JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Effects of Postharvest Preparation on Organophosphate Insecticide Residues in Apples

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Apples were sampled directly from orchard trees at 96, 45, and 21 days postapplication with one of three organophosphate insecticides (azinphos methyl, phosalone, or phosmet, respectively). Individual apples were prepared for analysis following one of three postharvest preparations: no preparation, rinsed with deionized water for 10–15 s, or rinsed and peeled. Azinphos methyl, phosalone, and phosmet concentrations ranged from below the level of detection to 5.26 ng/g, 94.7 to 5720 ng/g, and 0.011 to 663 ng/g in the apples that received no postharvest preparation, respectively. Although rinsed apples had lower maximum concentrations than observed in apples with no preparation, levels were not significantly lower. Concentrations of all three OP insecticides in apples that were rinsed followed by peeling, however, were much lower (below detection limits to 0.733 ng/g, azinphos methyl; 0.322–219 ng/g, phosalone; and below detection limits to 44.0 ng/g, phosmet) than observed in apples that had been rinsed alone. Rinsing and peeling of apples resulted in a 74.5−97.9% reduction in OP residues, while rinsing alone lowered mean concentrations by 13.5−28.7% relative to apples that received no postharvest preparation.

KEYWORDS: Organophosphate; preparation; residue reduction; rinse; peel

INTRODUCTION

Pesticides are used to control insects, weeds, and disease throughout the world. Although their use leads to increased crop yields and improvements to the quality of the food produced, pesticide residue levels in foods are of increasing concern to the public. Exposure and effects to exposed organisms, including humans, are considered as part of the Canadian risk assessment process. Regulatory activities also include the determination of maximum residue limits (MRLs) to ensure that pesticides are not present in food commodities at concentrations that could pose harm to individuals upon consumption.

Organophosphate (OP) pesticides are broad spectrum insecticides that have been used throughout the world on a variety of crops for many years. Because of their extensive use patterns, they have been the focus of much study. OP insecticides act via acetylcholinesterase (AChE) inhibition, and exposure to these compounds results in excess acetylcholine (ACh) in the nerve cells of both target and nontarget organisms, including humans (*1*). As a result of the association between the OP insecticides and the neurological impacts, OP insecticides are of concern to researchers involved in human health studies. Dietary intake is known to be an important route of exposure to pesticides (*2, 3*); therefore, regulatory agencies such as the Canadian Food Inspection Agency (CFIA) in Canada routinely measure pesticides in fruits and vegetables to ensure that residues meet with compliance levels (*4*). Composites of individual consumer units from a given lot are subsampled as part of the CFIA sampling protocol. Residue levels in foods also are determined for use in establishing dietary exposure estimates (*5*−*7*).

The reduction of pesticide concentrations in foods as a result of postharvest preparation has been studied for several classes of pesticides including some of the OP insecticides (*8*−*10*). While some researchers have compared different washing solutions (e.g., detergents, salt solutions, and chlorine washes), including water alone (*10*−*12*), others have quantified the impacts of brushing, blanching, and/or peeling (*9, 13*). Washing or rinsing with water alone is generally less effective than other preparation methods, such as washing with detergents and other solutions, peeling or blanching/cooking.

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10.1021/jf072408m Published 2008 by the American Chemical Society
Published on Web 01/04/2008

Table 1. Water Solubility of Selected OP Insecticides (*17*)

compound	water solubility (mg/L)	uses
azinphos methyl	28 (20 °C)	nonsystemic
phosalone	1.7–2.0 (room temperature)	nonsystemic
phosmet	22 (25 °C)	nonsystemic
chlorpyrifos	2 (25 °C)	nonsystemic
diazinon	40 (20 °C)	nonsystemic
malathion	145 (room temperature)	nonsystemic
parathion	11 (20 °C)	nonsystemic

Although rinsing with tap water has led to a significant reduction in residue concentrations for some pesticide classes, many OP insecticide residues are not significantly lowered by rinsing with water alone (*14, 15*). The removal of pesticides via washing with water is reported to be both compound- and commodity-specific (*9, 15, 16*). In contrast to most observations, Elkins (*16*) reported a dramatic reduction (95%) in malathion residues from tomatoes following rinsing with tap water. Malathion is a nonsystemic insecticide and has high water solubility (145 mg/L) relative to many of the OP insecticides (**Table 1**) (*17*).

In addition to water solubility, Krol et al. (*18*) have reported that a reduction in levels associated with washing or rinsing also is impacted by whether the pesticide is a systemic or surface-acting pesticide. Because systemic pesticides translocate throughout plants, removal of these pesticides via rinsing with water or other surface treatment is less effective. Although the reduction in mancozeb and ethylenethiourea residues in apples has been studied (*19, 20*), data on the reduction of OP insecticides in apples are not readily available.

Testing to determine pesticide reduction from a given commodity is sometimes performed on samples that have been harvested prior to pesticide treatment and subjected to laboratory fortification (*8*). Krol and co-workers (*18*) have reported that studying residue reduction resulting from postharvest preparation of produce with field-incurred residues more accurately represents commercially produced fruits and vegetables than using laboratory-fortified samples for this type of research. The extraction potential from field-applied compounds is different than laboratory-treated produce because in the field, translocation of pesticides, weathering, and interactions with the living plant occur (*18*). Laboratory application of pesticides does not allow for these additional factors to occur prior to the commencement of testing.

In the present study, residue reduction resulting from three postharvest preparation methods was determined in McIntosh apples treated with OP insecticides from a commercial orchard in Quebec, Canada. Many individuals eat apples directly from the market rather than rinsing with water prior to consumption; therefore, the impact of rinsing on OP insecticide residue levels in apples was investigated relative to no postharvest preparation. Parents of young children frequently rinse and peel apples prior to feeding them to children, so this postharvest preparation was also investigated to establish if it resulted in significantly lower residue levels.

MATERIALS AND METHODS

Field Application. During the 2003 agricultural season, three rows of apple trees (10 trees per row) from a commercial Canadian orchard were used for the study. Each row was treated with one of three OP insecticides (azinphos methyl, phosalone, or phosmet) following label directions (*21*). The OP compounds were applied using an air blast sprayer and application rates (azinphos methyl, 1.14 kg active ingredient (a.i.)/ha; phosalone, 1.5 kg a.i./ha; and phosmet, 2 kg a.i./ha) were consistent with recommended label rates for use on apples and corresponded to pest control requirements within the orchard. Although each compound was applied directly to one row, spray drift to the untreated rows was possible. Apples were collected one day in advance of the planned commercial harvesting and observed the required preharvest intervals for each insecticide.

Table 2. Parameters for the Mixed Effects Model Used in the Statistical Analyses

effect	description	nature of effect
P	preparation	fixed
H	height compartment	fixed
F	face compartment	fixed
	interactions of fixed effects (PH PF HF PHF)	fixed
T(R)	tree within row	random
R(AC)	replicate row within applied or not applied	random
S(C)	chemical analysis set	random
C	compound measured	fixed
A(C)	applied or not applied, within context of compound	fixed
	interactions of fixed and random effects	random
error (AC)	analysis to analysis differences in the effects above	random

Experimental Design and Harvest. Individual apples were sampled following an established protocol to ensure that equal numbers of apples were collected from each treatment row and apples were collected from all regions of the tree. Harvested apples were assigned to preparation (no preparation, rinse, and rinse and peel × tree zones [three heights, two faces]) according to a 3 × 3 × 2 factorial design (preparation, heights, and faces) arranged into blocks (trees) of six apples by partially confounding the three-way interaction with differences among trees. As apples were picked, they were given a unique code number, placed in a paper bag, and taken to the laboratory for further processing.

The relative frequency (log odds) of apples with residue concentrations greater than the limit of detection (Y) out of all apples harvested (N), pooled over trees in an orchard row and over chemical analysis sets, was modeled using a generalized mixed model: $\text{logit}(Y/N) \sim$ A|P + H|F + R(A) + error. A mixed effects model was used to describe variability among individual apple residue concentrations greater than LOD (Y) and treated chemical compound measurement as a repeated measure on the same apple (**Table 2**): $\ln(Y) =$ [P|C P|H P|F P|A(C) H|F A|H(C) A|F(C)] + [T(R) R(AC) S(C) error (AC)]. The data were compared and are reported using least-squares means (population marginal means) rather than simple means. Additionally, type III tests were performed to assess the significance of effects. This approach was used because the data set was unbalanced once the experimental design, missing or rejected observations, and residue concentrations less than the LOD were taken into account.

Chemicals and Reagents. Analytical standards of all analytes (azinphos methyl, phosalone, and phosmet) were purchased from AccuStandard (New Haven, CT). Deuterated (d_{10}) analogues of surrogate OP insecticides (diazinon and malathion) were purchased from Cambridge Isotope Laboratories (Andover, MA). Similarly, the performance standard ($^{13}C_{12}$ PCB 101) was purchased from Cambridge Isotope Laboratories. High-purity solvents (acetone, hexane, dichloromethane, and cyclohexane), suitable for liquid chromatography, gas chromatography, and residue analysis used in the extraction and cleanup steps, were purchased from EMD Biosciences Inc. (Mississauga, ON). Reagent grade sodium sulfate and sodium chloride also were purchased from EMD Biosciences Inc.

Postharvest Preparation of Apples. While the apples were undergoing sorting and preparation, they were stored at 4 °C. Samples were sorted according to preparation group. Apples subject to rinsing were held under running deionized water for 10–15 s and continuously rubbed with hands. Deionized water was used for these experiments to reduce the pesticide contribution from tap water. Apples requiring peeling were initially rinsed with hand rubbing followed by peeling with a paring knife. Following preparation, individual apples were then cored and sliced into 10 equal segments using a domestic corer/slicer. The apple slices were chopped manually using a knife and placed in a

Table 3. Apples Analyzed in the Study Relative to the Apples with Concentrations Exceeding the Limit of Detection

active ingredient		apples analyzed			number with residues > LOD		
		no preparation	rinse	rinse and peel	no preparation	rinse	rinse and peel
azinphos methyl	applied	24	23	24	23	22	20
	not applied	46	48	47	37	42	13
phosalone	applied	22	24	23	22	24	23
	not applied	48	47	48	48	47	48
phosmet	applied	24	24	24	24	24	24
	not applied	46	47	47	46	47	44

plastic bag for storage at −80 °C until extraction and analysis. The corer/slicers and knives used in apple preparation were thoroughly washed with detergent and rinsed with deionized water between apples.

Extraction and Cleanup. Extraction and clean up of samples was performed as described in Rawn et al. (*21*). Briefly, analytical samples were prepared by weighing a 25 g aliquot into a 500 mL Erlenmeyer flask to which deuterated (d_{10}) analogues of diazinon and malathion were added as surrogate standards. Homogenization with 5:1 acetone:hexane was performed using a Polytron, followed by filtration through glass wool into a separatory funnel, to which saturated NaCl was added. The aqueous layer was removed following gentle shaking and was extracted with an additional volume of hexane. The organic phases were dried over anhydrous Na_2SO_4 and evaporated to near dryness. Sample extracts were dissolved in dichloromethane (DCM):cyclohexane (1:1) and filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter, and high molecular weight impurities were removed using gel permeation chromatography (GPC) with 200−400 mesh Bio-Beads SX-3 (O-I Analytical, College Station, TX). Extracts were reduced to 2 mL and were cleaned up further using 6 g of Florisil (2% deactivated), eluting with 70 mL of 60% DCM:hexane followed by 100 mL of 15% acetone:hexane. A performance standard ($^{13}C_{12}$ PCB 101) was added to the final extracts, and all samples were concentrated to a final volume of 1 mL in iso-octane.

Gas Chromatography−Mass Spectrometry. Analysis was performed using a Micromass Autospec-Ultima (Manchester, United Kingdom) coupled to an Agilent 6890 gas chromatograph (Mississauga, ON, Canada) equipped with an on-column injection system. The injector was set to track oven temperatures. A 3 m × 0.53 mm retention gap (Chromatographic Specialties, Brockville, ON, Canada) was coupled to a 30 m DB-5 fused silica column with 0.25 mm i.d. × 0.25 μm film thickness for gas chromatographic separation (J&W Scientific, Folsom, CA). The temperature, initially set to 80 °C and ramped at 8 °C/min to 240 °C, was taken to a final temperature of 280 °C at a rate of 15 °C/min, where it remained for 5 min with a total run time of 28 min. Injection volumes were 1 μL for all analyses. Helium was used as the carrier gas with a constant pressure of 150 kPa. Samples were analyzed using selected ion monitoring (m/z = 160 and 132, 182 and 184, and 160 and 161 for azinphos methyl, phosalone, and phosmet, respectively).

The electron energy was set to 70 eV, with a photomultiplier voltage of 350 V. The trap current was 600 μA, and the source temperature was 250 °C. The re-entrant temperature and capillary line temperature were maintained at 280 °C, and perfluorokerosene-L (PFK) was used as the reference substance for tuning at m/z 393. The mass resolution was set to between 3000 and 4000 for all compounds.

Quality Assurance/Quality Control. Apples from an orchard with no OP insecticide application were obtained, prepared the same as the rinsed and peeled apples, and were used to prepare blank apple matrix for quality assurance testing. With each set of samples (8−10 samples per set) extracted and analyzed, two aliquots (2 × 25 g) of blank apple matrix were prepared for separate extraction. One was used as a blank, and the other was spiked with the analytes (azinphos methyl, 1.9 ng/g; phosalone, 0.90 ng/g; and phosmet, 0.92 ng/g) prior to processing, followed by extraction, cleanup, and analysis as for all other samples. Background levels of some analytes were periodically detected in the blank matrix samples and were used for background subtraction in the determination of recovery from spiked matrix only; residue concentrations in samples were not blank corrected. No traces of the OP insecticides were observed in any of the reagent blanks analyzed. Recoveries of all of the analytes from the spiked samples (n = 37), following blank subtraction, ranged from 74 (phosmet) to 107% (phosmet). The average d_{10}-diazinon and d_{10}-malathion recoveries were 78 and 91%, respectively.

Method detection limits (MDL) were established based on a 3:1 signal to baseline noise ratio and are reported as averages of individual chromatograms for all samples measured. Average MDLs ranged from 0.021 pg injected (phosmet) to 0.176 pg injected (azinphos methyl).

RESULTS AND DISCUSSION

In all cases, azinphos methyl and phosmet were below MRLs established for apples in Canada (2000 and 10000 ng/g, respectively). The MRL for phosalone in apples (5000 ng/g) was exceeded (5720 ng/g) in one of the 212 apples analyzed. The apple with very high phosalone concentration was part of the group not subjected to any postharvest preparation. The maximum phosalone concentration observed in the present study exceeded that measured in the initial study because a different set of apples was analyzed for the determination of the impact of compositing on residue levels (*21*) than used for the present study. This elevated concentration is consistent with variability of individual apples in an orchard.

All apples analyzed with no postharvest preparation had detectable levels of both phosalone and phosmet irrespective of its OP insecticide treatment row. Phosalone and phosmet concentrations in apples that received no postharvest preparation ranged from 94.7 to 5720 ng/g and from 0.011 to 663 ng/g, respectively. Azinphos methyl, however, was not detected in 10 (14%) of the apples analyzed where no postharvest preparation was performed (**Table 3**). Only one apple sprayed with azinphos methyl had residues below the level of detection, while the other apples with azinphos methyl concentrations below the MDL were obtained from the rows treated with phosalone (one apple) or phosmet (eight apples). The maximum azinphos methyl concentration (5.26 ng/g) was observed in an apple belonging to the group with no postharvest treatment and was collected from the row treated with this compound.

Maximum phosalone (3900 ng/g) and phosmet (436 ng/g) and least-squares mean concentrations (399–609 ng/g and 0.021–63.9 ng/g, respectively) in apples that were rinsed were lower than observed in apples with no postharvest preparation (**Table 4**). While all rinsed apples tested had detectable levels of phosalone and phosmet, azinphos methyl concentrations in seven (10%) rinsed apples were below the method detection limit (**Table 3**). The maximum concentration of azinphos methyl observed in an apple that had been rinsed prior to extraction and analysis was 3.15 ng/g, and the least-squares mean estimates ranged from 0.226 to 0.423 ng/g (**Table 4**).

The least-squares mean concentrations of both phosalone (6.92–12.2 ng/g) and phosmet (0.013–7.34 ng/g) in apples collected from all application rows following rinsing and peeling were lower than the least-squares mean concentration in apples that were rinsed only prior to extraction (**Table 4**). The

Table 4. Least Squares Mean Concentrations (ng/g) [Standard Error] in Apples Following Different Preparation Methods Based on the Model: ln(*Y*) = [PIC PIH PIF PIA(C) HIF AIH(C) AIF(C)] + [T(R) R(AC) S(C) Error (AC)]

active ingredient	treatment row	no preparation	rinse	rinse and peel
azinphos methyl	1[a]	0.515 [0.104]	0.423 [0.086]	0.082 [0.170]
	2	0.300 [0.062]	0.226 [0.045]	0.048 [0.014]
	3	0.191 [0.046]	0.233 [0.053]	0.021 [0.010]
phosalone	1	641 [144]	609 [138]	7.69 [1.71]
	2[a]	731 [168]	573 [129]	12.2 [2.73]
	3	461 [103]	399 [89.5]	6.92 [1.53]
phosmet	1	0.220 [0.045]	0.159 [0.033]	0.046 [0.009]
	2	0.039 [0.008]	0.021 [0.004]	0.013 [0.003]
	3[a]	125 [25.5]	63.9 [13.0]	7.34 [1.36]

[a] Treated with the active ingredient identified.

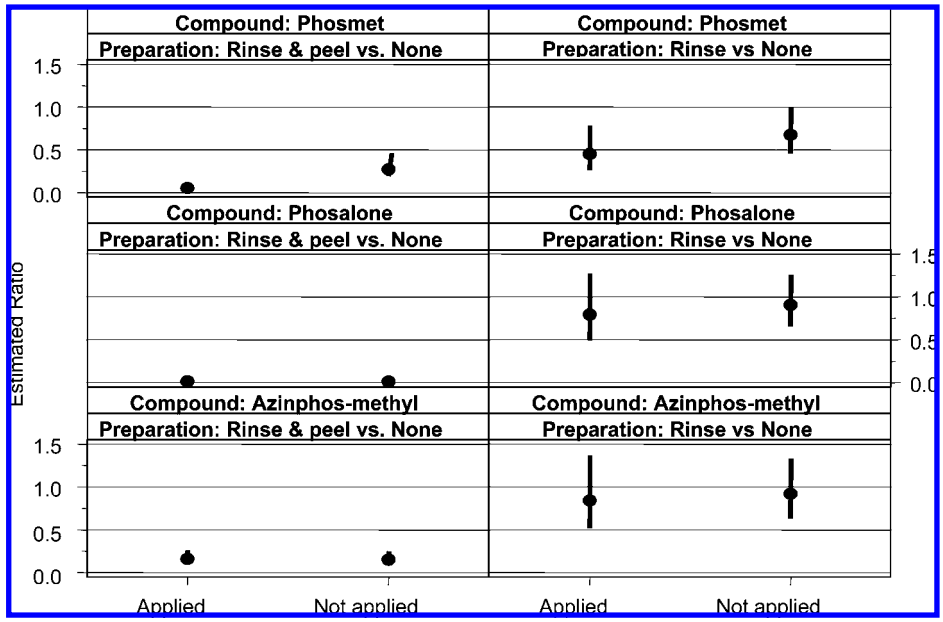

Figure 1. Ratio (point estimate, 95% confidence interval [bars]) of residue concentration, rinse vs no preparation (right-hand panels), and rinse and peel vs no preparation (left-hand panels) by compound; results are separated according to whether the OP insecticides were directly applied or not directly applied to orchard rows.

maximum concentrations of phosalone and phosmet observed in the rinsed and peeled apples were 219 and 44.0 ng/g, respectively. The maximum concentration of azinphos methyl observed in the apples that were both rinsed and peeled prior to extraction was 0.733 ng/g, with least-squares means levels ranging from 0.021 to 0.082 ng/g.

Although phosalone was detected in all rinsed and peeled apples tested, phosmet was below method detection limits in three (4%) of the apples subject to the two-step postharvest preparation (**Table 3**). Each apple with phosmet concentrations below the MDL was obtained from a row that was not directly sprayed with phosmet, while detectable levels were observed in all apples from the row treated with this OP insecticide.

The impact of apple preparation relative to no preparation was similar for phosalone and azinphos methyl, with rinsing and peeling having the greatest relative difference to residue levels. Mean phosalone and azinphos methyl residues were both lowered with preparation (rinse and rinse and peel) regardless of whether the apples were treated directly with these compounds or deposited via drift (**Figure 1**). Although phosmet residues were impacted by both preparation types tested, preparation was affected by whether phosmet was used to treat the apples directly (**Figure 1**), and the apples that received direct phosmet application were more greatly affected than those with residues solely the result of drift.

All compounds were found to be much lower in apples that had been rinsed and peeled rather than rinsed exclusively (**Figure 2**). Mean phosalone, phosmet, and azinphos methyl concentrations in rinsed apples were 13.5, 15.3, and 28.7% lower than mean concentrations in apples that received no postharvest preparation, respectively (**Figure 2**). Apples that were rinsed followed by peeling had 97.9, 74.5, and 86.5% lower mean phosalone, phosmet, and azinphos methyl concentrations than mean levels of apples with no preparation (**Figure 2**).

A type 3 test for fixed effects was used to evaluate the results of the residues greater than method detection limits. The overall impact of preparation was found to be significant ($p < 0.0001$), although rinsing relative to no preparation was not found to be significant ($p = 0.69$). Rinsing followed by peeling resulted in significantly lower OP residues ($p < 0.0001$) than no preparation. The interaction between postharvest preparation and compound application also was highly significant ($p < 0.0001$).

Phosalone concentrations in rinsed apples were not significantly different from those receiving no postharvest preparation ($p = 0.27$), although the apples that were rinsed followed by peeling had significantly lower residues than apples with no postharvest treatment ($p < 0.0001$). The fraction of apples with azinphos methyl residues greater than the method detection limit was significantly reduced in apples that were initially rinsed followed by peeling ($p < 0.0001$), although the rinsing of apples

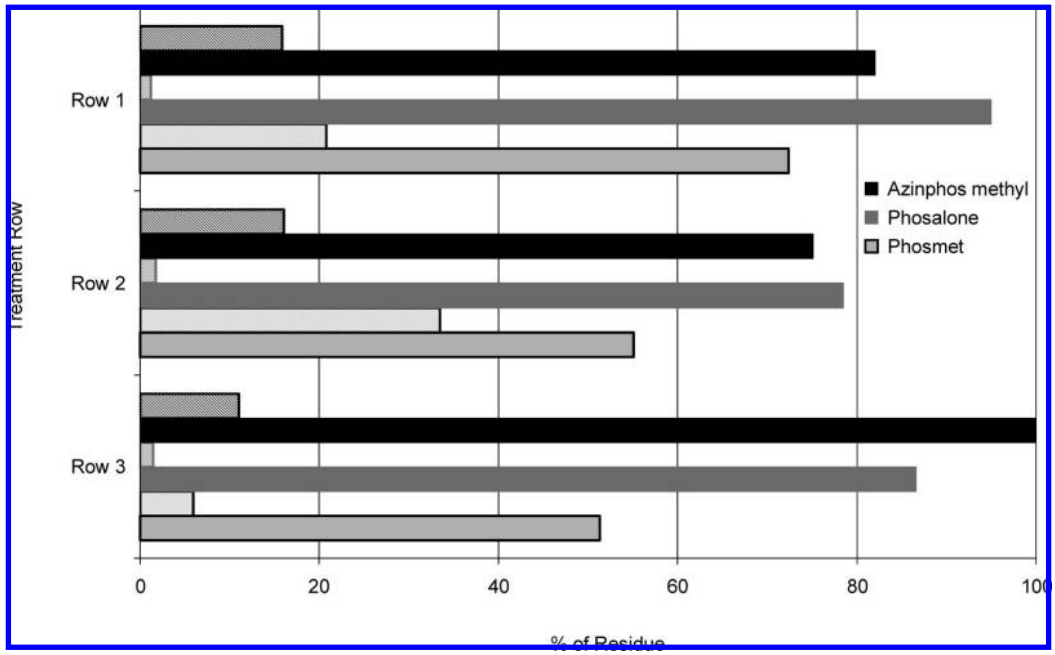

Figure 2. OP insecticide residue (%) in apples relative to apples receiving no postharvest preparation prior to extraction. Row 1 represents a row of apples sprayed with azinphos methyl; row 2 represents the application of phosalone, and row 3 represents phosmet application. Solid bars represent apples that were rinsed, and cross-hatched bars indicate rinsed and peeled apples.

alone did not significantly reduce residues to below method detection levels ($p = 0.69$).

The results in the present study agree well with previous reports that have focused on the determination of pesticide residue reduction resulting from rinsing vegetables and fruit with water. In this study, average OP residue reductions resulting from the rinsing of apples with deionized water alone ranged from 13.5 to 28.7%. A similar pattern was reported by Cabras et al. (*22*) who observed no reduction in residues to a 45% decrease in OP insecticide concentrations resulting from washing olives with water. Radwan et al. (*11*) reported 53−59% removal of pirimiphos methyl residues from peppers and eggplant following soaking in tap water, 5 days following application of this compound. Both studies reported in the literature were carried out under field conditions, although sampling and processing of produce began following very short preharvest intervals (1 and 5 days, respectively) (*11, 22*). During the present study, however, the preharvest intervals were 96, 45, and 21 days for azinphos methyl, phosalone, and phosmet, respectively, which reflected orchard needs for insect control. The difference in preharvest intervals could account for the slightly elevated removal rate observed in literature studies relative to this work.

Krol et al. (*18*) reported that although malathion residues were significantly reduced during washing, reduction of other OP insecticide (chlorpyrifos, diazinon) residues was not observed, consistent with their differing water solubilities (**Table 1**). A reduction of approximately 20% in OP residues was observed upon rinsing of tomatoes with water rather than using dilute acetic acid or salt solution, which resulted in reductions of up to 94% (*14*). Washing with water was, however, found to be effective in the removal of azinphos methyl (63 and 84%) from lemons and oranges (*23*). Although the results obtained in the present study differ from the data reviewed in Holland et al. (*23*), water alone was insufficient to remove dithiocarbamate fungicides from apples and washing of apples with a >50 ppm chlorine solution was required (*19*). Similar to the nonsystemic OP insecticides, fungicides undergo very little penetration of produce cuticles. This suggests that the type of cuticle also impacts the relative ability of water to remove OP pesticides from fruits and vegetables.

Guardia-Rubio and co-workers (*8*) studied the impact of repeated washing and found the initial wash to be the most effective with respect to reducing pesticide levels from olives. In the present study, only one rinse with water was tested prior to extraction and analysis, consistent with commonly accepted practices prior to apple consumption.

The OP insecticides analyzed were found to be most effectively reduced following peeling of apples in the present study. Similarly, peeling resulted in an 80−90% reduction in pesticide residues from tomatoes (*14*). Dichlorvos also was reduced by a large extent (53−58%) by peeling, while washing with water only resulted in a 21−25% reduction in cucumbers (*2*). Boulaid et al. (*24*) similarly reported that peeling resulted in a large reduction of three classes of pesticides (oxime fungicide, pyridazinone acaricide/insecticide, and pyrethroid insecticide) to below detection limits in tomatoes.

Residues of the three OP insecticides tested, azinphos methyl, phosalone, and phosmet, were significantly lower in apples rinsed followed by peeling relative to apples with no preparation. Although mean residue levels in apples that were rinsed alone were lower than observed in apples receiving no postharvest treatment, concentrations were not significantly different. The impact of postharvest preparations on phosmet residues was affected by whether phosmet was directly applied to apples or not. This phenomenon was not observed with azinphos methyl or phosalone residues.

LITERATURE CITED

(1) Roldán-Tapia, L.; Parrón, T.; Sánchez-Santed, F. Neurophysical effects of long-term exposure to organophosphate pesticides. *Neurotoxicol. Teratol.* **2005**, *27*, 259–266.

(2) Cengiz, M. F.; Certel, M.; Göçmen, H. Residue contents of DDVP (dichlorvos) and diazinon applied on cucumbers grown in greenhouses and their reduction by duration of a pre-harvest interval and post-harvest culinary applications. *Food Chem.* **2006**, *98*, 127–135.

(3) MacIntosh, D. L.; Spengler, J.; Ozkaynak, H.; Tsai, L-h.; Ryan, P. B. Dietary exposures to selected metals and pesticides. *Environ. Health Perspect.* **1996**, *104*, 202–209.
(4) CFIA (Canadian Food Inspection Agency). The chemical residue surveillance program for foods. http://www.inspection.gc.ca/english/fssa/microchem/chemchime.shtml (accessed 5 June, 2007).
(5) Rawn, D. F. K.; Cao, X-L.; Doucet, J.; Davies, D. J.; Sun, W.-F.; Dabeka, R. W.; Newsome, W. H. Canadian Total Diet Study in 1998: Pesticide levels in foods from Whitehorse, Yukon, Canada and corresponding dietary intake estimates. *Food Addit. Contam.* **2004**, *21*, 232–250.
(6) Newsome, W. H.; Doucet, J.; Davies, D.; Sun, W. F. Pesticide residues in the Canadian market basket survey−1992 to 1996. *Food Addit. Contam.* **2000**, *17*, 847–854.
(7) WHO (World Health Organization). Joint FAO/WHO consultation on food consumption and exposure assessment to chemicals in food. Geneva, Switzerland, 10–14 February 1997. 1997, http://www.who.int/food safety/publications/chem/exposure_feb1997/en/print.html.
(8) Guardia-Rubio, M.; Ayora-Cañada, M. J.; Ruiz-Medina, A. Effect of washing on pesticide residues in olives. *J. Food Sci.* **2007**, *72*, C139–C143.
(9) Chavarri, M. J.; Herrera, A.; Arinño, A. The decrease in pesticides in fruit and vegetables during commercial processing. *Int. J. Food Sci. Technol.* **2005**, *40*, 205–211.
(10) Pugliese, P.; Moltó, J. C.; Damiani, P.; Marín, R.; Cossignani, L.; Mañes, J. Gas chromatographic evaluation of pesticide residue contents in nectarines after non-toxic washing treatments. *J. Chromatogr. A* **2004**, *1050*, 185–191.
(11) Radwan, M. A.; Shiboob, M. H.; Abu-Alamayem, M. M.; Abdel-Aal, A. Pirimiphos-methyl residues on/in some field grown vegetables and its removal using various washing solutions and kitchen processing. *Int. J. Agric. Biol.* **2004**, *6*, 1026–1029.
(12) Krieger, R. I.; Brutsche-Keiper, P.; Crosby, H. R.; Krieger, A. D. Reduction of pesticide residues of fruit using water only or Plus Fit fruit and vegetable wash. *Bull. Envrion. Contam. Toxicol.* **2003**, *70*, 213–218.
(13) Taylor, K. C.; Bush, P. B. Influence of postharvest handling on the concentration of pesticide residues in peach peel. *HortScience* **2002**, *37*, 554–558.
(14) Abou-Arab, A. A. K. Behavior of pesticides in tomatoes during commercial and home preparation. *Food Chem.* **1999**, *65*, 509–514.
(15) Burchat, C. S.; Ripley, B. D.; Leishman, P. D.; Ritcey, G. M.; Kakuda, Y.; Stephenson, G. R. The distribution of nine pesticides between the juice and pulp of carrots and tomatoes after home processing. *Food Addit. Contam.* **1998**, *15*, 61–71.
(16) Elkins, E. R. Effect of commercial processing on pesticide residues in selected fruits and vegetables. *J. Assoc. Off. Anal. Chem.* **1989**, *72*, 533–535.
(17) Worthing, C. R.; Hance R. J. The pesticide manual. *A World Compendium*, 9th ed.; British Crop Protection Council: Old Woking, Surrey, United Kingdom, 1991; 1141 pp.
(18) Krol, W. J.; Arsenault, T. L.; Pylypiw, H. M., Jr.; Incorvia Mattina, M. J. Reduction of pesticide residues on produce by rinsing. *J. Agric. Food Chem.* **2000**, *48*, 4666–4670.
(19) Hwang, E.-S.; Cash, J. N.; Zabik, M. J. Degradation of mancozeb and ethylenethiourea in apples to postharvest treatments and processing. *J. Food Sci.* **2002**, *67*, 3295–3300.
(20) Sharma, I. D.; Patyal, S. K.; Nath, A.; Joshi, V. K. Effect of processing on mancozeb residues in apple. *J. Food Sci. Technol.* **2001**, *38*, 23–25.
(21) Rawn, D. F. K.; Quade, S. C.; Shields, J. B.; Conca, G.; Sun, W.-F.; Lacroix, G. M. A.; Smith, M.; Fouquet, A.; Bélanger, A. Organophosphate levels in apple composites and individual apples from a treated Canadian orchard. *J. Agric. Food Chem.* **2006**, *54*, 1943–1948.
(22) Cabras, P.; Angioni, A.; Garau, V. L.; Melis, M.; Pirisi, F. M.; Karim, M.; Minelli, E. V. Persistence of insecticide residues in olives and olive oil. *J. Agric. Food Chem.* **1997**, *45*, 2244–2247.
(23) Holland, P. T.; Hamilton, D.; Ohlin, B.; Skidmore, M. W. Effects of storage and processing on pesticide residues in plant products. *Pure Appl. Chem.* **1994**, *66*, 325–356.
(24) Boulaid, M.; Aguilera, A.; Camacho, F.; Soussi, M.; Valverde, A. Effect of household processing and unit-to-unit variability of pyrifenox, pyridaben and trahomethrin residues in tomatoes. *J. Agric. Food Chem.* **2005**, *53*, 4054–4058.

Received for review August 10, 2007. Revised manuscript received November 20, 2007. Accepted November 29, 2007.

JF072408M