Orthophenylphenol and Phenylhydroquinone Residues in Citrus Fruit and Processed Citrus Products after Postharvest Fungicidal Treatments with Sodium Orthophenylphenate in California and Florida

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Sodium orthophenylphenate (SOPP) has been used extensively for >40 years to control postharvest diseases of citrus fruits. Studies of the metabolism of [^{14}C]SOPP have identified orthophenylphenol (OPP) as the major metabolite with phenylhydroquinone (PHQ) as a minor metabolite. The whole-fruit tolerance in the United States for OPP is 10 ppm. This study was conducted to quantify terminal OPP and PHQ residues in whole Navel oranges, grapefruit, and lemons following SOPP applications at maximum application rates and following commercial application and fruit storage practices. OPP and PHQ residues also were determined in products processed from treated Navel oranges. OPP residues in lemons, Navel oranges, and grapefruit treated with SOPP using foamer wash and shipping wax applications remained below the 10 ppm tolerance, and PHQ residues were all ≤0.439 ppm. PHQ residues in whole fruit increased with time in commercial storage. OPP residues in all Navel orange matrices except oil remained relatively stable with time in commercial storage; residues in oil declined substantially while in storage.

Keywords: *Orthophenylphenol; phenylhydroquinone; sodium orthophenylphenate; citrus; postharvest application; concentration factors*

INTRODUCTION

The citrus industry enforces strict sanitation practices during handling and packing of fresh fruit to prevent microbial contaminations that cause decay during storage and distribution (*1*, *2*). Solutions of sodium orthophenylphenate (SOPP) have been used extensively for >40 years to control postharvest diseases of citrus fruits (*3*). The benefits of SOPP when properly applied are twofold: (1) spores of fungi and bacteria on the surface of the fruit or in the cleaning solution are inactivated, and (2) a residue of orthophenylphenol (OPP) is deposited in harvest injuries and prevents infection at these sites during storage or marketing. SOPP is registered by the U.S. Environmental Protection Agency (U.S. EPA) for postharvest application to commercial citrus species as a fungicide to control blue and green molds (*Penicillium* sp.). Applications to harvested fruit are applied in water solutions using various tank, spray, or foam-generating equipment and in water−wax emulsions applied with wax foamer or spray-brush equipment (*4*).

OPP residues in whole citrus have been shown to range from 5.6 to 8.2 ppm in Japan (*5*), from 1.8 to 8.3 ppm in Israel (*6*), and from 2.7 to 3.9 ppm in Belgium (*7*). In the United States, monitoring by the Food and Drug Administration (FDA) has shown that OPP residues in whole citrus are generally <4.5 ppm (*8*). Residues of OPP in juice processed from treated fruit range from nondetectable to 0.007 ppm (*9*, *10*). Citrus oil processed from treated fruit may contain nearly 150 ppm of OPP (*11*).

Studies of the metabolism of [^{14}C]SOPP have shown that OPP is the major metabolite with phenylhydroquinone (PHQ) as a minor metabolite (California Citrus Quality Council, unpublished data). A tolerance in the United States has been established for residues of OPP at 10 ppm in or on citrus fruits. Although most studies have shown OPP residues rarely approach these levels, higher residue levels have been found in shamouti oranges (*6*) and lemons (*12*) in Israel. We found no previously published studies that report PHQ levels in citrus treated with SOPP. In addition, there are few published data from U.S. studies reporting OPP residues in products processed from citrus for both human and livestock consumption, including oil and dried pulp. Therefore, the objectives of this study were to (1) quantify terminal OPP and PHQ residues in whole

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Navel oranges, grapefruit, lemons, orange juice, orange dry pulp, and orange oil following postharvest applications of SOPP made in accordance with current label use directions at maximum application rates and following commercial application and fruit handling practices, (2) evaluate OPP and PHQ dissipation rates under commercial storage conditions, and (3) determine OPP concentration factors in processed citrus products including juice, dried pulp, and oil. This study was conducted to satisfy U.S. EPA SOPP data requirements and followed then-current U.S. EPA residue chemistry guidelines and current Good Laboratory Practice standards.

MATERIALS AND METHODS

Fruit and Treatments. Most SOPP used in the United States is applied to lemons, oranges, and grapefruit. Commercially grown fruit from southern and central California (lemons, Navel oranges, and grapefruit) and central Florida (grapefruit only) were used for postharvest SOPP treatments. Scarred fruit were used for the study because chemical residues have generally been found to be higher with scarred than with higher grade fruit. Lemons (Lisbon variety) and Navel oranges were harvested in the field by study personnel and transported under ambient conditions to the postharvest treatment facility. Both California and Florida Ruby Red grapefruits were obtained from commercial packing houses and transported the same day to the treatment facility. All study treatments were made according to current label use directions and standard industry practices. Handling and storage procedures for the study fruit also were conducted according to standard industry practices. Postharvest applications to lemons, Navel oranges, and grapefruits in California were conducted using experimental packing line application equipment at the Sunkist Research Center in Ontario, CA. Florida grapefruit were treated using experimental packing line application equipment at the Florida Citrus Research and Education Center in Lake Alfred, FL.

Following standard industry practice, lemons used for the study were treated with storage wax containing 250 ppm of 2,4-D acid equivalents (ae) and 2000 ppm of active ingredient (ai) imazalil and placed in storage at 7−18 °C (*13*). The 2,4-D ae and imazalil treatment was made to inhibit abscission of buttons and control decay on lemons held in storage. The stored lemons were treated with SOPP following 6 weeks of commercial storage. Navel oranges and grapefruit were treated with SOPP within 4 days of harvest.

Foamer wash samples for the whole fruit residue study received a standard industry postharvest fungicide treatment consisting of a foamer wash treatment of ∼30 s of exposure containing 1.45% anhydrous SOPP (2.0% SOPP tetrahydrate) followed by a fresh water rinse. The pH of the foamer wash treatment solution was ∼11.7, and all solutions were made using tap water at ambient temperature. Treated fruit must be rinsed immediately with fresh water to avoid damage from exposure to nonionized OPP (*3*, *13*). Approximately 36 kg of lemons, 14 kg of Navel oranges, 14 kg of California grapefruits, and 156−173 kg of Florida grapefruits were placed through the foamer wash for each treatment. A sample of fruit was collected following this treatment for use as SOPP foamer wash samples. After rinsing and partial drying per standard industry practice, the remaining fruit that received the SOPP foamer wash treatment then received a treatment consisting of 1.00% anhydrous SOPP (1.4% SOPP tetrahydrate), 3500 ppm of ai thiabendazole (TBZ) and 2000 ppm of ai imazalil in shipping wax (Freshmark Fresh Wax 3330).

Following the wax treatment, the fruit samples were conveyed through a forced-air dryer to dry the wax. For each treatment described above, two individual solutions were prepared and applied as replicates for the treatment. Two fruit samples, each weighing ∼4.5 kg, were collected from each replicate treatment for each sampling occasion and storage period. Applications to lemons were made on February 8, 1995, and Navel oranges were treated on February 23−24, 1995. California grapefruits were treated on March 15, 1995, and Florida grapefruit on March 7, 1995.

The commercial SOPP foamer wash product label allows exposure times for foamer wash applications from 30 to 60 s. An exposure time of 30 s was selected for the whole-fruit residue study because 30 s is at the high end of exposure times used by packing houses in both California and Florida, and care is taken in the industry not to exceed 30 s because longer exposure times may cause phytotoxicity.

For treating Navel oranges for the processing study, we used an exaggerated exposure time of 120 s because it was anticipated from plant metabolism study data that exaggerated SOPP treatments would be required to detect PHQ in the processed products. The shipping wax treatment was similar to that used for the whole-fruit residue study. For each treatment, two individual solutions were prepared and applied as replicates for the treatment. One sample weighing ∼50 kg was collected for each replicate treatment and storage period. Approximately 45.5 kg from each sample was sent to the processing facility; the remaining 4.5 kg was frozen and shipped to the analytical laboratory for whole-fruit residue analysis.

Samples receiving the postharvest treatments designated for 0 days of storage were frozen after collection. The remaining samples were placed in storage to simulate the average low temperature commercial fruit is normally stored at between SOPP treatment and consumption. Storage rooms containing study samples were maintained at standard temperature and relative humidity for citrus storage. Lemon samples were stored at mean temperatures ranging from 10 to 11 °C and mean relative humidities ranging from 96 to 97%; Navel orange samples were stored at mean temperatures ranging from 5.5 to 10.5 °C and mean relative humidities ranging from 75 to 84%; California grapefruit samples were stored at mean temperatures ranging from 5.0 to 11.7 °C and mean relative humidities ranging from 71 to 83%; and Florida grapefruit samples were stored at temperatures ranging from ∼11.7 to 15.0 °C and relative humidities ranging from ∼74 to 98%.

Predesignated samples were removed from storage 28 and 56 days after the postharvest fungicide treatments, frozen, and submitted for residue analysis. The final sampling interval was set at 56 days because the maximum estimated normal interval between postharvest SOPP treatment of citrus and consumption is 8 weeks.

Processing. Processing of raw Navel oranges into juice, dried pulp, and oil was accomplished using procedures simulating standard industrial processing procedures. Prior to processing, fruit was tub-washed for 5 min. The washed fruit was hand-inspected for undesirable fruit and transferred to a modified vegetable peeler for scarifying. A total of 5−10 kg of fruit per batch was scarified for 3.0−3.67 min to scarify the flavedo for oil recovery. The collected oil−water emulsion was transferred to a vibrating sifter and screened using a ∼180 μm mesh screen to separate the flavedo solids from the oil−water emulsion. The oil−water emulsion was placed in freezer storage and frozen to aid in breaking the emulsion and then thawed. The thawed oil−water emulsion was clarified and then centrifuged. All oil available was removed for the required sample fraction. The scarified fruit was transferred to a juice extractor to extract juice from the fruit. The collected juice was transferred to a pulper finisher and screened to remove vesicular membranes, seeds, segment membranes, and peel fragments from the juice. A representative sample of the fresh juice was removed for the required sample fraction.

The peel and rag from the juice and finisher extraction were mechanically shredded to produce wet pulp. Lime was added to the wet pulp to a pH of 8−10 and mixed for 15−20 min. The limed pulp was pressed using a hydraulic press. The expressed liquid from the press was placed in a vacuum pan and evaporated to ∼50 °Brix to produce molasses. Samples of wet pulp and molasses were not analyzed because the U.S. EPA no longer requires residue data on these matrices for processed food/feed studies. An aliquot of the pressed pulp was

Table 1. Mean Recovery of OPP and PHQ in Citrus and Commercial Processed Products

commodity	concn range (ppm)	no. of replicates	mean recovery (%)	SE[a]
OPP				
whole lemons	0.25−5.0	18	83.5	2.5
whole Navel orange	0.05−5.0	18	82.5	3.1
California grapefruit	0.05−5.0	18	95.3	4.1
Florida grapefruit	0.05−5.0	18	89.8	2.7
Navel orange juice	0.25−5.0	6	82.8	2.9
Navel orange dry pulp	0.05−5.0	6	89.0	2.7
Navel orange oil	2−5	4	88.5	3.5
PHQ				
whole lemons	0.2−1.0	18	77.5	2.8
whole Navel orange	0.2−1.0	18	85.5	4.4
California grapefruit	0.2−1.0	18	79.0	2.5
Florida grapefruit	0.2−1.0	18	78.5	4.4
Navel orange juice	0.2−1.0	4	67.5	1.3
Navel orange oil	1−5	4	48.8	3.2

[a] Standard error.

placed on an air-dryer and dried to 1.3−7.1% moisture to produce dry pulp, and a representative sample of the dry pulp was removed for the required sample fraction.

Residue Analysis. For each ∼4.5-kg fruit sample, a subsample of 1.4−1.8 kg was randomly selected for analysis, and two 10-g aliquots from each of the subsamples were analyzed for OPP and PHQ. This design resulted in a total of eight analyses for each treatment and storage period. Whole fruits were chopped into small pieces using a knife. Samples were then ground using liquid nitrogen in a Robot Coupe blender (Robot Coupe USA, Inc., Jackson, MS). The ground samples were stored frozen at ∼−20 °C. Pulp samples were thoroughly mixed with a spatula before aliquots were taken for weighing, and oil and juice sample containers were thoroughly shaken before aliquots were taken for weighing. OPP was isolated from all citrus matrices except orange oil by a one-step hydrolysis/steam distillation/extraction procedure. Each sample was treated with aqueous HCl to generate a 1 N solution. A micro-Nielson-Kryger apparatus (Kontes, Vineland, NJ) was attached to the flask, and the sample was refluxed for 2 h to permit hydrolysis of OPP conjugates and extraction of OPP into isooctane contained in the extraction section of the apparatus.

The isooctane extract was derivatized with *N*,*N*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and analyzed on an HP5890 series II (Agilent Technologies, Inc., Palo Alto, CA) gas chromatograph (GC) equipped with an HP7673 autoinjector and an HP5972 mass selective detector (MSD), quantitating on the *m*/*z* 227 peak. OPP in oil was determined by direct injection of the oil into the GC-MSD. The quantitation ion was *m*/*z* 170. Recoveries ranged from 82.5% for Navel orange to 95.3% for California grapefruit (Table 1). The limit of quantitation (LOQ) for OPP in all matrices except oil was 0.05 ppm; the LOQ for OPP in oil was 1.0 ppm.

PHQ was isolated from all citrus samples except Navel orange oil by extraction. Each sample was first treated with ascorbic acid and ethylenediaminetetraacetic acid (EDTA) to minimize PHQ oxidation during sample preparation and analysis. The mixture was treated with aqueous HCl to generate a 0.3 N solution, and the headspace of the hydrolysis tube was purged with argon to eliminate oxygen. The mixture was heated at 100 °C for 1 h. The hydrolyzed mixture was then extracted with dichloromethane (3 × 10 mL), and the combined extracts were filtered and concentrated. For lemon samples, final extracts were in dichloromethane. For the other citrus samples, acetonitrile was added prior to final concentration. The concentrated extract was derivatized with BSTFA and analyzed with a GC-MSD, quantitating on the *m*/*z* 330 peak. PHQ in oil was determined by derivatization with BSTFA, followed by direct injection onto GC-MSD. The quantitation ion was *m*/*z* 330. PHQ recoveries ranged from 49% in orange oil to 85.5% in whole Navel orange (Table 1). The LOQ for PHQ in all matrices except oil was 0.2 ppm; the LOQ for PHQ in oil was 1.0 ppm.

Citrus samples were analyzed in sets consisting of one unspiked control sample to check for background interference, two fortified control samples run as process recoveries to monitor the analytical method, a series of samples, and a series of standards. Typically, eight concentration levels of standards were run, including a zero level (solvent). Each set began and ended with a standard, and no more than four samples were run between standards. Samples falling above the response range of the standards were diluted and reinjected along with standards. The ratio of the primary (quantitation) ion to the qualifier ion was monitored to ensure that it was acceptable relative to the ratio seen in standards, ensuring that no misidentification of peaks occurred.

Mean residue values were calculated for each matrix and storage interval. Each mean residue was based on eight values (two treatments × two samples/treatment × two assays/sample). The unit of replication for calculating standard errors was the treatment. OPP concentration/reduction factors were calculated for products processed from Navel orange samples collected following 0, 28, and 56 days of storage. Concentration factors were calculated by dividing the OPP residue concentration in each processed product by the corresponding OPP residue concentration in whole raw oranges treated at the same time and at the same application rate as those oranges treated for processing.

RESULTS

Whole Citrus. Mean OPP residues in whole fruit samples treated with just the 1.45% anhydrous SOPP foamer wash solution ranged from 0.566 ppm in Florida grapefruits to 2.93 ppm in lemons. After both the foamer wash and 1.00% anhydrous SOPP shipping wax applications had been made, day 0 OPP residues in whole fruit ranged from 2.18 ppm in California grapefruits to 6.59 ppm in Navel oranges (Table 2). OPP residues remained relatively stable during the 56-day commercial storage period in all fruits except lemons. Under commercial storage conditions, OPP residues in lemons increased from 4.34 ppm on day 0 to 5.08 ppm following 28 days in storage and to 5.28 ppm following 56 days of storage. Mean OPP residues were approximately twice as high in California grapefruits (1.21 ppm) as in Florida grapefruits (0.566 ppm) following the foamer wash application on day 0. After the subsequent shipping wax application, however, OPP residues in California and Florida grapefruits were relatively similar (1.78−2.41 ppm) throughout the 56-day storage period.

PHQ residues in all lemon, Navel orange, and grapefruit samples were <0.2 ppm on day 0 for samples treated with just the foamer wash as well as for all samples treated with both the foamer wash and shipping wax solutions (Table 3). PHQ residues remained <0.2 ppm in both Navel oranges and Florida grapefruits following 28 days in storage. PHQ residues averaged 0.339 ppm in lemons and 0.439 ppm in California grapefruits after 28 days of storage. After 56 days of storage, PHQ residues were detected in all samples, with mean concentrations ranging from 0.220 ppm in Florida grapefruits to 0.406 ppm in California grapefruits.

Processed Products. For day 0 treated samples, OPP residues in Navel orange juice averaged 0.297 ppm. OPP residues in juice remained relatively stable in commercial storage, averaging 0.366 ppm following 28 days and 0.337 ppm after 56 days in storage (Table 4). OPP residues in dry pulp averaged 38.2 ppm on day 0. OPP residues in dry pulp also remained relatively stable in commercial storage, averaging 41.1 ppm on day 56

Table 2. OPP Residues (Parts Per Million) in Whole Citrus Treated with 1.45% Anhydrous SOPP Foamer Wash for 30 s of Exposure Time Followed by Treatment with 1.00% Anhydrous SOPP in Shipping Wax

		treatment/storage interval							
		foamer wash		shipping wax					
		0 days		0 days		28 days		56 days	
commodity	state	mean	SE[a]	mean	SE	mean	SE	mean	SE
lemon	California	2.93	0.37	4.34	0.23	5.08	0.20	5.28	0.13
Navel orange	California	1.61	0.06	6.59	0.07	6.14	0.26	5.99	0.49
grapefruit	California	1.21	0.30	2.18	0.05	2.21	0.11	2.41	0.04
grapefruit	Florida	0.566	0.172	2.47	0.25	1.78	0.09	2.05	0.38

[a] Standard errors (SE) were calculated using mean residue values from two replicate treatments; each treatment comprised four residue values (two samples × two assays/sample).

Table 3. PHQ Residues (Parts per Million) in Whole Citrus Treated with 1.45% Anhydrous SOPP Foamer Wash for 30 s of Exposure Time Followed by Treatment with 1.00% Anhydrous SOPP in Shipping Wax

		treatment/storage interval							
		foamer wash		shipping wax					
		0 days		0 days		28 days		56 days	
commodity	state	mean	SE[a]	mean	SE	mean	SE	mean	SE
lemon	California	<0.2	0	<0.2	0	0.339	0.001	0.345	0.020
Navel orange	California	<0.2	0	<0.2	0	<0.2	0	0.277	0.025
grapefruit	California	<0.2	0	<0.2	0	0.439	0.018	0.406	0.042
grapefruit	Florida	<0.2	0	<0.2	0	<0.2	0	0.220	0.013

[a] Standard errors (SE) were calculated using mean residue values from two replicate treatments; each treatment comprised four residue values (two samples × two assays/sample).

Table 4. OPP Residues (Parts per Million) in Navel Oranges and Commercial Products Processed from Navel Oranges Treated with 1.45% Anhydrous SOPP Foamer Wash for 120 s of Exposure Time Followed by Treatment with 1.00% Anhydrous SOPP in Shipping Wax

	storage interval					
	0 days		28 days		56 days	
commodity	mean	SE[a]	mean	SE	mean	SE
whole Navel orange	15.3	1.8	10.2	1.6	9.18	0.81
juice	0.297	0.014	0.366	0.066	0.337	0.001
dry pulp	38.2	1.1	38.5	13.7	41.1	3.7
oil	1241	64	892	62	767	110

[a] Standard errors (SE) were calculated using mean residue values from two replicate treatments; each treatment comprised four residue values (two samples × two assays/sample).

Table 5. OPP Concentration Factors[a] in Products Processed from Navel Oranges Treated with 1.45% Anhydrous SOPP Foamer Wash for 120 s of Exposure Time Followed by Treatment with 1.00% Anhydrous SOPP in Shipping Wax

	storage interval					
	0 days		28 days		56 days	
commodity	mean	SE[b]	mean	SE	mean	SE
juice	0.020	0.001	0.036	0.001	0.037	0.003
dry pulp	2.5	0.3	3.7	0.7	4.5	0.8
oil	81.9	5.2	89.1	8.3	85.3	19.4

[a] Concentration factors calculated by dividing OPP residue concentration in processed products by OPP residue concentration in whole fruit. [b] Standard errors (SE) were calculated using mean concentration factor calculated from two replicate treatments; each treatment comprised four residue values (two samples × two assays/sample).

(Table 4). In oil, OPP residues averaged 1241 ppm on day 0 but declined substantially over time in commercial storage, averaging 767 ppm in fruit stored for 56 days (Table 4).

PHQ residues were below the LOQ in all juice (<0.2 ppm) and oil (<1.0 ppm) samples processed from Navel oranges during all storage periods. The liming procedure used to produce molasses before the pulp was dried resulted in the potential for significant degradation of any base-sensitive PHQ present. Therefore, PHQ residues in dry pulp were not determined.

Concentration Factors. Mean OPP residues in whole Navel oranges treated using the exaggerated SOPP foamer wash exposure time of 120 s were 15.3 ppm on day 0, 10.2 ppm on day 28, and 9.18 ppm on day 56 (Table 4). OPP concentration factors in juice following 0, 28, and 56 days of storage were 0.020, 0.036, and 0.037, respectively (Table 5). In dry pulp, OPP concentration factors following 0, 28, and 56 days of commercial storage were 2.5, 3.7, and 4.5, respectively. In oil, the OPP concentration factors were 81.9 on day 0, 89.1 on day 28, and 85.3 on day 56. PHQ concentration factors could not be calculated because all residue values were less than the LOQ (0.2 ppm, juice and pulp; 1.0 ppm, oil).

OPP Residues in Products Treated at Standard Commercial Application Rates. To estimate OPP residue levels expected in juice, dried pulp, and oil in samples treated using the industrial standard of 30 s, rather than the exaggerated 120-s foamer wash exposure time used in this study, OPP concentration factors calculated above were applied to Navel oranges treated using a 30-s foamer wash exposure time. OPP residues in juice processed from oranges treated with standard commercial applications of SOPP were estimated to be 0.132 ppm on day 0 and 0.221 ppm on both days 28 and 56 (Table 6). In dry pulp, OPP residues on days 0, 28, and 56 were estimated to be 16.5, 22.7, and 26.9 ppm, respectively. OPP residues in oil were estimated to be 539 ppm on day 0, 547 ppm on day 28, and 510 ppm on day 56 (Table 6).

DISCUSSION

Treatment of grapefruit, Navel oranges, and lemons with SOPP at maximum labeled use rates and following

Table 6. Estimated OPP Residues (Parts per Million) in Navel Orange Juice, Dry Pulp, and Oil Assuming That Oranges Were Treated with the Industry Standard Foamer Wash Exposure Time of 30 s

	storage interval					
	0 days		28 days		56 days	
commodity	mean	SE[a]	mean	SE	mean	SE
juice	0.132	0.001	0.221	0.009	0.221	0.018
dry pulp	16.5	0.2	22.7	1.0	26.9	2.2
oil	539	6	547	23	510	42

[a] Standard errors (SE) were calculated using mean residue values obtained by multiplying mean concentration factor from Table 5 by mean OPP residue concentration from two replicate treatments; each treatment comprised four residue values (two samples × two assays/sample).

commercial practices resulted in terminal OPP residues in/on whole fruit well below the 10 ppm U.S. tolerance for OPP. OPP residues in all processed Navel orange matrices except oil remained relatively stable with time in commercial storage; residues in oil declined substantially while in storage. OPP did not concentrate in juice, indicating that the vast majority of OPP residues on whole fruit remain on the peel. Numerous other studies with oranges, grapefruit, and lemons have also found that residues of OPP remain almost exclusively in the peel portion (*5*, *6*, *9*, *10*, *14*, *15*). OPP residues in juice were well below the 10 ppm U.S. tolerance for OPP residues in the raw agricultural commodity. Because OPP did concentrate in dry pulp and oil, estimated OPP residues in dry pulp and oil processed from Navel oranges treated with SOPP at industry standard use rates exceeded the whole fruit tolerance immediately following treatment and throughout the 56-day commercial storage period. Although OPP residues did concentrate in dry pulp, this item comprises no more than 20% of feed for beef and dairy cattle, and a metabolism study with lactating goats determined that no identifiable residues of OPP (LOQ = 0.002 ppm) were detected in milk, liver, or kidney of goats provided a total dose of 68.5 or 276.5 mg of OPP over a 5-day period (Covance Laboratories, Madison, WI, unpublished data).

Concentration of OPP in citrus oil was expected due to its low solubility in water and high solubility in organic solvents. However, the potential intake of OPP is insignificant from use of citrus oils as flavoring agents in processed foods. OPP residues in oil were much higher than expected, even when the exaggerated SOPP treatment used in this study was taken into consideration. OPP residues in oil following commercial SOPP applications are typically <100 ppm, although residues of up to 200 ppm are occasionally detected (Dr. Dennis Nelson, Sunkist Research Center, personal communication). On the bais of residue results obtained during this study, we calculated that OPP residues in oil extracted from fruit treated using commercial rather than exaggerated rates would average ~500 ppm (Table 6). Our oil extraction procedure was apparently not as efficient as commercial extraction procedures. The amount of oil recovered during this study averaged 0.10% of the whole-fruit sample weight. This represents only 20−25% of typical oil recovery achieved commercially. Essentially all OPP residues on whole fruit are on the peel. Because OPP is very soluble in oil, OPP on the peel of oranges will partition into the oil as it is extracted from the fruit. In this study, the amount of oil available for OPP to partition into was much less than typical under commercial practices; therefore, OPP residues were excessively concentrated in oil.

PHQ residues were below the LOQ at the time of application in all study fruits. PHQ apparently forms in fruit treated with SOPP under commercial storage conditions, as PHQ residues increased in whole fruit with time in commercial storage. However, PHQ residues remained ≤0.439 ppm following 56 days of commercial storage. On the basis of U.S. EPA review of this study, it was concluded that PHQ needs not to be in the tolerance expression for the parent compound (OPP) and its sodium salt (SOPP) because PHQ accounts for <10% of the combined residue amount.

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LITERATURE CITED

(1) Wardowski, W. F.; Brown, G. E. *Postharvest Decay Control Recommendations for Florida Citrus Fruit*; University of Florida Cooperative Extension Service Circular 359-A; 1993; pp 1−5.

(2) California Citrus Quality Council (CCQC). *California Citrus Industry Microbial Contamination Prevention Practices*; CCQC Bulletin; CCQC: Diamond Bar, CA, 1999; pp 1−3.

(3) Eckert, J. W.; Kolbezen, M. J.; Kramer, B. A. Accumulation of *o*-phenylphenol by citrus fruit and pathogenic fungi in relation to decay control and residues. *Proc. 1st Int. Citrus Symp.* **1969**, *2*, 1097−1103.

(4) Brown, G. E. Citrus diseases-postharvest. In *Proceedings of Citrus Flowering and Fruiting Short Course*; Futch, S. H., Kender, W. J., Eds.; Citrus Research and Education Center: Lake Alfred, FL, 1997; p[145−152.

(5) Isshiki, K.; Tsumura, S.; Watanabe, T. Post-harvest fungicides in edible parts of citrus fruits. *Agric. Biol. Chem.* **1982**, *46*, 993−999.

(6) Rajzman, A.; Heller, H. The fate of sodium 2-phenylphenate and biphenyl applied to citrus fruit in wax coatings. *Pestic. Sci.* **1972**, *3*, 457−463.

(7) Steurbaut, W.; Dejonckheere, W.; Kips, R. H. *Residues of Benomyl, OPP and Thiabendazole in Citrus Fruits, Bananas, and Derived Products*; Laboratorium voor Fytofarmacie Faculteit van de Landbouwwetenschappen Rijksuniversiteit: Gent, Belgium, 1973.

(8) Yess, N. A.; Gunderson, E. L.; Roy, R. R. U.S. Food and Drug Administration monitoring of pesticide residues in infant foods and adult foods eaten by infants/children. *J. AOAC Int.* **1993**, *76*, 492−507.

(9) Maekawa, Y.; Yamaha, K.; Kubota, F.; Morita, K. Removal of *o*-phenylphenol and thiabendazole in citrus fruits. *Food Sanit. Res.* **1981**, *31*, 483−490.

(10) Goto, M.; Soda, T. Microanalysis of diphenyl and orthophenylphenol in fruit juices and citrus. *Res. Rep. Shimane Prefect. Public Health Lab.* **1978**, *20*, 90−91.

(11) Ito, Y.; Toyoda, M.; Suzuki, H.; Iwaida, M. A systematic analysis of diphenyl, o-phenylphenol and thiabendazole in citrus oil. *J. Food Hyg. Soc. Jpn.* **1977**, *18*, 450−454.

(12) Mestres, R. Pesticides in citrus fruits on the French market. *Proc. 1st Int. Citrus Symp.* **1969**, *2*, 1035−1042.

(13) Dawson, A. J.; Eckert, J. W. Problems of decay control in marketing citrus fruits: strategy and solutions, California and Arizona. *Proc. Int. Soc. Citric.* **1977**, *1*, 255−259.

(14) Rajzman, A.; Apfelbaum, A. Survey of *o*-phenylphenol residues found in marketable citrus fruit. Volcani Institute of Agricultural Research, Israel, 1968 Series 1351-E. *J. Sci. Food Agric.* **1968**, *19*, 740−744.

(15) Ito, Y.; Toyoda, M.; Ogawa, S.; Iwaida, M.; Yanagida, F. Occurrence of orthophenylphenol during manufacture of lemon marmalade. *J. Food Prot.* **1979**, *42*, 292−293.

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