

Chlorine and ozone washes for pesticide removal from apples and processed apple sauce

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The effectiveness of chlorinated and ozonated water dips in the dissipation of azinphos-methyl, captan and formetanate hydrochloride in solution and on fresh and processed apples was examined. All three pesticides in model systems solution decreased 50–100% with chlorine and ozone treatment. Captan and formetanate-HCl were both rapidly degraded in 50 and 500 mg liter⁻¹ chlorine solutions at pH 7 and 10.7. Ozonation was also effective in degrading the pesticides. Rate of degradation of the pesticides generally increased at higher pH and temperature. Pesticide residues on fresh apples and in processed products were also reduced by chlorine and ozone washes; chlorine (500 mg liter⁻¹) being the most effective wash treatment. Ozone wash at 0.25 mg liter⁻¹ was not as effective owing to its low concentration, its instability in water and the high organic content of the wash water.

INTRODUCTION

The demand by consumers for produce with good sensory quality has continued to sustain the use of pesticides for control of insects and diseases in apple fruits. As a result, there is a need to develop methods for removing or reducing the levels of pesticide residues on fresh and processed apples after harvest. Such methods could alleviate concerns about the hazard of these chemicals to humans and the environment. Postharvest treatments, such as the postharvest water wash and scrub that have been traditionally employed to remove debris and dirt, have been shown to reduce pesticide residues (El-Hadidi, 1993). The use of postharvest chlorine dips has also shown potential as an effective postharvest treatment in the reduction of pesticide residues on apple fruits (Hendrix, 1991). The use of ozonated water dips has similar potential as an alternative postharvest treatment method.

Apples (*Malus × domestica* Borkh.) are a major agricultural product with substantial economic value. In terms of annual tonnage produced, apples are the third most important fruit crop grown in the United States (Downing, 1989). 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 growth, significant quantities of pesticides are often necessary for the protection of this crop. This leads to pesticide residues on (or in) the fruit at harvest. Although residue levels are generally well below established tolerances, consumer wariness warrants efforts to further reduce pesticide residues.

Three pesticides, azinphos-methyl (guthion), captan and formetanate hydrochloride (carzol), were selected for this study. Application of these pesticides before harvest is often necessary for the protection of fruits during the preharvest period. Only pesticides with no evidence of carcinogenicity according to Environmental Protection Agency (EPA) standards were selected for this study.

The objective of the present study was to determine the effectiveness of chlorine and ozone as postharvest washes used in the dissipation of pesticide residues in solution and on fresh and processed apples.

MATERIALS AND METHODS

Pesticides

The three pesticides selected are used in the control of the major diseases, insects and mites that affect apples. Azinphos-methyl (guthion or *O,O*-dimethyl-*S*-[(4-oxo-1,2,3 benzotrizazin-3(4H)-yl)-methyl]-phosphorodithio-

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ate) is a non-systemic organophosphorous insecticide that acts both by contact and ingestion. Captan which is the common name adopted for *N*-trichloromethylthio-4-cyclohexene-1,2-dicarboximide is used widely as a non-systemic organosulphur fungicide in the prevention of fungal diseases of pome fruits and grapes. Formetanate-HCl (carzol or [*m*-[[[(dimethylamino)methylene]amino]phenyl-methylcarbamate]-hydrochloride) is an insecticide/acaricide that is characterized by its ability to evoke a variety of behavioral and other effects in several plant insects, beet fly, mites and thrips.

Orchard application and fruit sampling

Golden Delicious apples were grown at the Botany Field Research Laboratory at Michigan State University in East Lansing. Maintenance sprays of pesticides were applied throughout the growing season, and a final application of guthion, captan and carzol were applied just before harvest. Pesticides were applied with an airblast sprayer at 80 gallons per acre and 300 psi. For the final application, all three products (captan 50W, carzol 92SP and guthion 50W) were tank mixed and applied as a single application at rates of 6, 1.25 and 2 lbs per acre, respectively. The apples were harvested by hand the following day (1 day Preharvest Interval) to ensure the maximum amount of residue on the fruits. The apples were hand-picked randomly from various regions of the treated trees, thoroughly mixed and representative samples of eight fruits were used for each replication. All sample fruits were stored at -20°C for 10 days before analysis.

Wash treatments and sample preparation

Eight apples were used per replication (three replications per treatment) and placed in a 15-liter bucket containing 5 liters of water. The five treatments were: (1) no wash; (2) water wash; (3) ozone wash @ $0.25\text{ mg liter}^{-1}$; (4) chlorine wash @ 50 mg liter^{-1} ; and (5) chlorine wash @ 500 mg liter^{-1} . The apples were agitated every minute and the temperature, pH, chlorine and ozone concentration monitored before and after each wash treatment. A preliminary study, with 5, 10 and 15 min dip times, was carried out to determine the appropriate time that would be sufficient for an effective wash. It was deemed likely that any of these dip times could be easily incorporated into a process schedule in a commercial apple processing facility. A 15 min dip time was subsequently chosen for the present study.

After the wash treatments, the eight apples in each replication were divided into two batches. One batch (four fruits) was chopped in a Hobart food chopper (Hobart Mfg. Co., Troy, OH) and thoroughly mixed to ensure homogeneity. The chopped apples were stored in plastic ziplock bags to be used for pesticide analysis. The remaining four apples were first sliced, steam blanched and processed into apple sauce, and the sauce was subsequently analyzed for residue. The apple sauce was prepared from unpeeled apples which is typical

of commercial processing practices. Samples of water (400 ml) used in the wash treatments were saved for analysis to determine the amount of pesticides that were washed off the fruits and had not undergone degradation either on the fruits or in solution. All samples were stored at -20°C prior to residue analysis.

Aqueous solution study

In order to study the degradation of the three pesticides in aqueous solution, laboratory studies were conducted in a model system to determine the effects of: (i) chlorination (calcium hypochlorite at 50 and 500 mg liter^{-1}) and ozonation ($0.25\text{ mg liter}^{-1}$); (ii) three pHs (4.5–4.8, 7, 10.7); and (iii) two temperatures [ambient (21°C) and elevated (44°C)] on each pesticide over a 30 min period. There were three replications per treatment. Aqueous solutions unbuffered at pH 4.5–4.8 and buffered at pH 7 (0.2 M sodium phosphate) and pH 10.7 (0.2 M carbonate-bicarbonate) were prepared. Degradation of the pesticides was studied over a 30 min period because the typical water contact time (i.e. washing and fluming) for apples in a commercial plant is about 10–15 min and under normal conditions would rarely exceed 30 min.

For the chlorination study, an appropriate amount of calcium hypochlorite stock solution ($5000\text{ mg liter}^{-1}$) was added to each pH solution to bring the final chlorine concentration to either 50 or 500 mg liter^{-1} . Each pH solution was spiked with 4 ml of the pesticide stock solution (500 mg liter^{-1}) to give a final concentration of 2 mg liter^{-1} . The sample solutions were stirred with a magnetic stirrer to ensure thorough mixing. A 40 ml aliquot of the sample was transferred at 0, 5, 15 and 30 min intervals into 200 ml glass bottles. A 0.5 M sodium thiosulfate solution (Segall, 1968) and 40 ml of methylene chloride were immediately added to the samples to quench the reaction. Approximately 1 min elapsed between transferring the sample to the bottle and quenching of the reaction.

For the ozonation study, 1 liter of the water solution was pumped from a 2 liter glass beaker through a Lifex EV 200 ozone water system (Lifex Corporation, Birmingham, MI) using a Variostatic pump (Manostat, New York, NY) at a flow rate of $1.4\text{--}1.5\text{ ml min}^{-1}$. The solution was recirculated during the entire sampling period and 40 ml aliquots were pipetted from the glass beaker at 0, 5, 15 and 30 min intervals into 200 ml glass bottles. The samples were quenched as described for the chlorination study. Ozone concentration ($0.25\text{ mg liter}^{-1}$) in the solution was monitored before and after the sampling period using the indigo colorimetric method (APHA, 1987). All samples were stored at -20°C for subsequent pesticide residue analysis.

Residue analysis

Both azinphos-methyl and captan were extracted from water and apple samples with a modification of the method described by Liang & Lichtenstein (1976). Final extracts of formetanate-HCl were dissolved in

acetonitrile, while captan and azinphos-methyl were dissolved in hexane in known volumes and subsequently analyzed using either HPLC or GC. Residues of azinphos-methyl were detected with a Hewlett Packard Series II 5890 gas chromatograph equipped with a nitrogen phosphorus detector. The GC was equipped with a DB-5 fused silica capillary column (30 m \times 0.25 mm i.d.) with a film thickness of 0.25 μ m (J.W. Scientific, Folsom, CA). The oven temperature was programmed isothermally at 230°C, while the injector and detector temperatures were set at 250°C and 250°C, respectively. Residues of captan were detected with a Ni⁶³ electron capture detector. The GC was equipped with a DB-5 fused capillary (60 m \times 0.25 mm i.d.) with a film thickness of 0.25 μ m. The oven temperature was programmed isothermally at 180°C, while the injector and detector temperatures were 220°C and 275°C, respectively. The limit of detection for both pesticides was 0.002 mg liter⁻¹ in apple and 0.003 mg liter⁻¹ in solution. Formetanate-HCl residues were analyzed using a Milton Roy Spectrophotometer 3100 variable wavelength UV-visible detector, set at a wavelength of 254 nm, 0.05 absorbance unit full scale (AUFS) and 0.1 s response time. The column used was a Brownlee Spheri-5, RP-18 (5 μ m, 220 \times 4.6 mm i.d.). The mobile phase was 35% acetonitrile in 0.01 N NH₄H₂PO₄ (pH 8) filtered through a 0.45 μ m filter and degassed prior to use. An Anspec 3113 HPLC pump was used for solvent delivery at a flow rate of 2 ml min⁻¹. The limit of detection for both pesticides was 0.050 mg liter⁻¹ in apple and 0.003 mg liter⁻¹ in solution.

Statistical analysis

The study on effect of wash treatments on dissipation of pesticides on apple fruits was designed as a two factor (treatments \times replication) and (treatments \times product) randomized model. The model study was designed as a split plot (treatments \times pH \times temperature) randomized model, split across the duration of treatment. All determinations for both studies were made in triplicate. Mean, standard errors, mean square errors, two factor

ANOVA, correlation and interaction of main effects were calculated using SuperANOVA software (Abacus Corp., Inc., Berkeley, CA). Bonferroni's 't' was used to determine significant differences between treatment means.

RESULTS AND DISCUSSION

Aqueous solution study

The concentration of ozone in water generated from a Lifex ozone system was 0.251 mg liter⁻¹. Chlorine concentration of each sample solution was monitored, and determined to be within ± 2 mg liter⁻¹ (for 50 mg liter⁻¹) and ± 10 mg liter⁻¹ (for 500 mg liter⁻¹) of the intended final concentrations.

In the GC analysis, azinphos-methyl appeared as a single sharp peak at a retention time of 9.2 min. The percent recovery of azinphos-methyl in solution spiked with 0.5 and 5 μ g ml⁻¹ pesticide standards was 91.30 \pm 7.09%. Azinphos-methyl was stable in pH 4.5 and 7 solutions at both 21 and 44°C with very little degradation (0–4% at 21°C and 4–7% at 44°C) of pesticide after 31 min (Figs 1 and 2). Azinphos-methyl was relatively less stable at pH 10.7, with about 50 and 43% remaining after 31 min in solution at 21 and 44°C, respectively. These results are in agreement with various studies that have been carried out to show the behavior of azinphos-methyl in aqueous solutions over a wide range of pH and temperature. Faust & Gomma (1972) have shown that azinphos-methyl was less stable under basic than acidic conditions. The half-lives of azinphos-methyl at 21°C in buffered solutions ranged from 24 h at pH 1 to 0.6 h at pH 9.

Maximum degradation of azinphos-methyl by ozone was observed at pH 4.5 which decreased with increasing pH (Fig. 1). Between 17 and 39% of azinphos-methyl remained after 30 min at both 21 and 44°C for all three pH treatments. Degradation of azinphos-methyl at pH 7 at both 21 and 44°C was significantly ($P < 0.05$) different compared to pH 4.5, except at $t = 15$ min. The ozone

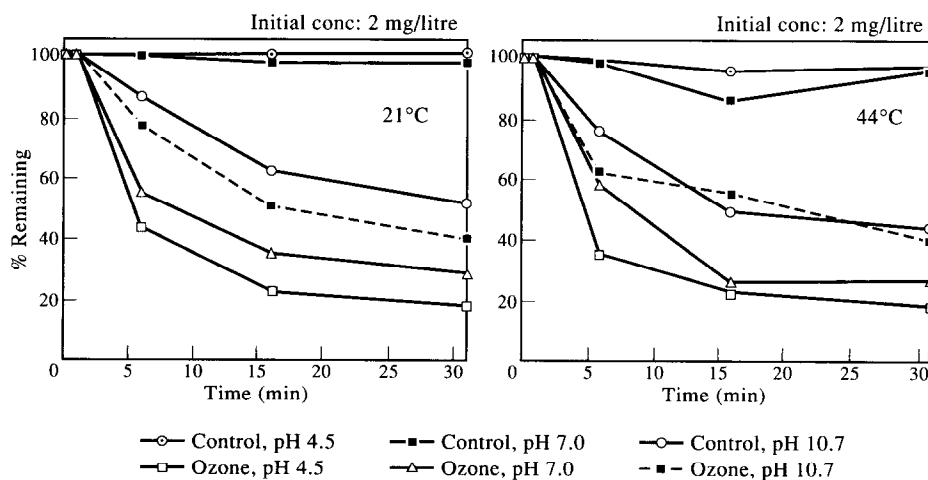


Fig. 1. Effect of ozone treatment on the degradation of azinphos-methyl at 21 and 44°C in a model system.

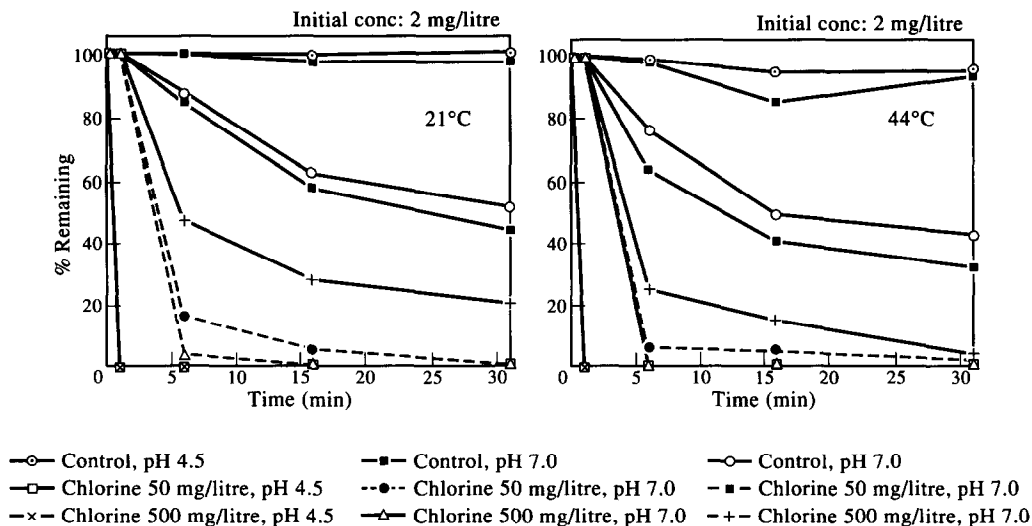


Fig. 2. Effect of chlorine treatment on the degradation of azinphos-methyl at 21 and 44°C in a model system.

treatment at pH 10.7 was the least effective at both 21 and 44°C. Increased temperatures did not significantly ($P < 0.05$) increase the rate of degradation of azinphos-methyl.

In 50 mg liter⁻¹ chlorine solution, azinphos-methyl was completely degraded at pH 4.5 at both 21 and 44°C (Fig. 2). At pH 7, almost 85% of the initial amount of azinphos-methyl was degraded after only 6 min in a 50 mg liter⁻¹ chlorine solution. The 50 mg liter⁻¹ chlorine treatment at pH 10.7 was the least effective resulting in only 15 and 56% degradation after 5 and 31 min, respectively. At both pH 7 and 10.7, higher temperature increased the degradation of azinphos-methyl by about 10%. Chlorination at 500 mg liter⁻¹ significantly ($P < 0.05$) increased the rate of degradation of azinphos-methyl at all three pHs (both temperatures). The most effective treatment was chlorination at 500 mg liter⁻¹ in the pH 4.5 solution, while pH 10.7 was the least effective treatment.

When chlorine as calcium hypochlorite is added to water, a mixture of hypochlorous acid (HOCl) and hydrochloric acids are formed; HOCl has the highest

oxidation potential of all of the chlorine species formed. Wei *et al.* (1985) has shown that the percent of HOCl is greatest at low pH and decreases as the pH and temperature of a solution increase. Under these circumstances the oxidation reaction of HOCl with azinphos-methyl was greatest at pH 4.5 and least at pH 10.7, as was observed in this study. Also, the organophosphate insecticide used contains a phosphoric acid ester linkage that is relatively unstable and more susceptible to oxidation in a strong oxidizing medium. This was shown to be true owing to the strong correlation between the rate of azinphos-methyl degradation and increasing hypochlorite concentration.

In the GC analysis, captan appeared as a sharp peak with a retention of 46 min. The recovery of captan spiked with 0.5 and 5 mg liter⁻¹ of the standard was $105.9 \pm 1.71\%$. The degradation of captan (2 mg liter⁻¹) in solutions due to hydrolysis, ozonation and chlorination is shown in Fig. 3. At 21°C, captan degradation due solely to hydrolysis was not significant ($P > 0.05$) at pH 4.5 and 7, and significant ($P < 0.05$) at pH 10.7. Captan was completely unstable at pH 10.7 in both the control

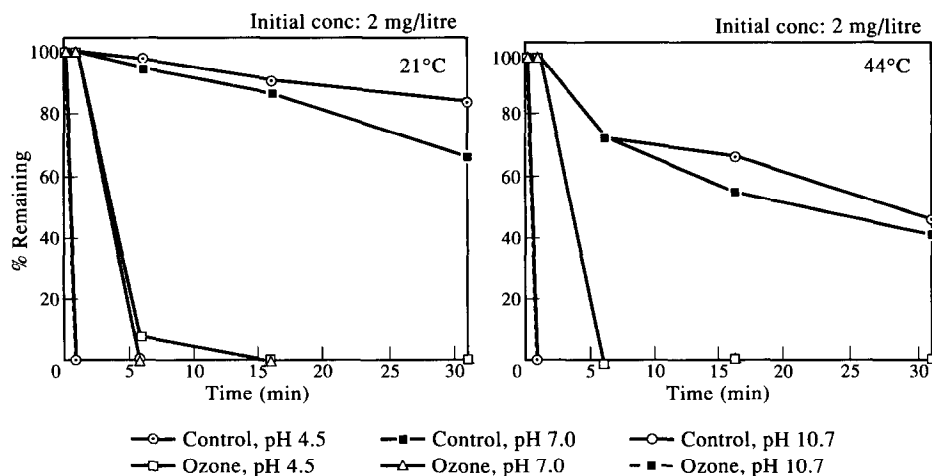


Fig. 3. Effect of ozone treatment on the degradation of captan at 21 and 44°C in a model system.

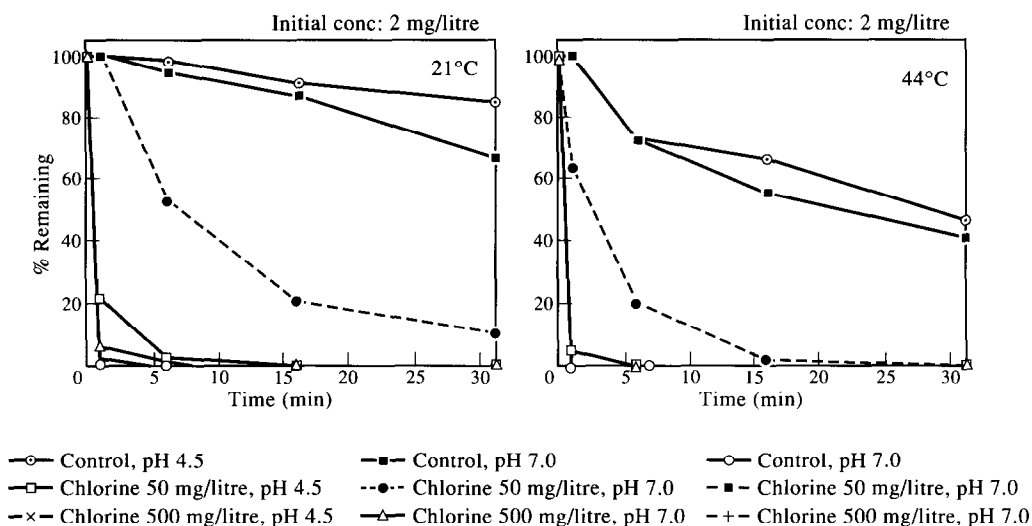


Fig. 4. Effect of chlorine treatment on the degradation of captan at 21 and 44°C in a model system.

and ozonated samples, even at $t=1$ min. After 6 min of ozone treatment at 21°C at pH 4.5 and 7, only 7.3 and 0% of captan remained respectively. Captan degradation was accelerated at 44°C. After 30 min in pH 4.5 and 7 control solutions, about 47 and 42% of captan remained, respectively (Fig. 4). With ozonation, captan was completely degraded after 5 min at all three pHs. The rate of degradation of captan due to ozonation was significantly greater at 44°C than at 21°C. Earlier investigators have reported the relative instability of captan in solution. Melnikov (1971) reported that captan was hydrolyzed by moisture and the reaction was accelerated by alkali. Von Rümker & Horay (1972) presented data showing that the half-life of captan at 20°C at pH 4 was 4 h, and at pH 10 it was less than 2 min. Wolfe *et al.* (1976) reported that the degradation of captan was independent of pH over the pH range 2–6, and pH dependent above pH 7.

Chlorine treatment at both ambient and elevated temperatures caused significantly ($P < 0.05$) greater captan degradation compared to the control (hydrolysis

only) (Fig. 4). Captan in a 50 mg liter⁻¹ chlorine solution was most stable at pH 7 and very unstable at pH 4.5 and 10.7. Almost all the pesticide was degraded at pH 4.5 and 10.7; however, the degradation of captan at pH 10.7 was due almost entirely to hydrolysis and not as a result of chlorine treatment. Captan was completely degraded in 500 mg liter⁻¹ chlorine solutions at all three pHs. At pH 7 at both 21 and 44°C, residual captan was detected in the 50 mg liter⁻¹ solution but not in the 500 mg liter⁻¹ solution indicating that captan was extremely unstable at high chlorine concentrations. Temperature significantly ($P < 0.05$) influenced the effect of chlorination on captan degradation in all treatments. A 20–30% increase was observed in the degradation of captan at the higher temperature between the 5 and 30 min treatment interval at pH 7.

In the HPLC analysis, formetanate-HCl as formetanate appeared as a broad peak with a retention time of 3.4 min. The average recovery for formetanate-HCl, spiked at 0.5 and 5 mg liter⁻¹ in solution, was $103.2 \pm 6.19\%$. The rate of degradation of formetanate-

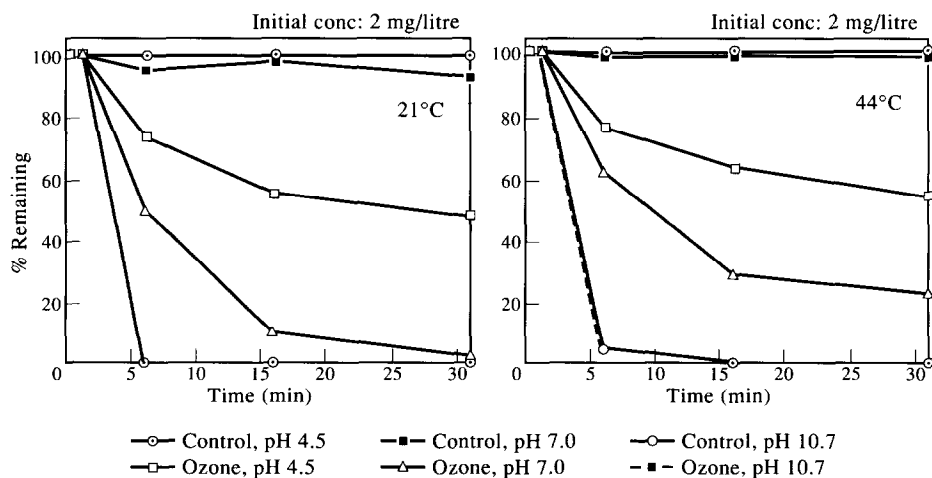


Fig. 5. Effect of ozone treatment on the degradation of formetanate-HCl at 21 and 44°C in a model system.

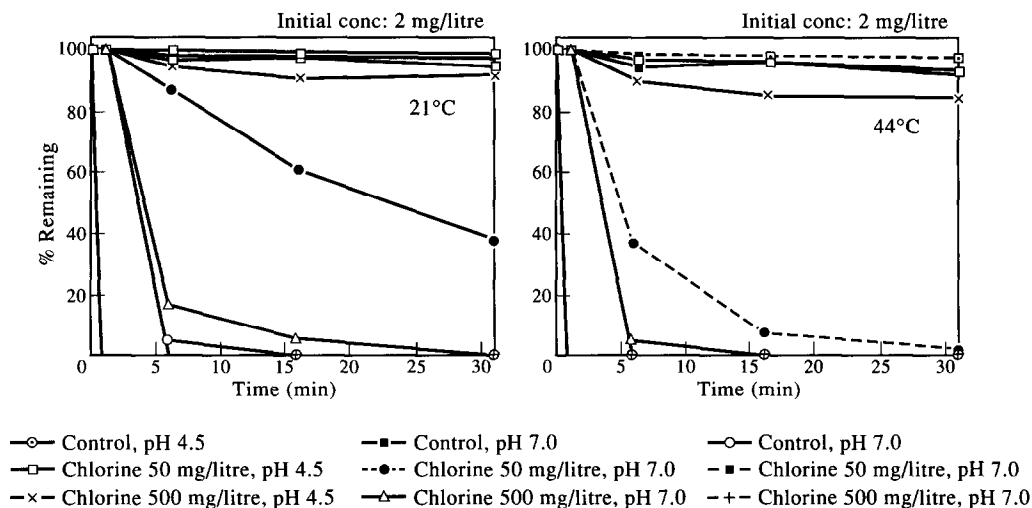


Fig. 6. Effect of chlorine treatment on the degradation of formetanate-HCl at 21 and 44°C in a model system.

HCl due to hydrolysis generally increased with increased pH and temperature. Formetanate-HCl as formetanate was unstable and degraded rapidly at alkaline pH (Fig. 5). Almost no degradation was observed in solution at pH 4.5 and 7 and at both 21 and 44°C. Ozonation at pH 4.5 was the least effective treatment. Almost 50% of formetanate-HCl remained after 31 min of ozone treatment at both 21 and 44°C. Higher temperature did not significantly ($P > 0.05$) accelerate degradation of the pesticide by ozonation. At pH 10.7, most of the formetanate-HCl degradation was due to hydrolysis rather than oxidation by ozone.

Formetanate-HCl in chlorinated solution was relatively stable at low pH, and extremely unstable in its basic form at pH 10.7 (Fig. 6). Formetanate-HCl was degraded by 80–100% at pH 10.7 in both 50 and 500 mg liter⁻¹ calcium hypochlorite solutions at both 21 and 44°C. Elevated temperature significantly ($P < 0.05$) increased the degradation of the pesticide in chlorinated water at pH 7. Of the three treatments (ozone, 50 and 500 mg liter⁻¹ chlorination), chlorination at 500 mg liter⁻¹ was the most effective treatment in the degradation of formetanate-HCl.

Due to the chemical structure of formetanate-HCl and the form it takes in different pH medium, it

appeared that the acidic form was relatively stable while its basic salt was unstable and subject to both hydrolysis and chemical oxidation. Jenny & Kossmann (1978) reported that formetanate-HCl hydrolyzed slowly in acid medium, and was extremely susceptible to hydrolysis in neutral or basic medium.

Residue removal by various wash treatments

Data presented in Fig. 7, show the effects of the various wash treatments on reduction of azinphos-methyl residue in/on apple fruit and sauce. The total amount of residue on the control unwashed fruit was determined to be 401.78 μg or 0.67 mg liter⁻¹. Almost 53% of azinphos-methyl residue was removed from the fruit with the water wash. Apples dipped in ozonated water had reduced residue levels by about 75%. Chlorine wash at 50 and 500 mg liter⁻¹ removed about 76 and 83% of the pesticide residue, respectively. The various wash treatments significantly ($P < 0.05$) reduced residue levels as compared to the unwashed samples. While there appeared to be a decrease in the amount of azinphos-methyl removed from the water-washed fruits to those washed with either ozone or chlorine, there was no significant difference ($P > 0.05$) between treatment means. Processing apples into apple sauce significantly ($P < 0.05$) reduced the levels of azinphos-methyl residue (Fig. 7). About 96% of azinphos-methyl was removed when the unwashed apples were processed into sauce. Washing the apples followed by processing reduced the amount of residue by 98%. The amount of azinphos-methyl remaining in the sauce from fruit washed with either ozonated or chlorinated water was between 2 and 3% of the unwashed fruits. The results from the present study were all in agreement with those reported by Gunther *et al.* (1963) and El-Hadidi (1993).

The amount of captan on the control apples (unwashed) was 291.54 μg or 0.488 mg liter⁻¹ (Fig. 8). The effect of a simple water-wash treatment reduced the amount of captan by about 50%. Ozone wash removed 72% of captan, while the 50 and 500 mg liter⁻¹ chlorine

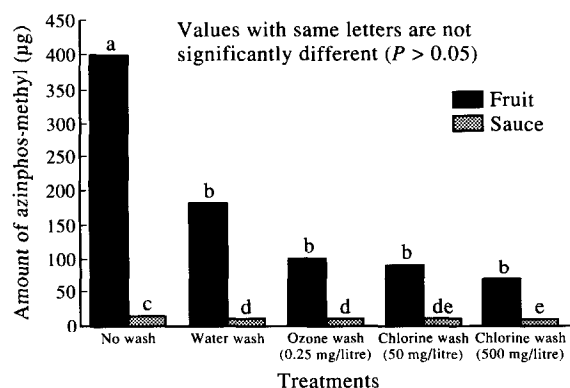


Fig. 7. Amount of azinphos-methyl residue on/in apple fruit and sauce.

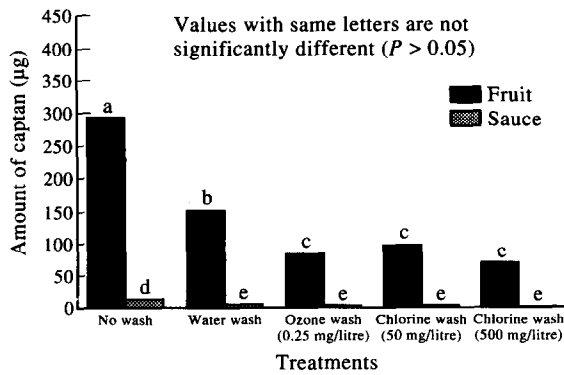


Fig. 8. Amount of captan residue on/in apple fruit and sauce.

wash removed 66 and 77% pesticides, respectively. There was a significant ($P < 0.05$) difference between the unwashed and washed fruit. Chlorine wash at 500 mg liter⁻¹ was the most effective treatment for captan removal. Frank *et al.* (1983) reported that washing apples with water removed 43% of the captan residue. Hendrix (1991) reported that 0.42 ppm captan remained on apples washed with water, while 500 ppm chlorine wash for 5 min reduced residues to less than detectable levels. The percent reduction of residue from the water-washed fruit to the 500 mg liter⁻¹ chlorine wash in this study was about 56%. Processing the apples into apple sauce significantly ($P < 0.05$) reduced the amount of captan. Almost 97% was removed from the unwashed fruits by processing, while 99% was removed when the fruits were water-washed and processed. No detectable amount of captan was found in the apple sauces from apples that were first washed with ozonated or chlorinated water.

In general, there were significant ($P > 0.05$) differences between the washed fruits compared to the unwashed fruits in terms of captan reduction. Although there was a reduction in the residue levels between the water-washed apples and the ozone and 50 mg liter⁻¹ chlorine-washed fruits, there was no significant ($P > 0.05$) difference. Also, increasing the chlorine concentration to 500 mg liter⁻¹ did not significantly ($P > 0.05$) increase the effectiveness of the chlorine wash.

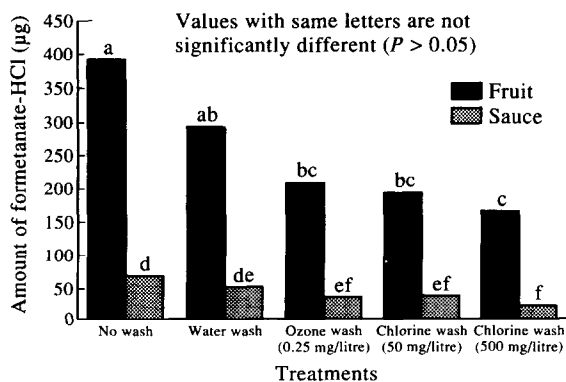


Fig. 9. Amount of formetanate-HCl residue on/in apple fruit and sauce.

The significant ($P < 0.05$) decrease in captan residue due to processing could be due to the heat used during the blanching of the apples. According to Worthing & Hance (1991), the melting point of captan is 160–170°C, and it decomposes at or near its melting point. Therefore, it would be expected that most of the residual captan would be degraded during the blanching process where temperature is maintained at 110°C for about 10 min. Frank *et al.* (1983) reported that boiling the whole apple for 5 min or cooking the peeled and diced apple removed and/or destroyed 70–98% of captan residue. They also showed that the combination of thorough washing and cooking gave almost 100% removal. Ritcey *et al.* (1984) reported that washing and cooking strawberries for 5 min reduced captan by more than 95%.

The amount of formetanate-HCl found on/in unwashed apples was 392.23 µg or 0.657 mg liter⁻¹. Reduction in residual formetanate-HCl was significantly ($P < 0.05$) influenced by the effect of various wash treatments, except for the water-washed fruits where the reduction was not significant ($P < 0.05$) as compared to the unwashed apples (Fig. 9). While water-washing of fruits reduced levels by 23%, the ozone and chlorine washes reduced formetanate-HCl by about 46 and 50% respectively. The 500 µg ml⁻¹ chlorine wash was the most effective treatment. However, there appeared to be no statistical difference between the three washes (ozone, 50 and 500 mg liter⁻¹ chlorine) at the 5% level. Processing of apples into sauce significantly ($P < 0.05$) reduced the amount of formetanate-HCl (Fig. 9). Unwashed apples that were processed into sauce showed an 84.2% reduction in residue level. Apples that were water-washed and subsequently processed into sauce had pesticide residue reduction of 87.3%. Ozone- and chlorine-washed apples processed into sauce had pesticide reductions of 91–96%.

The amount of captan, azinphos-methyl and formetanate-HCl recovered in the wash water was 137, 420 and 253 µg, respectively (Fig. 10). There was significant ($P < 0.05$) reduction of the three pesticides in the ozonated water-wash treatment as compared to the simple water wash. The reduction of the three pesticides

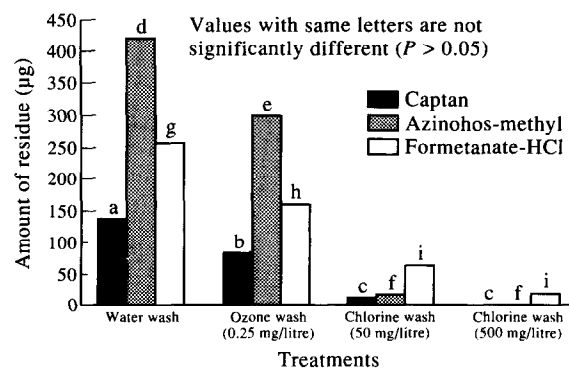


Fig. 10. Azinphos-methyl, captan and formetanate-HCl residues in wash water.

ranged between 29 and 42%. The 50 and 500 mg liter⁻¹ chlorine-wash treatment resulted in significantly ($P < 0.05$) less pesticide residue in wash water as compared to the water-wash treatment. In the 50 mg liter⁻¹ chlorine wash treatment, 93, 96 and 76% of captan, azinphos-methyl and formetanate-HCl, were removed from the wash water, respectively, as compared to the water-wash (control) treatment. The 500 mg liter⁻¹ chlorine wash removed 93% of formetanate-HCl and all detectable levels of captan and azinphos-methyl in the wash water. Results indicate that the ozone- and chlorine-wash treatments were effective in reducing the amount of pesticide residues in the wash water after the pesticides have been rinsed off the apples. This would ensure that the wash water would be 'detoxified' before it is disposed of as waste. This is an advantage in terms of reducing chemical waste and ensuring the safe disposal of pesticide waste. In general, the ozone washes were not as effective in reducing the three pesticides from the fruit, sauce and in the wash water as compared to the chlorine washes. Possible reasons for this could be the low concentration of ozone (0.25 mg liter⁻¹), its instability in water and the high organic content in the wash water. The presence of organic materials has been reported by Glaze (1987) to accelerate the decomposition of ozone.

CONCLUSIONS

A laboratory-scaled model system was developed which was shown to be effective in monitoring the degradation and/or disappearance of azinphos-methyl, captan and formetanate-HCl through the use of various pH, temperature, ozone and chlorine treatments. Residue analysis of fresh and processed fruit showed that post-harvest and processing treatments were effective in reducing pesticide residue levels on the fruit and in processed products.

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