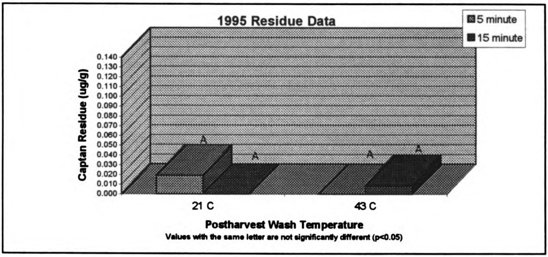
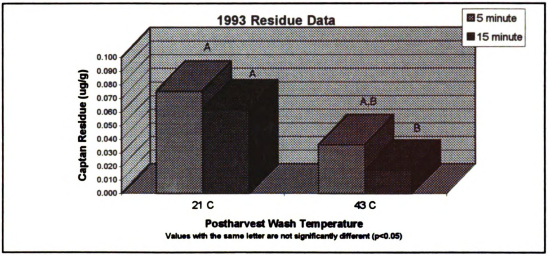
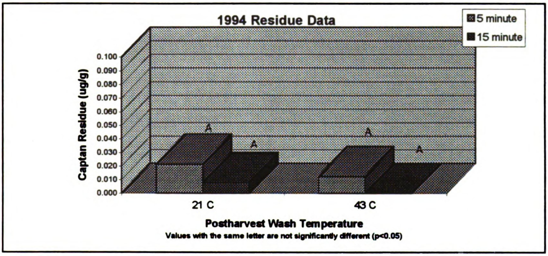


Figure 54: Effect of Postharvest Wash Temperature on the Removal of Captan at pH 7 in Apple Juice





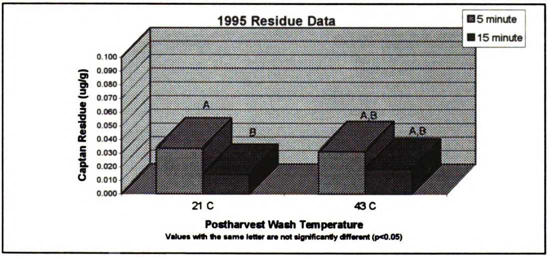


Figure 55: Effect of Postharvest Wash Temperature on the Removal of Captan at pH 7 in Apple Slices

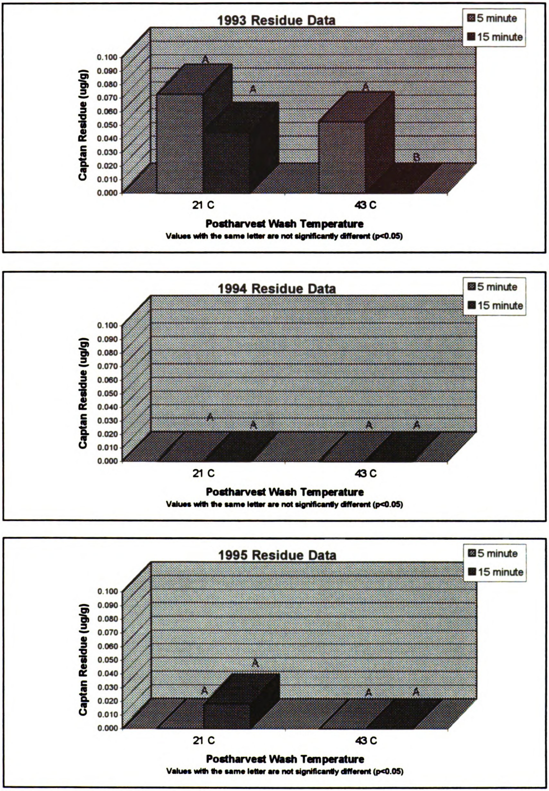


Figure 56: Effect of Postharvest Wash Temperature on the Removal of Captan at pH 11 in Apple Juice

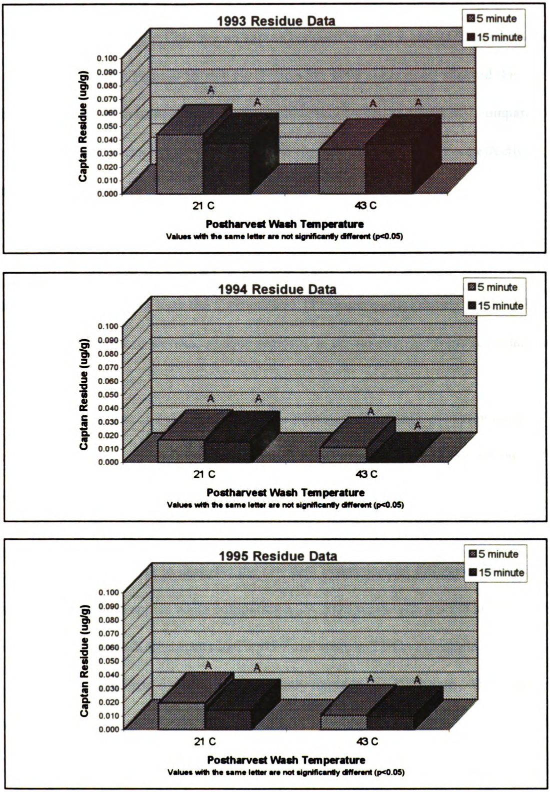


Figure 57: Effect of Postharvest Wash Temperature on the Removal of Captan at pH 11 in Apple Slices

e. Effect of 500 μg/g Chlorine in Postharvest Wash

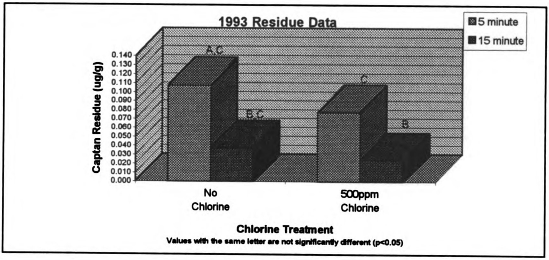
The effects of 500 μg/g Chlorine on captan residues in a pH 7 and 21°C postharvest wash are illustrated in Figures 58 and 59. Figure 58, 1993 apple juice, showed the 15 minute, Chlorine wash to be more effective in lowering captan resides when compared to the 5 minute, no-chlorine wash. A longer wash time was shown to be more effective in the 1993, chlorine wash.

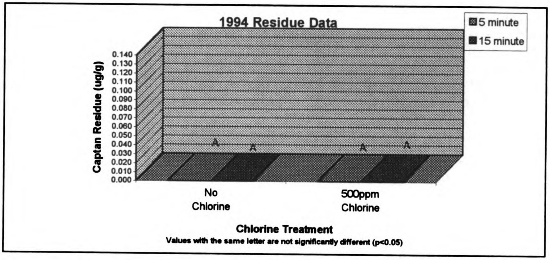
Apple slice data, Figure 59, showed the 500 μg/g Chlorine wash to increase the removal of captan residues over the no-chlorine wash. This was determined to be statistically significant for both the 5 minute and 15 minute washes during 1993. A longer wash time was shown to increase residue removal in the no-chlorine wash according to 1995 data.

A longer wash time and the use of Chlorine increased the chance of captan residue removal. Again, we see few observations but those that are made are in agreement with previous work by Ong *et al.* (1995).

f. Effect of 2% Sodium Dodecyl Sulfate in Postharvest Wash

Figures 60 and 61 help to illustrate the raw data examining the difference in captan residue removal from apples when comparing a 2% SDS wash with a wash lacking SDS. These postharvest wash treatments had a pH 7 and were at 21°C. For apple Juice, Figure 60, statistically significant observations were only found in the 1993 data. This exhibited 2% SDS to have an increased ability to remove Captan residues over the no-SDS wash. This was found to be true for both the 5 minute and 15 minute wash treatments. The longer wash time was also found to increase residue removal in both the 2% SDS and no-SDS washes for 1993.





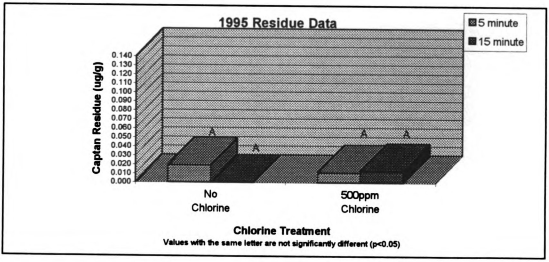


Figure 58: Effect of 500 ppm Chlorine on the Removal of Captan at 21°C and pH 7 in Apple Juice

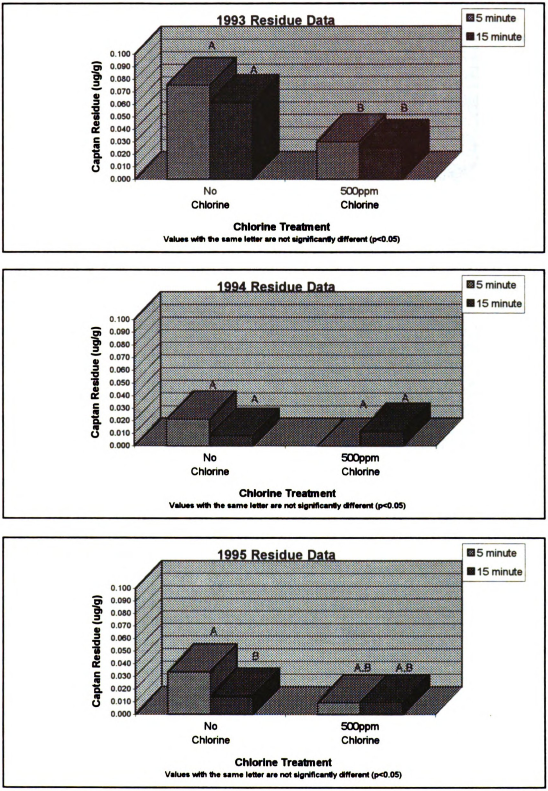
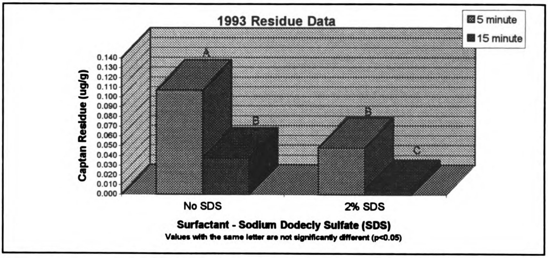
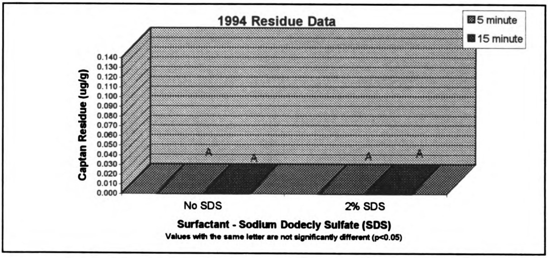


Figure 59: Effect of 500 ppm Chlorine on the Removal of Captan at 21°C and pH 7 in Apple Slices





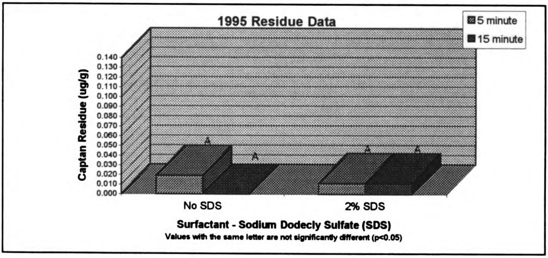


Figure 60: Effect of 2% SDS on the Removal of Captan at 21°C and pH 7 in Apple Juice

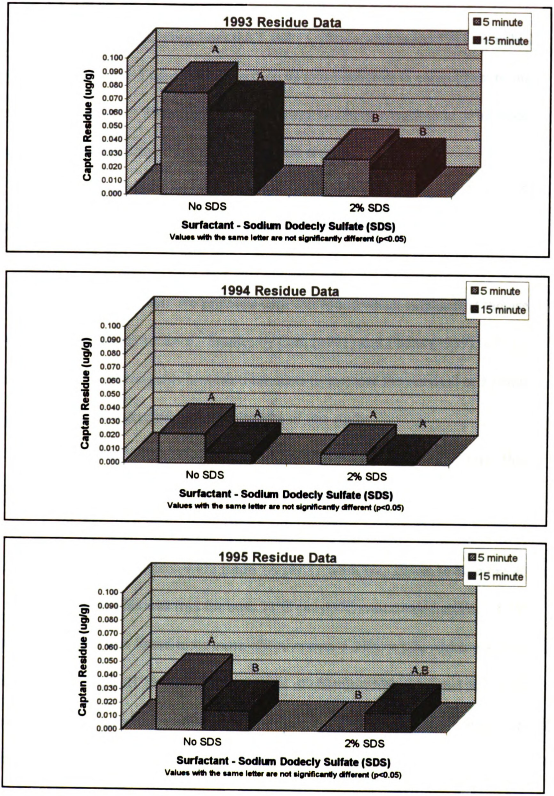


Figure 61: Effect of 2% SDS on the Removal of Captan at 21°C and pH 7 in Apple Slices

Figure 61, apple slices, also found the presence of SDS in the postharvest wash to increase residue removal during both the 5 and 15 minute washes for 1993. Similarily, 1995 data showed the 5 minute SDS wash to be more effective in comparison to the 5 minute, no-SDS wash. Data for 1995 also illustrates a longer wash time to be more adequate at residue removal in the no-SDS wash treatment.

Data for 1993 showed a lot of potential, in both apple juice and apple slice, for SDS to increase captan residue removal. Both products indicated a longer wash time to be more advantageous in terms of captan residue removal. Captan showed similar susceptibility to SDS as did azinphosmethyl. No previous data was found which emphasized the use of SDS for captan residue removal. Studies by Chin (1991) and Elkins (1989), which reported the use of detergents in wash treatments to increase the removal of a parathion in vegetables, were in agreement with the results of this study.

Postharvest Wash Treatment Results. The preceeding sections illustrated the effectiveness of wash treatment variables, in combination with processing, on reducing captan residues. The following conclusions were drawn based on the statistically significant observations which were made. A pH 11 wash was shown to be more effective over a pH 7 wash. This was true for both 21°C and 43°C wash temperatures. A 43°C wash temperature was found to be more effective over a 21°C wash, which was true for both the a pH 7 and pH 11 wash. The addition of chlorine (500 µg/g) and SDS (2%) were both shown to be more effective in removing residues over a plane water wash. A longer wash was shown to increase the effectiveness of the wash variables, as well as the individual wash. These findings are in agreement with previous studies. The wash treatments were found to have similar effects on both the apple juice and apple slices. SDS was found to be particularly effective in the removal of captan in both apple juice and apple slices during 1993.

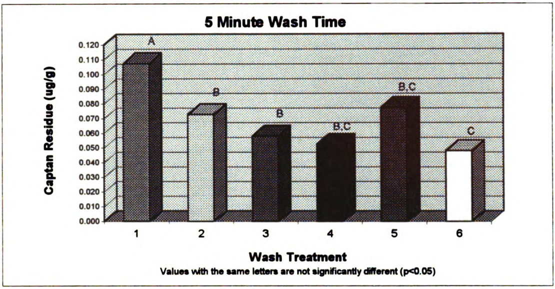
The absence of captan residues from peeled and unpeeled applesauce was determined to be a result of heat processing (blanching) and not due to wash treatment variables. Captan residues in apple juice and apple slices showed a similar susceptibility to the wash treatment variables as did azinphosmethyl. Similar to azinphosmethyl data, captan residues were higher during 1993 which resulted in the occurance of more statistically significant observations. Referring back to Figure 8 and Table 6, captan residues in the raw apples showed a similar pattern as that found in the processed apples. Again, it is unknown whether the higher captan residue observed for 1993 data may be responsible for the increased influence of the wash treatments.

(2) Comparison of Postharvest Wash Treatments

Figures 62-67 illustrate the average captan residues observed in each of the six wash treatments so that they may be compared as to their relative effectiveness in relation to one another. Upon review of these figures, residue levels between the various wash treatments were not found to differ to any great extent. Among the four products, only a small number of cases were observed in which wash treatments differed statistically but with no patterns observed in which to base any conclusions concerning a more effective wash treatment(s).

(3) Comparison of Raw Apple and Processed Apple Residues

The percent reduction in captan residues in peeled applesauce, unpeeled applesauce, apple juice, and apple slices are illustrated in Figures 68-69, respectively. To determine the



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

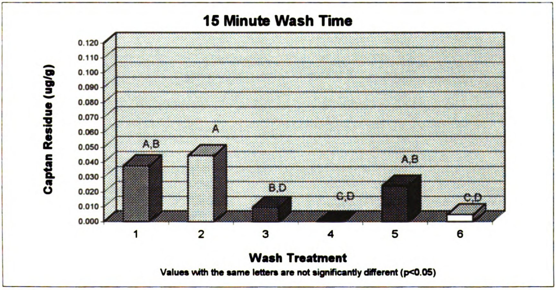
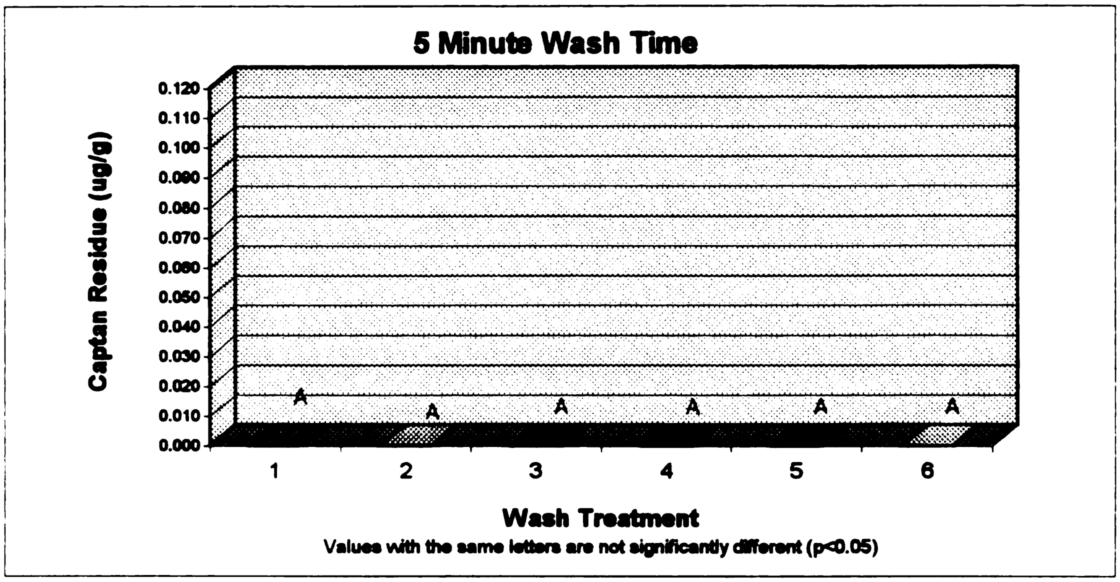


Figure 62: Comparison of Postharvest Wash Treatments - Captan Residue in Apple Juice, 1993 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

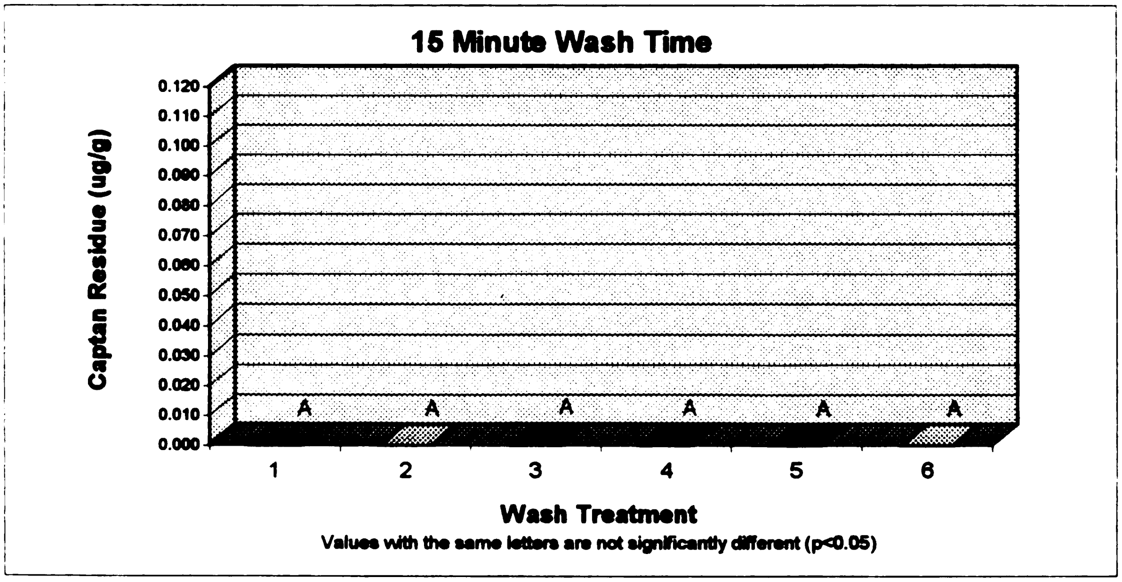
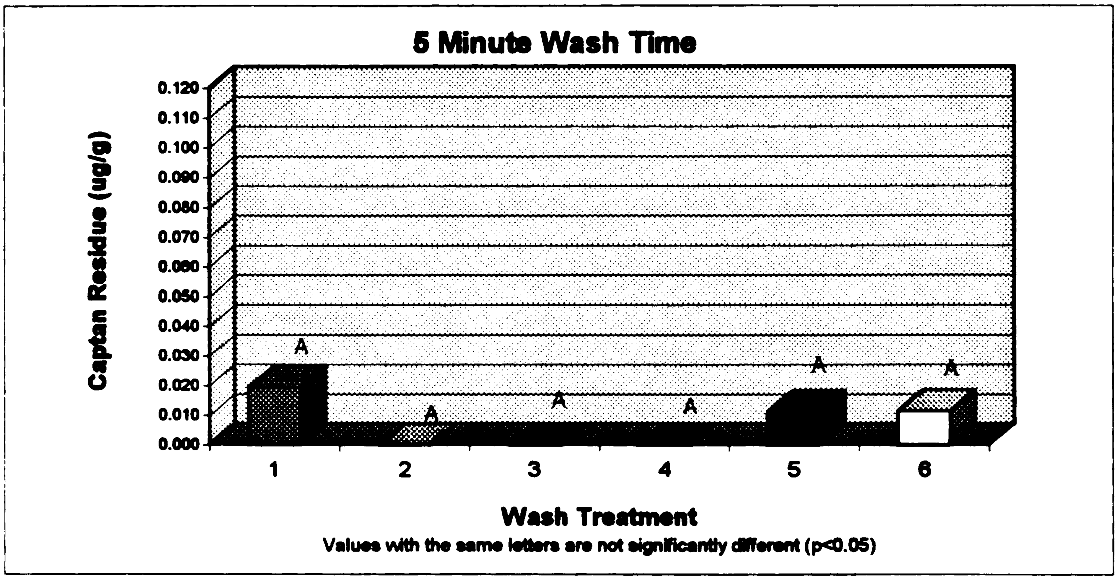


Figure 63: Comparison of Postharvest Wash Treatments - Captan Residue in Apple Juice, 1994 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

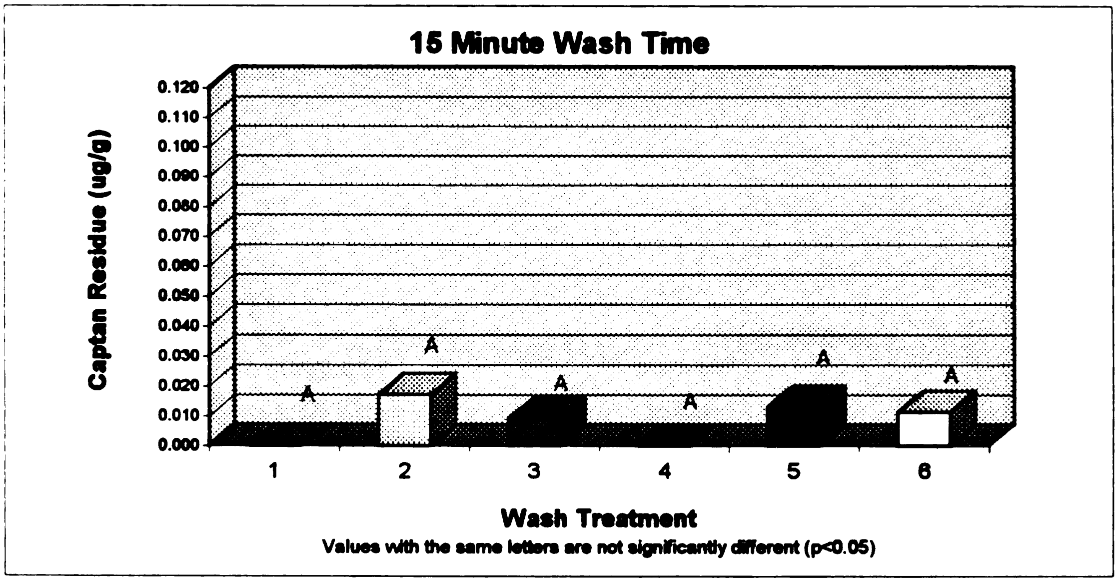
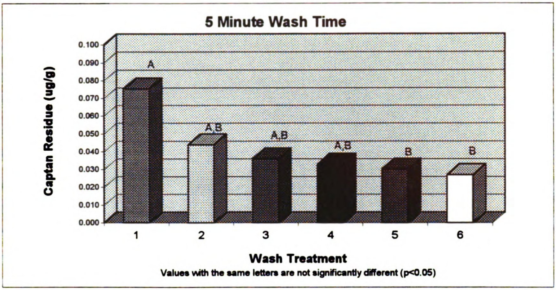


Figure 64: Comparison of Postharvest Wash Treatments - Captan Residue in Apple Juice, 1995 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

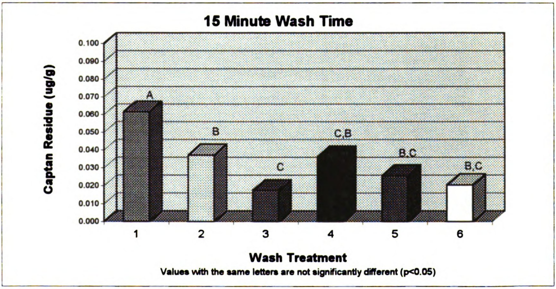
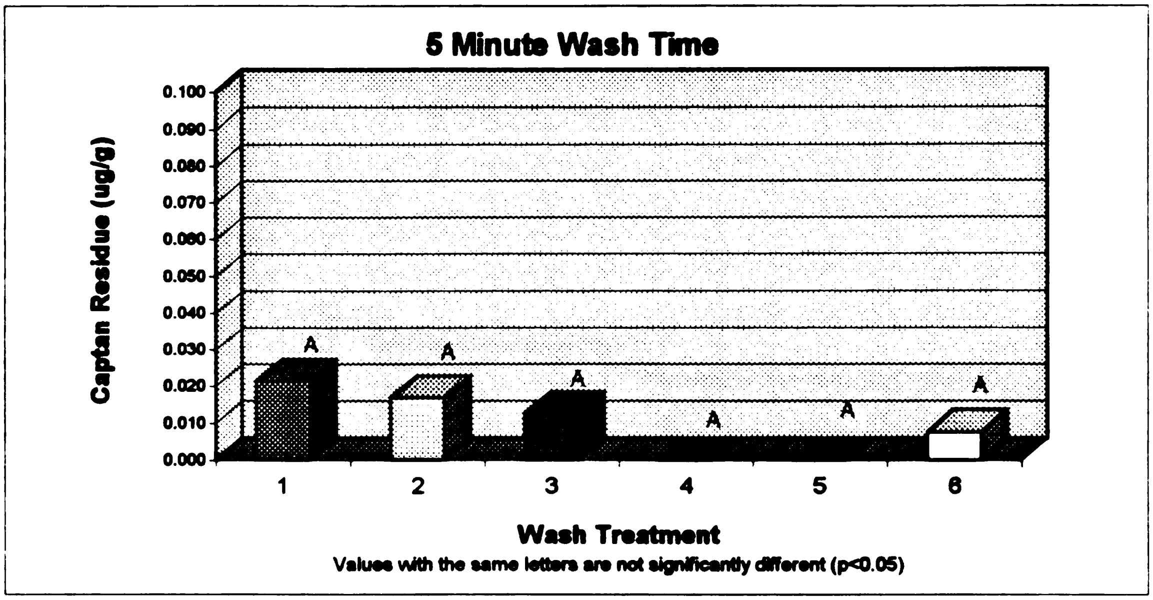


Figure 65: Comparison of Postharvest Wash Treatments - Captan Residue in Apple Juice, 1993 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

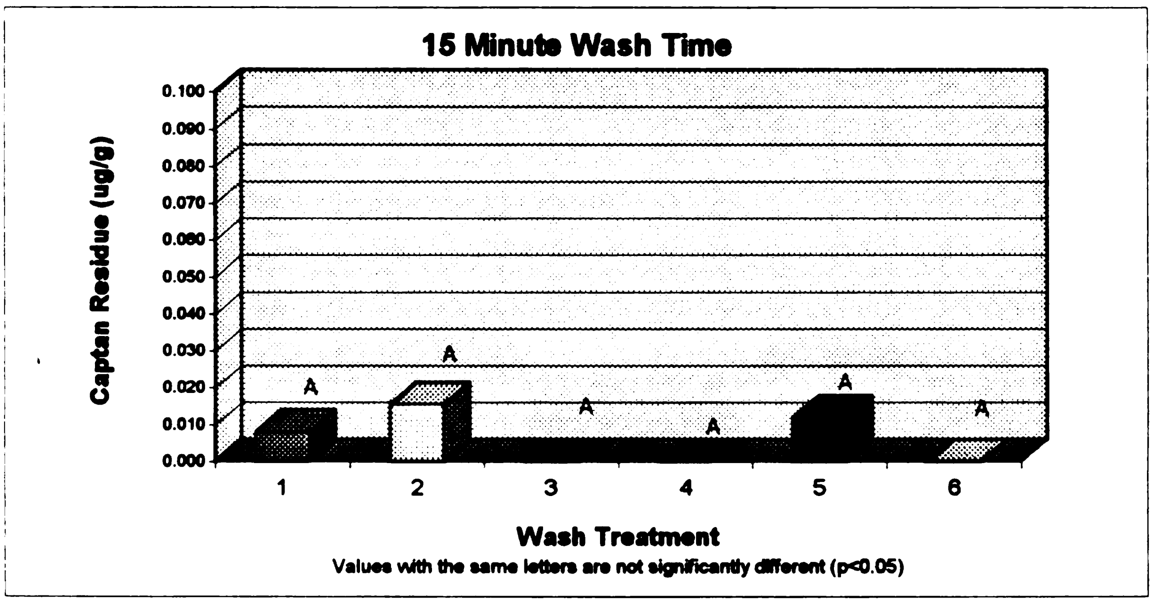
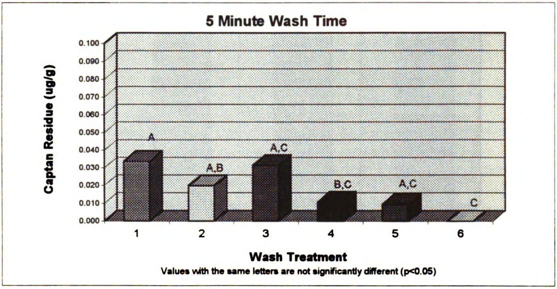


Figure 66: Comparison of Postharvest Wash Treatments - Captan Residue in Apple Juice, 1994 Data



Wash Treatments

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

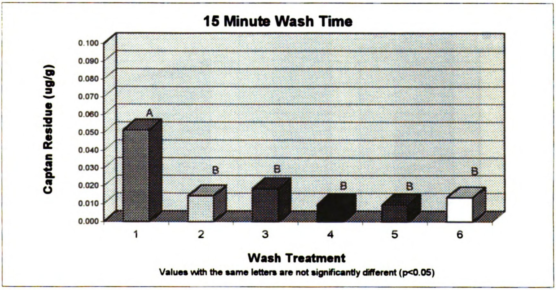


Figure 67 Comparison of Postharvest Wash Treatments - Captan Residue in Apple Juice, 1995 Data

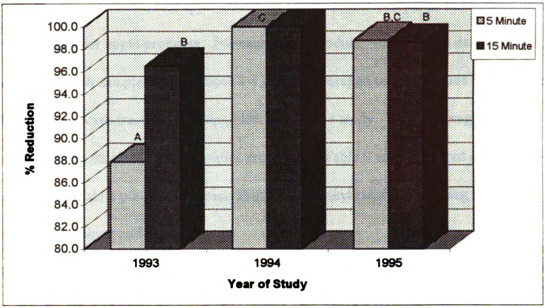


Figure 68: Percent Reduction of Captan Residues in Apple Juice

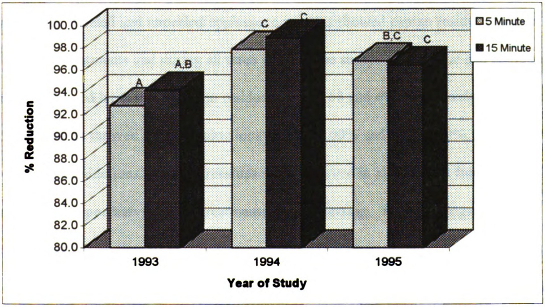


Figure 69: Percent Reduction of Captan Residues in Apple Slices

percent residue reduction, raw apple residues (Table 6) were compared to residues found in each of the four apple products. For each apple product, the residues determined in the postharvest wash samples (Appendices 8-11) were averaged to yield values for both the 5 and 15 minute wash treatments during each year of the study. These average residue levels and those obtained for raw apples are listed in Table 9 and compared on a one to one basis to obtain a percent reduction in azinphosmethyl residues resulting from postharvest washing and processing.

Table 9 indicates similar residue patterns in both the raw and processed apples (juice and slices) as that observed for azinphosmethyl. Residue levels in raw apples were at their highest during 1993, followed by 1995 and 1994, respectively. This same residue pattern was observed for apple juice and apple slices, following postharvest washing and processing. The percent reduction in captan was shown to decrease in relation to higher initial residue levels. Residue loss was lowest during 1993, followed by 1995 and 1994, respectively. Peeled and unpeeled applesauce samples showed captan residue losses of a 100% in all treatments and during all three years of the study. Apple juice and apple slice data also showed large reductions in residues, Figure 68 and 69, respectively. Apple juice and apple slices showed percent reductions of 87.9-100% and 92.8-98.9%, respectively. Overall, high reductions in captan residues were observed in all products from the combination of postharvest wash treatments and processing. These findings are in agreement with previous studies by Ong *et al.* (1995), Koivistoinen et al. (1965), Frank et al. (1983), and El-Zemaity (1988) on the ability of washing and processing to significantly reduce captan residues in apples as well as other fruits and vegetables.

Table 9: Percent Reduction in Captan Residues Following Postharvest Washing and Processing

Year / Product	*Captan Residue in Raw Apple	** Captan Residue in Postharvest Washed and Processed Apples (ug/g)		% Reduction in Captan Residue	
Peeled Applesauce		5 Minute Wash	15 Minute Wash	5 Minute Wash	15 Minute Wash
1993	1.67 +/- 1.1	0	0	100%	100%
1994	0.71 +/- 0.18	0	0	100%	100%
1995	1.12 +/- 0.54	0	0	100%	100%
Unpeeled Applesauce					
1993	1.67 +/- 1.1	0	0	100%	100%
1994	0.71 +/- 0.18	0	0	100%	100%
1995	1.12 +/- 0.54	0	0	100%	100%
Apple Juice					
1993	1.67 +/- 1.1	0.069 +/- 0.01	0.02 +/- 0.014	87.9%	96.5%
1994	0.71 +/- 0.18	0	0	100%	100%
1995	1.12 +/- 0.54	0.007 +/- 0.011	0.008 +/- 0.009	98.8%	98.6%
Apple Slices					
1993	1.67 +/- 1.1	0.041 +/- 0.013	0.033 +/- 0.01	92.8%	94.2%
1994	0.71 +/- 0.18	0.012 +/- 0.011	0.006 +/- 0.009	97.9%	98.9%
1995	1.12 +/- 0.54	0.018 +/- 0.012	0.02 +/- 0.003	96.8%	96.5%

* Values obtained from Table 6

** Each values represent a captan residue mean for the six postharvest wash treatment samples (Appendices 8-11)

Note: A 50 gram sample size was used for both the raw and processed apple samples.

Figures 68, apple juice, showed a longer wash time to significantly increase residue reduction in 1993 samples. Apple slices, Figure 69, did not indicate wash time to be a statistically significant factor in the reduction of azinphosmethyl residues.

(4) Comparison of Residue Levels between Products

Figure 70 compares the different residue levels found among the four apple products. The mean residue levels for the six postharvest wash treatments (Tables 8-11) were combined to give an average azinphosmethyl residue observed for each of the four apple products. The differences observed in the residue levels between products is a direct result of the different processing methods used.

Figure 70 shows the dramatic effects of the heat processing step (blanching) on captan residues in both the peeled and unpeeled applesauce. Residue levels observed for apple juice and apple slices were not found to be significantly different.

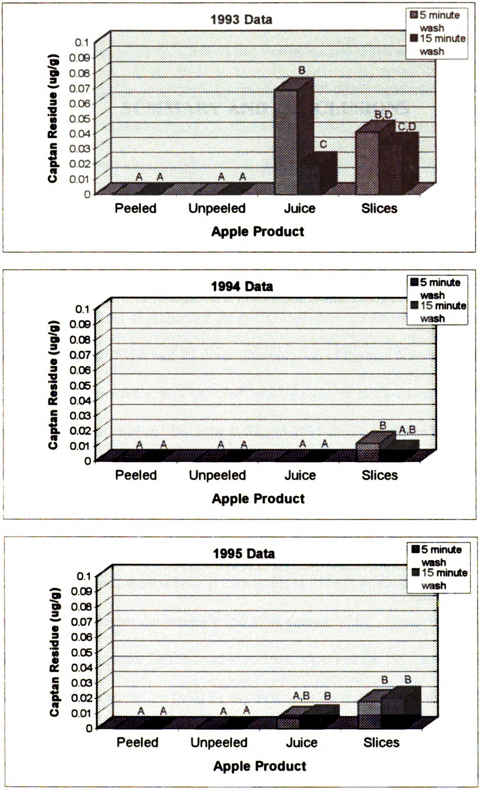


Figure 70: Comparison of Captan Residues in Apple Products

SUMMARY AND CONCLUSIONS

The objective of this study was to examine the effectiveness of preharvest intervals (PHI), postharvest wash treatments, and processing on pesticide residues in raw and processed apple fruits. This study was conducted over a three year period.

To study the effects of preharvest intervals, final spray treatments were altered to yield apples with PHI's of 7, 14, and 21 days. Examination of the raw (unwashed and unprocessed) PHI treated apples revealed residue patterns inconsistent with those observed in previous studies. Data for 1993 and 1995 showed residue levels, for both azinphosmethyl and captan, to be at their highest in the 14 day PHI samples, followed respectively by 7 day and 21 day samples. Data for 1994 indicated azinphosmethyl and captan to be highest in the 7 day PHI samples, followed by 14 day and 21 day samples, respectively. Previous studies have shown residues of both pesticides to decrease with an increase in PHI. This was observed in the 1994 data only.

A possible explanation for the residue patterns observed for 1993 and 1995 data point to the spray treatment. In the field, 14 day PHI samples were located directly between both the 7 and 21 day PHI samples, with only on buffer row separating each treatment. The close vicinity of the treatment rows, particularly the 14 day PHI treatment, creates a lot of potential for problems resulting from spray drift. This would help to explain the residue pattern observed for both pesticides during the 1993 and 1995 data years.

Previous field studies indicate rainfall to be effective in the removal of both captan and azinphosmethyl from apple fruit, particularly when closely following a spray application. Rainfall was recorded shortly following application of the 14 day final spray in 1994. This would most likely resulted in lower than expected residue levels for the 14 day PHI samples. Thus, it is the combination of rainfall and spray drift which help to explain the residue patterns of both pesticides observed in 1994 data.

Residues were also found to vary significantly from year to year for both pesticides, with 1993 being the highest, followed by 1995 and 1994, respectively. The reason for variations in residue levels from year to year can not be explained. This is most likely a direct result of the different climatic conditions which are encountered from year to year. Due to the unexpected results encountered during the PHI study the effect of PHI on postharvest washed and processed apple samples was not discussed.

Raw apples sprayed with both pesticides were used to determine the effectiveness of postharvest washing and processing on the removal of the pesticides in apple products. Postharvest wash treatments included: (1) 21° C and pH 7; (2) 21° C and pH 11; (3) 43° C and pH 7; (4) 43° C and pH 11; (5) 21° C and pH 7, 500 ug/g Chlorine; (6) 21° C and pH 7, 2% Sodium Dodecyl Sulfate (SDS). Following postharvest wash treatment, apples were processed into peeled applesauce, unpeeled applesauce, apple juice, and apple slices. Examination of the statistically significant observations, from the postharvest washed and processed apple samples, revealed similar findings for both pesticides, excluding captan applesauce (peeled and unpeeled) samples. A pH 11 wash was shown to be more effective in reducing residues over a pH 7 wash. This was true for both 21° C and 43° C wash temperatures. A 43° C wash temperature was found to be more effective over a 21°C wash, which was true for both a pH 7 and pH 11 wash. Chlorine (500 µg/g) and SDS (2%) were both shown to be more effective in removing residues over plain water washes. A longer wash time was found to increase the effectiveness of the wash variables, as well as the individual wash. These findings were not found consistently for any of the apple products or during any year of the study. Data for 1993, which had the highest initial residues prior to postharvest washing and processing, showed the largest number of statistically significant observations.

Examination of peeled and unpeeled applesauce for captan revealed no detectable residues. The absence of captan residues was concluded to be a result of the blanching step involved in the processing of both applesauce types. Previous works have indicated captans high susceptibility to heat. This fact, combined with the presence of captan in both apple juice and apple slice samples, point towards the processing as being the limiting factor responsible for its removal from applesauce samples.

Comparing the effects of the six postharvest wash treatments to one another, revealed no significant observations. No one particular wash treatment was identified as having more potential for reducing residue levels. This was found to be true for both azinphosmethyl and captan residue studies.

The percent reductions in azinphosmethyl and captan residues were examined by comparing residues found in the raw apple with the preharvest washed and processed apple samples. Azinphosmethyl and captan residue losses resulting from postharvest washing and processing were significant for both pesticides and in all products. Azinphosmethyl losses in peeled applesauce, unpeeled applesauce, apple juice, and apple slices were between 93.7-96.5%, 84.2-97.4%, 88.1-100%, and 88.9-97.0%, respectively. Captan losses in peeled applesauce, unpeeled applesauce, apple juice, and apple slices were 100%, 100%, 87.9-100%, and 92.8-98.9%, respectively. The lowest residue losses for both pesticides were observed during 1993 in all products, with the highest losses observed during 1994 and 1995, respectively. Residues for both pesticides were found to the highest in the raw apple samples during 1993, followed by 1995 and 1994, respectively. Thus, higher percent reductions for both pesticides were achieved in relation to the lower initial residues found in the raw apples samples.

To conclude, well regulated spray treatments with the implementation of appropriate PHIs can be used to lower residue levels observed at harvest. This, combined with postharvest wash treatments and processing can greatly reduce or eliminate pesticide residues.

FUTURE WORK

Possible future research efforts include:

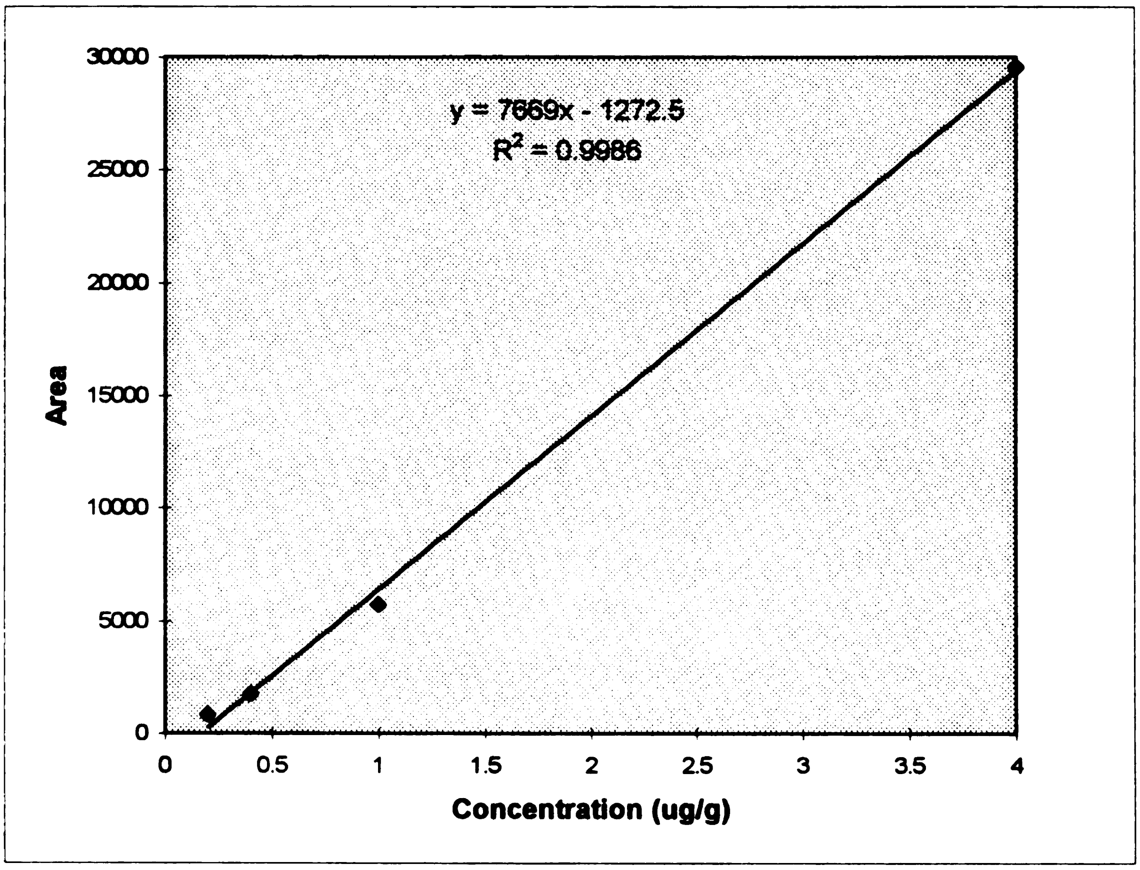
1. This study looked at the combined effects of postharvest wash treatments and processing on the removal of azinphosmethyl and captan residues in apple products. This study was not able to distinguish between the effects of the wash treatments and processing on residue levels. Future work should include analysis of the residue levels following both the wash and processing steps.

2. The use of detergents, such as SDS, to aid in the removal of pesticide residues has not been explored to a large extent. This study indicated SDS have some potential in postharvest wash treatments for the removal of pesticide residues. More research should be carried out to further investigate SDS and the concentrations which may be used to maximize reductions of pesticide residue levels.

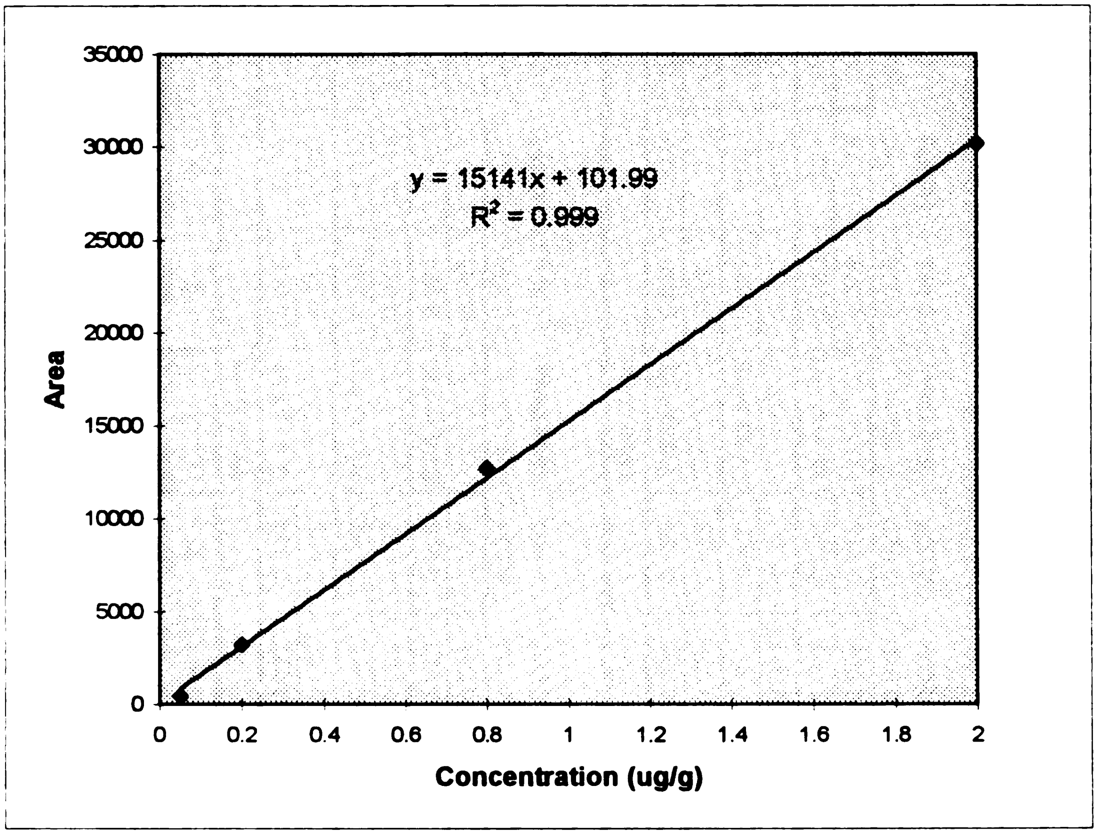
3. Future work should include a look at the degradative pathways of these two pesticides during postharvest washing and processing. Assessment of toxicity should also be carried out on the degradation products.

APPENDICES

Appendix 2: A Typical Standard Curve For Azinphosmethyl Standards



Appendix 3: A Typical Standard Curve For Captan Standards



Appendix 4: Raw Data for Azinphosmethyl Residues in Peeled Applesauce

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1993 Data						
0.034	0.033	0.037	0.042	0.027	0.033	**7 day PHI**	0.046	0.036	0.043	0.033	0.036	0.031
0.026	0.031	0.043	0.04	0.036	0.038		0.041	0.033	0.036	0.033	0.04	0.037
0.054	0.038	0.041	0.038	0.042	0.042	**14 day PHI**	0.047	0.043	0.04	0.038	0.055	0.05
0.052	0.035	0.041	0.038	0.042	0.037		0.041	0.044	0.04	0.044	0.041	0.043
0.04	0.028	0.03	0.028	0.028	0.028	**21 day PHI**	0.024	0.02	0.023	0	0	0
0.043	0.025	0.029	0.03	0.031	0.027		0.035	0	0	0	0.035	0
0.042	0.032	0.037	0.036	0.034	0.034	**Mean**	0.039	0.029	0.030	0.025	0.035	0.027
0.011	**0.005**	**0.006**	**0.006**	**0.007**	**0.006**	**Std Dev.**	**0.009**	**0.017**	**0.016**	**0.020**	**0.018**	**0.022**
						1994 Data						
0.026	0.028	0.024	0.024	0.025	0.029	**7 day PHI**	0.048	0.02	0.035	0.037	0.021	0.026
0.029	0.024	0.025	0.023	0.025	0.025		0.02	0	0.021	0.02	0	0.02
0.02	0.02	0.02	0.02	0	0.02	**14 day PHI**	0.021	0.02	0.022	0.022	0.021	0.02
0.022	0.021	0	0.02	0.021	0.02		0.022	0.021	0.022	0.021	0.021	0
0.022	0.021	0.021	0	0.022	0.023	**21 day PHI**	0.022	0.022	0.024	0.021	0.022	0.026
0.021	0.021	0.023	0.02	0.021	0.023		0.023	0.022	0.024	0.023	0.025	0.02
0.023	0.023	0.019	0.018	0.019	0.023	**Mean**	0.026	0.018	0.025	0.024	0.018	0.019
0.003	**0.003**	**0.009**	**0.009**	**0.009**	**0.003**	**Std Dev.**	**0.011**	**0.009**	**0.005**	**0.006**	**0.009**	**0.010**

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for azinphosmethyl in applesauce.

* Wash Treatments:

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 4 (cont'd)

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6	1995 Data	1	2	3	4	5	6
0.044	0.04	0.034	0.034	0.025	0.026	7 day PHI	0.027	0.03	0.029	0.024	0.028	0.024
0.028	0.04	0.028	0.034	0.026	0.026		0.04	0.028	0.029	0	0.029	0.03
0.04	0.037	0.039	0	0.031	0.034	14 day PHI	0.026	0.027	0.029	0.021	0.032	0.022
0.027	0	0.023	0	0	0.021		0.03	0.029	0.057	0.025	0.03	0.02
0.025	0	0	0	0	0	21 day PHI	0.022	0.029	0.02	0.023	0.024	0.022
0.02	0	0.024	0	0	0.026		0.024	0.02	0.022	0.026	0.021	0.026
0.031	0.020	0.025	0.011	0.014	0.022	Mean	0.028	0.027	0.026	0.020	0.027	0.024
0.009	**0.021**	**0.014**	**0.018**	**0.015**	**0.012**	**Std Dev.**	**0.006**	**0.004**	**0.004**	**0.010**	**0.004**	**0.004**

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for azinphosmethyl in applesauce.

2. A value which is shaded represents a statistical outlier which has been eliminated from the data.

* Wash Treatments:

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 5: Raw Data for Azinphosmethyl Residues in Unpeeled Applesauce

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1993 Data						
0.11	0.085	0.092	0.072	0.069	0.069	7 day PHI	0.096	0.077	0.079	0.082	0.061	0.05
0.152	0.095	0.097	0.102	0.095	0.075		0.077	0.078	0.072	0.085	0.07	0.073
0.129	0.088	0.132	0.08	0.109	0.091	14 day PHI	0.077	0.102	0.088	0.068	0.046	0.057
0.174	0.151	0.078	0.103	0.146	0.118		0.129	0.143	0.088	0.127	0.085	0.082
0.084	0.07	0.064	0.068	0.066	0.051	21 day PHI	0.051	0.052	0.051	0.033	0.037	0.047
0.073	0.065	0.05	0.073	0.072	0.059		0.043	0.04	0.045	0.035	0.045	0.03
0.120	0.081	0.086	0.083	0.093	0.077	**Mean**	0.079	0.082	0.071	0.072	0.057	0.057
0.039	**0.013**	**0.029**	**0.016**	**0.031**	**0.024**	**Std Dev.**	**0.031**	**0.037**	**0.019**	**0.035**	**0.018**	**0.019**
						1994 Data						
0.044	0.027	0.03	0.032	0.026	0.022	7 day PHI	0.025	0.024	0	0.021	0.02	0.02
0.029	0.026	0.024	0.023	0	0.024		0.037	0.031	0.032	0.031	0	0.022
0	0	0	0	0	0	14 day PHI	0.024	0	0	0	0	0
0	0.022	0	0	0	0		0.022	0.021	0	0.02	0	0
0.036	0.024	0.022	0.028	0	0.021	21 day PHI	0.029	0.027	0.029	0.026	0.03	0.026
0	0	0.024	0.027	0.026	0.03		0	0	0	0	0	0.033
0.018	0.017	0.017	0.018	0.009	0.016	**Mean**	0.023	0.017	0.010	0.016	0.008	0.017
0.020	**0.013**	**0.013**	**0.014**	**0.013**	**0.013**	**Std Dev.**	**0.012**	**0.014**	**0.016**	**0.013**	**0.013**	**0.014**

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for azinphosmethyl in applesauce.
2. A value which is shaded represents a statistical outlier which has been eliminated from the data.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 5 (cont'd)

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1995 Data						
0.031	0.028	0.022	0	0	0	**7 day PHI**	0.026	0	0.024	0	0	0
0.025	0	0.029	0.02	0.021	0		0.029	0	0	0	0	0.02
0.047	0.047	0.043	0.033	0.032	0.021	**14 day PHI**	0.03	0.03	0.027	0.033	0.021	0.03
0.051	0.05	0.038	0.037	0.026	0.036		0.05	0.041	0.03	0.026	0.025	0
0.029	0	0.059	0.045	0.026	0.046	**21 day PHI**	0.022	0.023	0.023	0	0.022	0.02
0.046	0.025	0.039	0.02	0.037	0.024		0.046	0.036	0.051	0.021	0.041	0.038
0.038	0.025	0.038	0.026	0.024	0.021	**Mean**	0.034	0.022	0.026	0.013	0.018	0.018
0.011	**0.022**	**0.013**	**0.016**	**0.013**	**0.019**	**Std Dev.**	**0.011**	**0.018**	**0.016**	**0.015**	**0.016**	**0.015**

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for azinphosmethyl in applesauce.

* Wash Treatments:

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 6: Raw Data for Azinphosmethyl Residues in Apple Juice

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1993 Data						
0.055	0.061	0.04	0.041	0.046	0.071	7 day PHI	0.056	0.078	0.035	0.037	0.044	0.051
0.055	0.04	0.092	0.049	0.046	0.062		0.043	0.07	0.037	0.047	0.036	0.037
0.143	0.059	0.048	0.044	0.055	0.057	14 day PHI	0.074	0.083	0.041	0.038	0.041	0.038
0.082	0.076	0.047	0.051	0.045	0.046		0.134	0.089	0.046	0.044	0.042	0.04
0.117	0.073	0.098	0.054	0.069	0.067	21 day PHI	0.044	0.065	0.037	0.037	0.038	0.036
0.23	0.144	0.074	0.068	0.085	0.05		0.053	0.038	0.039	0.039	0.04	0.04
0.114	0.062	0.067	0.051	0.058	0.059	Mean	0.054	0.071	0.039	0.040	0.040	0.040
0.067	0.014	0.025	0.009	0.016	0.010	Std Dev.	0.013	0.018	0.004	0.004	0.003	0.005
						1994 Data						
0.024	0.058	0	0	0	0	7 day PHI	0	0	0	0	0	0
0.029	0.02	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	14 day PHI	0	0	0	0	0	0
0.021	0	0	0	0	0		0	0	0	0	0	0
0.022	0	0	0	0	0	21 day PHI	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0.016	0.004	0	0	0	0	Mean	0	0	0	0	0	0
0.012696	0.008944	0	0	0	0	Std Dev.	0	0	0	0	0	0

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for azinphosmethyl in apple juice.
2. A value which is shaded represents a statistical outlier which has been eliminated from the data.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 6 (cont'd)

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6	1995 Data	1	2	3	4	5	6
0	0	0	0	0	0	7 day PHI	0	0.047	0.02	0	0	0
0.02	0	0	0	0.022	0		0.021	0	0	0	0.02	0
0.024	0.025	0.026	0	0.022	0	14 day PHI	0.025	0.024	0	0.02	0.022	0.022
0.032	0.025	0.025	0	0.02	0.024		0.023	0.024	0.024	0.022	0.027	0.02
0.02	0.021	0.022	0.023	0.021	0	21 day PHI	0.02	0	0	0	0.021	0
0.023	0	0.022	0.024	0	0.02		0	0	0.022	0	0	0.02
0.020	0.012	0.016	0.008	0.014	0.007	Mean	0.015	0.016	0.011	0.007	0.015	0.010
0.011	**0.013**	**0.012**	**0.012**	**0.011**	**0.011**	**Std Dev.**	**0.012**	**0.019**	**0.012**	**0.011**	**0.012**	**0.011**

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for azinphosmethyl in apple juice.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 7: Raw Data for Azinphosmethyl Residues in Apple Slices

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1993 Data						
0.051	0.076	0.047	0.068	0.038	0.045	**7 day PHI**	0.049	0.05	0.041	0.072	0.05	0.056
0.067	0.062	0.054	0.063	0.04	0.02		0.07	0.043	0.043	0.072	0.05	0.03
0.122	0.099	0.101	0.051	0.089	0.065	**14 day PHI**	0.097	0.051	0.052	0.058	0.066	0.052
0.121	0.084	0.084	0.055	0.086	0.055		0.087	0.057	0.048	0.051	0.05	0.061
0.059	0.051	0.029	0.049	0.051	0.087	**21 day PHI**	0.047	0.038	0.038	0.035	0.042	0.042
0.103	0.032	0.032	0.043	0.054	0.044		0.05	0.032	0.044	0.039	0.055	0.04
0.087	0.067	0.058	0.055	0.060	0.053	**Mean**	0.067	0.045	0.044	0.055	0.052	0.047
0.032	0.024	0.029	0.009	0.022	0.023	**Std Dev.**	0.022	0.009	0.005	0.016	0.008	0.012
						1994 Data						
0.031	0.029	0.023	0.022	0.028	0.033	**7 day PHI**	0.036	0.034	0.027	0.026	0.033	0.039
0.031	0.025	0.024	0.021	0.027	0.038		0.037	0.029	0.028	0.024	0.032	0.046
0	0	0	0	0	0	**14 day PHI**	0	0	0	0	0	0
0	0.021	0	0	0	0		0.023	0	0	0	0	0
0.024	0.02	0.023	0	0.036	0.023	**21 day PHI**	0.02	0.037	0.028	0.02	0.022	0.022
0.021	0.021	0.029	0	0.028	0.022		0.023	0.041	0.023	0.023	0.024	0.021
0.018	0.019	0.017	0.007	0.020	0.019	**Mean**	0.023	0.024	0.018	0.016	0.019	0.021
0.014	0.010	0.013	0.011	0.016	0.016	**Std Dev.**	0.013	0.019	0.014	0.012	0.015	0.019

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for azinphosmethyl in apple slices.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 7 (cont'd)

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6	1995 Data	1	2	3	4	5	6
0.042	0.026	0.042	0.023	0	0.022	7 day PHI	0.038	0.025	0	0.029	0	0
0.033	0.023	0.057	0.029	0.021	0.024		0.051	0	0	0	0	0
0.042	0.052	0.04	0.028	0.044	0.032	14 day PHI	0.04	0.032	0.028	0.038	0.029	0.036
0.045	0.066	0.04	0.031	0.043	0.036		0.04	0.029	0.029	0.038	0.037	0.041
0.027	0.03	0.021	0.021	0	0.023	21 day PHI	0	0.024	0.028	0.021	0.029	0.025
0.026	0.02	0.025	0	0	0.027		0.024	0.022	0.031	0.022	0.028	0.026
0.036	0.036	0.038	0.022	0.018	0.027	**Mean**	0.032	0.022	0.019	0.025	0.021	0.021
0.008	**0.019**	**0.013**	**0.011**	**0.021**	**0.006**	**Std Dev.**	**0.018**	**0.011**	**0.015**	**0.014**	**0.016**	**0.018**

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for azinphosmethyl in apple slices.

* Wash Treatments:

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 8: Raw Data for Captan Residues in Peeled Applesauce

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1993 Data						
0	0	0	0	0	0	**7 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**14 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**21 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0.000	0.000	0.000	0.000	0.000	0.000	**Mean**	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	**Std Dev.**	0.000	0.000	0.000	0.000	0.000	0.000
						1994 Data						
0	0	0	0	0	0	**7 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**14 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**21 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0.000	0.000	0.000	0.000	0.000	0.000	**Mean**	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	**Std Dev.**	0.000	0.000	0.000	0.000	0.000	0.000

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for captan in applesauce.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 8 (cont'd)

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1995 Data						
0	0	0	0	0	0	7 day PHI	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	14 day PHI	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	21 day PHI	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0.000	0.000	0.000	0.000	0.000	0.000	Mean	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	Std Dev.	0.000	0.000	0.000	0.000	0.000	0.000

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for captan in applesauce.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 9: Raw Data for Captan Residues in Unpeeled Applesauce

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1993 Data						
0	0	0	0	0	0	**7 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**14 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**21 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0.000	0.000	0.000	0.000	0.000	0.000	**Mean**	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	**Std Dev.**	0.000	0.000	0.000	0.000	0.000	0.000
						1994 Data						
0	0	0	0	0	0	**7 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**14 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**21 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0.000	0.000	0.000	0.000	0.000	0.000	**Mean**	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	**Std Dev.**	0.000	0.000	0.000	0.000	0.000	0.000

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for captan in applesauce.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 9 (cont'd)

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6	1995 Data	1	2	3	4	5	6
0	0	0	0	0	0	7 day PHI	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	14 day PHI	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	21 day PHI	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0.000	0.000	0.000	0.000	0.000	0.000	Mean	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	Std Dev.	0.000	0.000	0.000	0.000	0.000	0.000

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for captan in applesauce.

* Wash Treatments:

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 10: Raw Data for Captan Residues in Apple Juice

5 Minute Wash Interval, * Wash Treatment 1	2	3	4	5	6		15 Minute Wash Interval, Wash Treatment 1	2	3	4	5	6
						1993 Data						
0.099	0.086	0.043	0.05	0.066	0.047	**7 day PHI**	0.045	0.029	0.022	0	0.041	0.074
0.118	0.059	0.051	0.067	0.107	0.042		0	0.108	0.036	0.03	0.012	0
0.114	0.053	0.05	0.019	0.048	0.04	**14 day PHI**	0.041	0.027	0	0	0.018	0
0.083	0.081	0.048	0.028	0.043	0.043		0.087	0.066	0	0	0.03	0.024
0.122	0.09	0.072	0.075	0.063	0.053	**21 day PHI**	0.022	0.037	0	0	0.01	0
0.109	0.068	0.085	0.076	0.138	0.064		0.031	0	0	0	0.033	0
0.108	0.073	0.058	0.053	0.078	0.048	**Mean**	0.038	0.045	0.010	0.000	0.024	0.004
0.014	0.015	0.017	0.024	0.037	0.009	**Std Dev.**	0.029	0.038	0.016	0.000	0.013	0.010
						1994 Data						
0	0.021	0	0	0	0	**7 day PHI**	0	0	0	0	0	0
0.021	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**14 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0	0	0	0	0	0	**21 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0	0	0	0	0
0.000	0.000	0.000	0.000	0.000	0.000	**Mean**	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	**Std Dev.**	0.000	0.000	0.000	0.000	0.000	0.000

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for captan in apple juice.
2. A value which is shaded represents a statistical outlier which has been eliminated from the data.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 10 (cont'd)

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1995 Data						
0	0	0	0	0.023	0.031	**7 day PHI**	0	0.034	0.023	0	0.025	0
0.028	0	0	0	0	0		0	0	0	0	0	0
0.042	0.055	0	0	0	0	**14 day PHI**	0	0.041	0	0	0.032	0
0.046	0	0	0	0.044	0.038		0.037	0	0	0	0	0
0	0	0	0	0	0	**21 day PHI**	0	0.028	0.03	0	0.021	0.034
0	0	0.028	0	0	0		0	0	0	0	0	0.034
0.019	0.000	0.000	0.000	0.011	0.012	**Mean**	0.000	0.017	0.009	0.000	0.013	0.011
0.022	**0.000**	**0.000**	**0.000**	**0.019**	**0.018**	**Std Dev.**	**0.000**	**0.019**	**0.014**	**0.000**	**0.015**	**0.018**

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for captan in apple juice.

2. A value which is shaded represents a statistical outlier which has been eliminated from the data.

* Wash Treatments:

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 11: Raw Data for Captan Residues in Apple Slices

5 Minute Wash Interval							15 Minute Wash Interval					
* Wash Treatment							Wash Treatment					
1	2	3	4	5	6		1	2	3	4	5	6
						1993 Data						
0.044	0.072	0.033	0.037	0.02	0	**7 day PHI**	0.043	0.027	0	0.021	0	0
0.033	0.043	0.026	0.058	0.02	0		0.054	0.037	0	0.026	0	0
0.062	0.059	0.105	0	0.025	0.026	**14 day PHI**	0.09	0.051	0.043	0.082	0.059	0.046
0.063	0.054	0.052	0	0.037	0.026		0.082	0.044	0.032	0.088	0.051	0.046
0.112	0.035	0	0.102	0.036	0.065	**21 day PHI**	0.049	0.032	0	0	0	0.031
0.138	0	0	0	0.043	0.045		0.051	0.032	0.029	0	0.044	0
0.075	0.044	0.036	0.033	0.030	0.027	**Mean**	0.062	0.037	0.017	0.036	0.026	0.021
0.041	0.025	0.039	0.042	0.010	0.025	**Std Dev.**	0.019	0.009	0.020	0.039	0.029	0.023
						1994 Data						
0.068	0.04	0.042	0.031	0.022	0.026	**7 day PHI**	0	0.039	0	0	0.033	0.028
0.06	0.04	0.033	0.037	0	0.02		0.024	0.033	0.025	0	0.038	0
0	0.021	0	0	0	0	**14 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0.024	0	0	0	0	0
0	0	0	0	0	0	**21 day PHI**	0	0	0	0	0	0
0	0	0	0	0	0		0	0.021	0	0	0	0
0.021333	0.016833	0.0125	0.011333	0	0.007667	**Mean**	0.008	0.0155	0	0	0.011833	0
0.033146	0.019702	0.019573	0.01766	0	0.012028	**Std Dev.**	0.012394	0.017942	0	0	0.0184	0

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for captan in apple slices.
2. A value which is shaded represents a statistical outlier which has been eliminated from the data.

* Wash Treatments:
1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

Appendix 11 (cont'd)

5 Minute Wash Interval: * Wash Treatment 1	2	3	4	5	6	1995 Data	15 Minute Wash Interval: Wash Treatment 1	2	3	4	5	6
0.071	0.02	0.062	0.023	0	0	7 day PHI	0.085	0.034	0.023	0.034	0	0
0.058	0.023	0.075	0.021	0	0		0.065	0.032	0.022	0.024	0	0
0.04	0.029	0.025	0.02	0.029	0	14 day PHI	0.059	0.021	0.033	0	0	0.041
0.033	0.027	0.026	0	0.028	0		0.043	0	0.033	0	0	0.04
0	0.02	0	0	0	0	21 day PHI	0.035	0	0	0	0.03	0
0	0	0	0	0	0		0.022	0	0	0	0.027	0
0.034	0.020	0.031	0.011	0.010	0.000	**Mean**	0.052	0.015	0.019	0.010	0.010	0.014
0.029	**0.010**	**0.031**	**0.012**	**0.015**	**0.000**	**Std Dev.**	**0.023**	**0.016**	**0.015**	**0.015**	**0.015**	**0.021**

Note: 1. The number 0 for a given sample represents a value <0.02 ug/g, which is the method detection limit for captan in apple slices.

* Wash Treatments:

1. 21°C and pH 7
2. 21°C and pH 11
3. 43°C and pH 7
4. 43°C and pH 11
5. 21°C and pH 7, 500 ppm Chlorine
6. 21°C and pH 7, 2% SDS

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