Residue Levels of Dichlorvos, Chlorpropham, and Pyrethrins in Postharvest-Treated Potatoes during Storage or Processing into Starch

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The effects of storage or processing on residue levels of dichlorvos, chlorpropham, and six components of natural pyrethrin in postharvest-treated potatoes were investigated. Potatoes were sprayed with a mixed solution of pesticides and stored at ambient temperature or refrigerated for 85 days. The residue levels of pesticides were then determined at intervals of a few days. The pesticides gave single-phase and double-phase semilogarithmic dissipation curves, the former for pesticides of slower dissipation rate and the latter for pesticides of quicker dissipation rate. The dissipation of dichlorvos and chlorpropham was slower during refrigeration than at ambient temperature. The effects of temperature were less on the reduction rate of pyrethrins. At the sixth week of storage, the potatoes were processed into starch, and residue levels of the pesticides were determined at each step of processing. Less than 1% of the initial residues was present in the final starch product.

INTRODUCTION

Postharvest application of pesticides to agricultural products has become a subject of great interest in Japan. Since Japanese producers rarely treat commodities with chemicals after harvesting, pesticide application has not been on a regular basis. The present Japanese Law for Food Hygiene holds tolerances for only 26 pesticides in 53 kinds of agricultural commodities. However, about 52% of foods consumed in Japan (calorie based) is imported from foreign countries, and thus specification of tolerance levels for more pesticides is quite essential. The Ministry of Health and Welfare is considering 53 additional pesticides, including those for postharvest usage. This should be put into effect within this year. Residue data on these pesticides are thus required to facilitate settlement of tolerance levels.

In recent years, about a hundred thousand tons of potatoes are being imported to Japan per year, mainly from the United States. The U.S. Environmental Protection Agency permits several pesticides on potatoes following harvest. However, there is not adequate information on the effects of storage or processing on the residues of pesticides. There are some reports on dichlorvos (Deura, 1972; Ishikura et al., 1984; Kawamura et al., 1980; Wen et al., 1985a,b), chlorpropham (Gard, 1959; Coxon and Filmer, 1985; Hajšlová and Davídek, 1986), and pyrethrin (Uno et al., 1984; Hasegawa et al., 1991), but they do not refer to general rules for the dissipation of pesticides. This paper presents data on residues of dichlorvos, chlorpropham, and pyrethrins in postharvest-treated potatoes during storage or processing into starch. Dichlorvos and pyrethrins are used as insecticides, and chlorpropham is used as a sprout suppressant. Tolerance levels for these three chemicals in commercial potatoes have not been specified by the Japanese government.

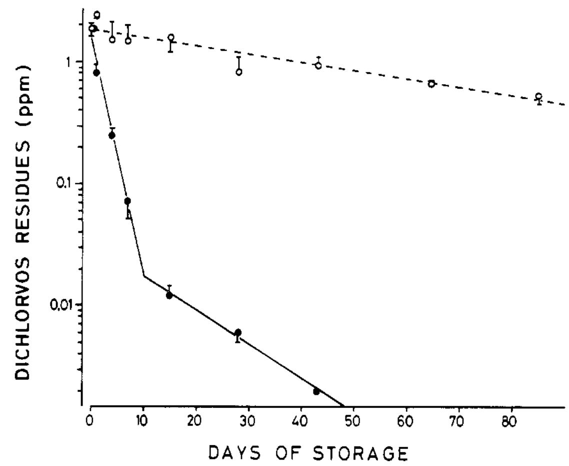

Figure 1. Dichlorvos residues in treated potatoes during storage at ambient temperature (●) or under refrigeration at 5 °C (○). Vertical lines indicate standard deviation for triplicates. The initial dichlorvos level was 1.79 ppm.

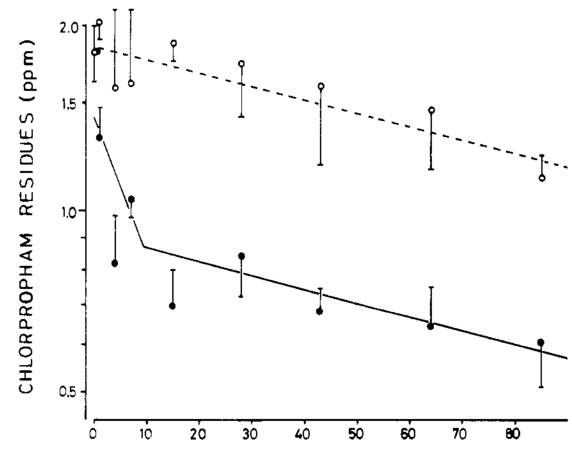

Figure 2. Chlorpropham residues in treated potatoes during storage at ambient temperature (●) or under refrigeration at 5 °C (○). Vertical lines indicate standard deviation for triplicates. The initial chlorpropham level was 1.81 ppm.

EXPERIMENTAL PROCEDURES

Analytical Standards and Reagents. Dichlorvos and chlorpropham for the analytical standards were provided by Wako Pure Chemical Industries, Chuo-ku, Osaka. The standards were colorless and showed no extraneous peaks in GC analysis. Pyrethrum as an analytical standard was provided by Dainihon-jochugiku, Nishi-ku, Osaka. It was a light yellow oil and shown to contain 13.21 w/w % pyrethrin Is (pyrethrin I plus cinerin I plus jasmolin I) and 12.00 w/w % pyrethrin IIs (pyrethrin II plus cinerin II plus jasmolin II) by the official analytical method (Ministry of Health and Welfare, Japan, 1990). The concentrations of individual components were calculated on the basis

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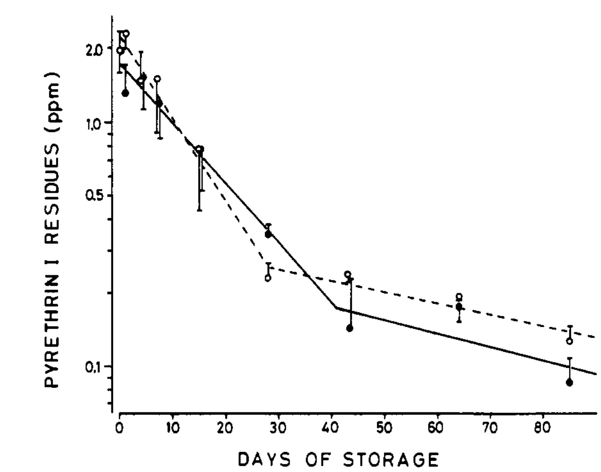


Figure 3. Pyrethrin I residues in treated potatoes during storage at ambient temperature (●) or under refrigeration at 5 °C (○). Vertical lines indicate standard deviation for triplicates. The initial pyrethrin I level was 1.96 ppm.

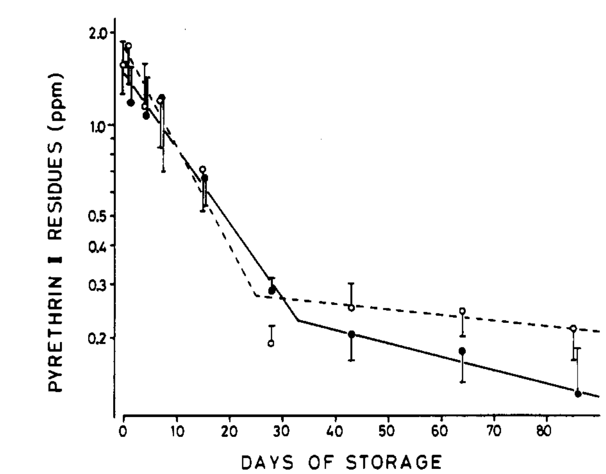


Figure 4. Pyrethrin II residues in treated potatoes during storage at ambient temperature (●) or under refrigeration at 5 °C (○). Vertical lines indicate standard deviation for triplicates. The initial pyrethrin II level was 1.57 ppm.

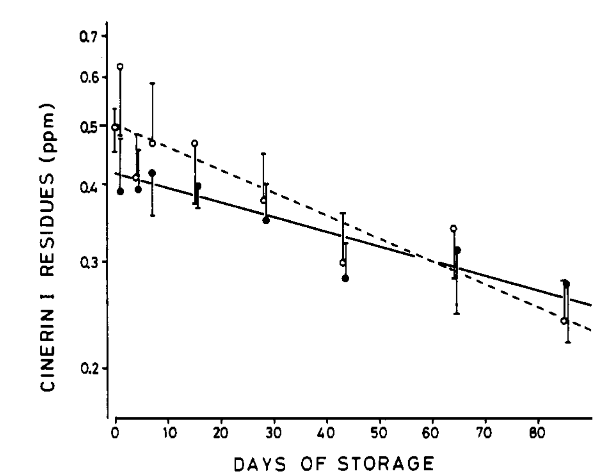


Figure 5. Cinerin I residues in treated potatoes during storage at ambient temperature (●) or under refrigeration at 5 °C (○). Vertical lines indicate standard deviation for triplicates. The initial level of cinerin I was 0.49 ppm.

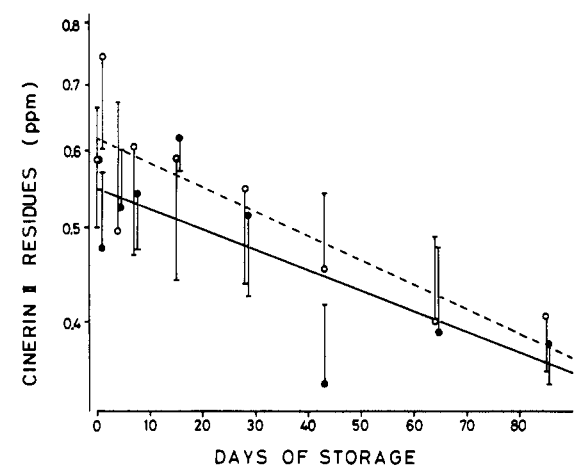


Figure 6. Cinerin II residues in treated potatoes during storage at ambient temperature (●) or under refrigeration at 5 °C (○). Vertical lines indicate standard deviation for triplicates. The initial cinerin II level was 0.58 ppm.

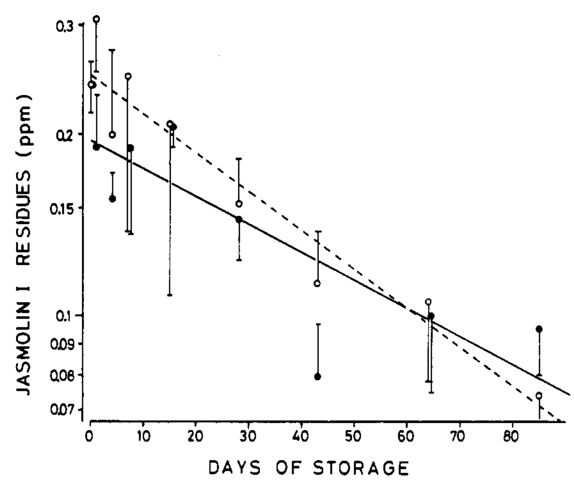


Figure 7. Jasmolin I residues in treated potatoes during storage at ambient temperature (●) or under refrigeration at 5 °C (○). Vertical lines indicate standard deviation for triplicates. The initial level of jasmolin I was 0.24 ppm.

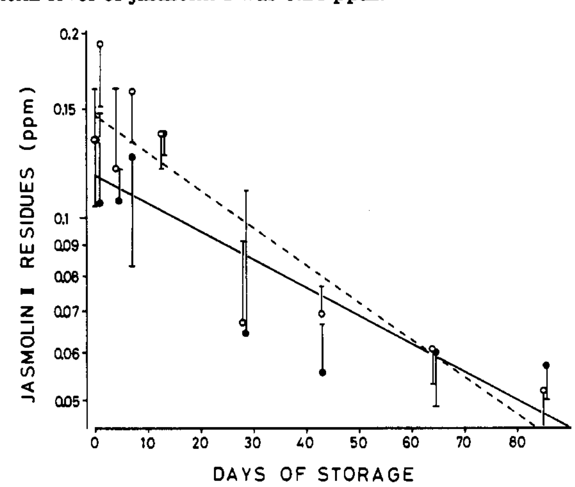


Figure 8. Jasmolin II residues in treated potatoes during storage at ambient temperature (●) or under refrigeration at 5 °C (○). Vertical lines indicate standard deviation for triplicates. The initial jasmolin II level was 0.13 ppm.

of the data of Tomizawa et al. (1989) as follows: pyrethrin I 35%, pyrethrin II 32%, cinerin I 10%, cinerin II 14%, jasmolin I 5%, and jasmolin II 4%. Commercial pesticides such as 50.0% dichlorvos (Takeda Pharmaceutica), 45.8% chlorpropham (Nissan Chemical Industries), and 3.0% pyrethrin (Dainihon-jochugiku), each with emulsifiers, were mixed to prepare solutions for potato spraying. Organic solvents were of pesticide analysis grade and inorganic reagents of special grade. None interfered with the gas chromatographic conditions.

Treatment. The potatoes (*Solanum tuberosum*) were grown at Shirotori, Gifu, without pesticides, and harvested in July 1990. Immediately after harvest, 348 potatoes were selected by weight,

Table I. Values for Semilogarithmic Plots[a] Shown in Figures 1–8

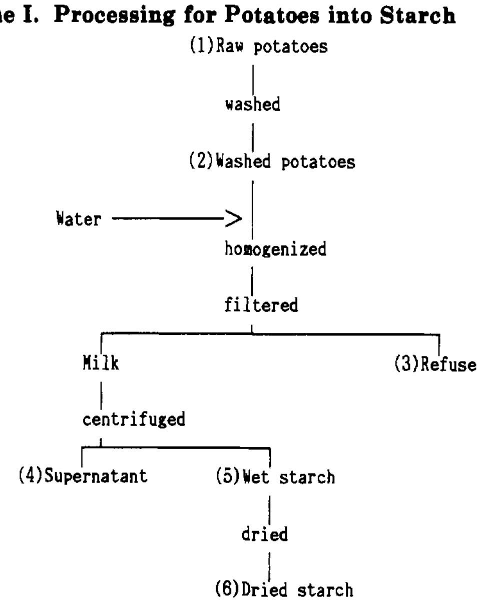
			first phase			second phase		
figure	pesticide	storage temp, °C	k	r	$t_{1/2}$	k	r	$t_{1/2}$
1	dichlorvos	ambient[b]	–0.445	–0.994	1.6	–0.0642	–0.996	11
1	dichlorvos	–5	–0.0155	–0.935	45		(single phase)	
2	chlorpropham	ambient	–0.0518	–0.822	13	–0.00524	–0.917	132
2	chlorpropham	–5	–0.00467	–0.841	148		(single phase)	
3	pyrethrin I	ambient	–0.0570	–0.981	12	–0.0128	–0.710	54
3	pyrethrin I	–5	–0.0790	–0.989	8.8	–0.0107	–0.920	65
4	pyrethrin II	ambient	–0.0565	–0.976	12	–0.0102	–0.994	68
4	pyrethrin II	–5	–0.0757	–0.982	9.2	–0.00385	–0.999	180
5	cinerin I	ambient	–0.00557	–0.881	124		(single phase)	
5	cinerin I	–5	–0.00854	–0.897	81		(single phase)	
6	cinerin II	ambient	–0.00515	–0.775	135		(single phase)	
6	cinerin II	–5	–0.00567	–0.845	122		(single phase)	
7	jasmolin I	ambient	–0.0105	–0.838	66		(single phase)	
7	jasmolin I	–5	–0.0147	–0.962	47		(single phase)	
8	jasmolin II	ambient	–0.0106	–0.837	65		(single phase)	
8	jasmolin II	–5	–0.0141	–0.898	49		(single phase)	

[a] Formula: $y = ae^{kx}$; y, residue level (ppm); a, initial level (ppm); x, storage period (days); k, slope; r, correlation coefficient; $t_{1/2}$, half-life (days). [b] Ambient temperature, 19.7 °C (average).

Table II. Residue Levels of Pesticides in Potatoes at Various Times during Starch Processing

		residue levels (first value, pesticide level in sample, ppm; second value, ratio to amount in unprocessed potatoes, %)							
processing step	potato wt, g	dichlorvos	chlorpropham	pyrethrin I	pyrethrin II	cinerin I	cinerin II	jasmolin I	jasmolin II
(1) unprocessed potatoes	450.5	0.919 100.0	1.59 100.0	0.235 100.0	0.250 100.0	0.297 100.0	0.453 100.0	0.113 100.0	0.069 100.0
(2) washed potatoes	450.5	0.031 3.4	0.192 12.0	0.187 79.6	0.188 75.2	0.112 37.7	0.133 29.4	0.041 36.3	0.023 33.3
(3) refuse	365.0	0.005 0.5	0.123 6.3	0.057 19.6	0.049 15.7	0.080 21.8	0.087 15.6	0.036 25.8	0.018 21.1
(4) supernatant	2232.1	0.003 1.6	0.018 5.6	ND	ND	0.009 15.0	0.010 10.9	0.002 8.8	0.002 14.4
(5) wet starch	44.4	ND	ND	ND	ND	0.021 0.7	0.049 1.1	0.009 0.8	ND
(6) dried starch	31.9	ND	ND	ND	ND	0.016 0.4	0.066 1.0	0.007 0.4	ND
detection limits		0.001	0.001	0.002	0.01	0.001	0.005	0.001	0.002

Scheme I. Processing for Potatoes into Starch



from 20 to 30 g. Similarly to commercial treatment, they were sprayed with emulsified solutions of pesticides, containing dichlorvos 0.2%, chlorpropham 0.1%, and pyrethrin 0.4%. The volume of spray was 50 mL for 8.7 kg of potatoes.

Storage. Half of the treated potatoes were packed into a carton (18 × 26 × 40 cm) and stored at ambient temperature for 85 days in the dark. The average air temperature was 19.7 °C. The other half were placed in the same size box and stored in a refrigerator at 5 °C for the same period. Analysis of individual potatoes taken at random was made prior to and following various periods of storage.

Processing. At the sixth week of storage, some potatoes stored in the refrigerator were processed into starch as described below. They were placed in beakers followed by the addition of 5 times their weight of distilled water. They were shaken at a speed of 120 shakes/min for 1 min, and the water was drained off. The same amount of water was again added followed by similar processing for 2 min and then once more. The washed potatoes were put in a stainless steel basket, and the water drops were drained off. After the potatoes were cut into pieces and 2 times their weight of distilled water was added, the potatoes were mechanically homogenized for 3 min and filtered through a stainless filter of 80 mesh. The refuse was repeatedly rinsed with twice the volume of water. The filtrate was left for 2 h until the starch settled. The sediment was transferred to a tube and centrifuged at 3000 rpm for 10 min to separate the starch from the supernatant fluid. The wet starch was transferred to filter paper, made into a powder, and dried in a desiccator at 145 °C for 3 min. The powder was placed in a closed glass vessel with silica gel and allowed to stand for 24 h to obtain dry starch. Analysis of pesticide residues was made at each step of processing.

Analysis. Analysis of pesticide residues was made in triplicate for each sample as previously described (Hasegawa, 1991), as follows: 20 g of sample was put in a stainless steel cup to which 100 mL of acetone was added, followed by homogenization for 2 min. The mixture was filtered through filter paper, and the residues were rinsed with 50 mL of acetone. The filtrate was evaporated in vacuo at 40 °C and then reduced to ca. 50 mL. The residue was transferred to a separating funnel followed by the addition of 100 mL of 10% NaCl solution. The pesticides were extracted two times with 100 mL of ethyl acetate. The organic layers were gathered, dehydrated with 20 g of anhydrous sodium sulfate, filtered through filter paper, and reduced by a rotary evaporator at 40 °C to ca. 2 mL. The solution was then quantitatively transferred to a graduated tube which was filled to 5 mL with ethyl acetate. Two microliters of the extract was injected into GC for pesticide analysis.

Equipment. For dichlorvos, a gas chromatograph (Shimadzu GC-14A) equipped with a flame photometric detector (P-mode) and capillary column (J&W Scientific DB-210, 30 m × 0.248 mm i.d., 0.25-μm film thickness) was used under the following conditions: injector, splitless mode at 240 °C; column oven, 60–235 °C at a rate of 10 °C/min; carrier gas, 1 kg/cm^2 helium. For chlorpropham and pyrethrins, a double-focusing mass spectrometer with a gas chromatograph and high-speed data acquisition system (JEOL JMS-DX302) was used. The gas chromatograph was equipped with a capillary column (Shimadzu Hi Cap CBP-1, 25 m × 0.2 mm i.d., 0.25-μm film thickness) directly facing the mass spectrometer.

Conditions for GC were as follows: injector, splitless mode at 270 °C; column oven, initially held at 60 °C for 2 min followed by a ramp of 32 °C/min to 250 °C; carrier gas, 1 kg/cm^2 helium.

Mass spectrometer conditions were as follows: 70-eV electron impact ionization; trap current, 300 μA; source temperature, 250 °C; ion monitoring at m/z 127 for chlorpropham, at m/z 123 for cinerin I, jasmolin I, and pyrethrin I, at m/z 107 for cinerin II and jasmolin II, and at m/z 161 for pyrethrin II; dwelling time, 0.1 s.

RESULTS AND DISCUSSION

Storage. Dichlorvos residues in the potatoes are shown in Figure 1. In storage at ambient temperature, dichlorvos residues dissipated rapidly during the first few days and thereafter at a slower rate. However, in storage at 5 °C, they dissipated at a constant rate throughout the storage period, and the rate was somewhat less than that at ambient temperature. Figure 2 shows residue levels of chlorpropham in potatoes. The dissipation rate for chlorpropham was also faster at ambient temperature than in the refrigerator. Dissipation occurred in a double phase during storage at ambient temperature.

The dissipation rates for six components of pyrethrin were the same at ambient temperature and refrigeration. Pyrethrins I and II dissipated the fastest, as shown in Figures 3 and 4. Pyrethrins I and II dissipated with a double-phase slope at ambient temperature and with refrigeration. Dissipation occurred in a single phase for cinerins I and II and jasmolins I and II, as shown in Figures 5–8. Table I mathematically depicts the lines drawn in Figures 1–8.

The double-phase curve means two different modes of dissipation. The initial rapid dissipation is considered to be due to pesticide loss on the surface of potatoes, such as by evaporation. The slower dissipation is considered to arise by a more continuous and slower mechanism, enzymatic or biological. Some studies indicate double-phase dissipation of chlorpyrifos or pirimiphos-methyl on and in agricultural products (Iwata et al., 1983; Sendra et al., 1985). Others show single-phase dissipation (El-Zemaity, 1988; Hadjidemetriou, 1988). In this study, slower rate dissipation usually gave a single phase and that of faster rate a double phase. Dissipation at the slower rate may thus not be a single one, but the initial one prior to still slower dissipation. Evidence for this is shown in Figure 1 for dichlorvos. It follows then that the pesticide dissipation rate based on short-term observation may be too large. Sufficiently long-term observation is necessary for correct evaluation of stability of pesticides in foods.

The effects of temperature on the dissipation rate suggest a mechanism for the dissipation of each pesticide. The considerable effect of dichlorvos indicates the main factor of dissipation to be evaporation, while the minor effect of pyrethrins, decomposition.

Processing into Starch. Pesticide residues in potatoes following processing to make potato chips (Gard, 1959) or French fries (Hasegawa, 1991) have been investigated. However, there is no information on chemical residues in starch manufactured from treated potatoes. A stepwise study has been made on this matter. The outline of this is shown in Scheme I. The process for starch is based on commercial processing except that in commercial processing the wet starch is dried by mechanical air blowing, but in the experiment it was dried in a desiccator. The results are shown in Table II. Water washing removed 96.6% of dichlorvos and 88.0% of chlorpropham, with more than half of pyrethrins I and II remaining. The potatoes were homogenized and separated into refuse and milk. Most of the residual pesticides remained in the refuse. The reason for this may be that the refuse includes the skin. Chemicals have been shown to remain mainly in the outer layers of treated potato tubers (Coxon, 1985; Hasegawa, 1991). Refuse from potato starch manufacturing is used as feed for cattle, and thus care should be taken to eliminate pesticide residues present in the feed. Residue levels in the supernatant were rather low, as also in the case of wet starch. The residues were further decreased by drying. Pesticide levels in starch products were thus quite small, less than 1% or below the limits of detection.

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LITERATURE CITED

Coxon, D. T.; Filmer, A. A. E. The fate and distribution of chlorpropham when applied to stored potatoes as a sprout suppressant. *Pestic. Sci.* **1985**, *16*, 355–363.

Deura, H. Studies on removal of residual pesticides from vegetables (II) removal of residual pesticides from shantung greens and other vegetables by washing. *J. Food Hyg. Soc. Jpn.* **1972**, *13*, 68–73.

El-Zemaity, M. S. Degradation behavior of captan and folpet on greenhouse tomatoes. *Bull. Environ. Contam. Toxicol.* **1988**, *40*, 80–85.

Gard, L. N. Determination of isopropyl N-(3-chlorophenyl)carbamate residues in potatoes treated for sprout inhibition. *J. Agric. Food Chem.* **1959**, *7*, 339–341.

Hadjidemetriou, D. G. Persistence of pirimiphos-methyl in stored potatoes. *Bull. Environ. Contam. Toxicol.* **1988**, *41*, 299–303.

Hajšlová, J.; Davídek, J. Sprout inhibitors IPC and CIPC in treated potatoes. *Nahrung* **1986**, *30*, 75–79.

Hasegawa, Y.; Tonogai, Y.; Nakamura, Y.; Ito, Y. Reduction of post-harvest applied pesticides in potatoes during storage and the process of preparing French fries. *J. Food Hyg. Soc. Jpn.* **1991**, *32*, 128–136.

Ishikura, S.; Onodera, S.; Sumiyashiki, S.; Kasahara, T.; Nakayama, M.; Watanabe, S. Evaporation and thermal decomposition of organophosphorus pesticides during cooking of rice. *J. Food Hyg. Soc. Jpn.* **1984**, *25*, 203–208.

Iwata, Y.; O'Neal, J. R.; Barkley, J. H.; Dinoff, T. M.; Düsch, M. E. Chlorpyrifos applied to California citrus: residue levels on foliage and on and in fruit. *J. Agric. Food Chem.* **1983**, *31*, 603–610.

Kawamura, Y.; Takeda, M.; Uchiyama, M.; Sakai, K.; Ishikawa, H. Organophosphorus pesticides in flour. *J. Food Hyg. Soc. Jpn.* **1980**, *21*, 70–74.

Ministry of Health and Welfare, Japan. Pyrethrum. In *The guidelines for insecticides*; The second section of drug examination, department of medicine, Nihon Yakugyo Shinbun-sha: Osaka, 1990.

Sendra, J. M.; Escamilla, J. C.; Santaballa, E.; Cuñat, P. Pirimiphos-methyl applied to Spanish citrus trees: residue decay and final residue levels at harvest time in precocious fruits. *Pestic. Sci.* **1985**, *16*, 152–158.

Tomizawa, C.; Ueji, M.; Koshioka, M. *Pesticide data book*, 2nd ed.; Soft Science: Tokyo, 1989.

Uno, M.; Onji, Y.; Tanigawa, K. Removal of pyrethroid insecticides from agricultural products by washing and boiling. *J. Food Hyg. Soc. Jpn.* **1984**, *25*, 261–263.

Wen, K.; Kawanishi, Y.; Kiyota, N.; Okamoto, K.; Nishihara, T.; Kondo, M. Behavior of pesticides during cooking treatments. *Eisei Kagaku* **1985a**, *31*, 101–106.

Wen, K.; Shimamoto, T.; Nishihara, T.; Kondo, M. Behavior of pesticides during cooking treatments. II. food samples. *Eisei Kagaku* **1985b**, *31*, 256–259.

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Registry No. Dichlorvos, 62-73-7; chlorpropham, 101-21-3; pyrethrin I, 121-21-1; pyrethrin II, 121-29-9; cinerin I, 25402-06-6; cinerin II, 121-20-0; jasmolin I, 4466-14-2; jasmolin II, 1172-63-0; starch, 9005-25-8.