Canada for provision of the crops and plots used in this study, and to G. Hergert, Engineering Research Service, Agriculture Canada for design and provision of the spray apparatus. This study was conducted with the technical assistance of L. Hierlihy, D. Davies, L. Panopio, and G. Lacroix.

LITERATURE CITED

Engst, R., Schnaak, W., Rattba, H., *Nachrichtenbl. Pflanzenschutzdienst* **22**, 26 (1968).
Newsome, W. H., *J. Agric. Food Chem.* **22**, 886 (1974).
Newsome, W. H., *J. Agric. Food Chem.* **23**, 348 (1975).
Newsome, W. H., *J. Agric. Food Chem.* **24**, 420 (1976).
Newsome, W. H., Shields, J. B., Villeneuve, D. C., *J. Agric. Food Chem.* **23**, 756 (1975).
Pecka, Z., Baulu, P., Newsome, H., *Pestic. Monit. J.* **8**, 232 (1975).
Watts, R. R., Storherr, R. W., Onley, J. H., *Bull. Environ. Contam. Toxicol.* **12**, 224 (1974).

Received for review March 23, 1976. Accepted June 9, 1976.

Changes of Thiofanox Residues in Potatoes Resulting from Storage and Cooking

Wei-Tsung Chin,* Warren C. Duane, J. Ralph Meeks, and Don E. Stallard

Dacamox, the 5–15% granular formulation of thiofanox (P), 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime, was applied to potato crops in furrow at planting as an insecticide in the U.S. and Canada. Less than 0.5 ppm of the anticholinesterase carbamate residues derived from P was found in the tubers harvested from plots treated at the 3 lb (active ingredient) rate in the U.S. and Canada. These residues in potatoes may be reduced significantly by three mechanisms: (1) storage of the tubers at room temperature for 10–20 weeks reduced 48 to 97% of these residues through metabolic degradation; (2) baking and frying potatoes reduced the initial residues 50–90% due to hydrolysis of these residues; and (3) boiling potatoes reduced 30–60% of the initial residues due to water extraction.

Thiofanox (P), 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime, a potent systemic and contact insecticide, effectively controls a wide range of insects which attack potato plants and other crops (Schauer, 1976). Cholinesterase-inhibiting residues were determined in the tubers harvested from P-treated potato plants in different locations of the U.S. and Canada. Metabolic studies indicated that a two-step oxidation of P is the primary mode of degradation in plants (Whitten and Bull, 1974; Holm et al., 1975), animals (Tallant and Sullivan, 1974), and soils (Duane, 1974). The present paper reports the qualitative and quantitative changes of the residues derived from P in potatoes during storage and cooking.

EXPERIMENTAL SECTION

Reagents. Besides the parent material P, the following derivatives of P were prepared as standards: the sulfoxide (P_1), 3,3-dimethyl-1-(methylsulfinyl)-2-butanone *O*-[(methylamino)carbonyl]oxime; the sulfone (P_2), 3,3-dimethyl-1-(methylsulfonyl)-2-butanone *O*-[(methylamino)carbonyl]oxime; the three hydrolytic products of P, P_1, and P_2: (O), 3,3-dimethyl-1-(methylthio)-2-butanone oxime, (O_1), 3,3-dimethyl-1-(methylsulfinyl)-2-butanone oxime, and (O_2), 3,3-dimethyl-1-(methylsulfonyl)-2-butanone oxime, respectively; and the ketone (K_2), 3,3-dimethyl-1-(methylsulfonyl)-2-butanone. Radioactive analogues of the three carbamates were also prepared with radioactive carbon-14 at the methyl carbon attached to the sulfur atom (Wolfe and Magee, 1975). The specific activities were from 19.1 to 21.7 mCi/g. All the standards were greater than 99% pure.

Methods. For residue analysis, potato plants were treated with different rates of Dacamox (5–15% granule P) in furrow at planting in different locations. The P and P_1 residues in the potato samples were first oxidized to P_2 and the total anticholinesterase carbamate residues derived from thiofanox (P_t, $P_t = P + P_1 + P_2$) were determined in the form of total P_2 (Chin et al., 1975). For studying the relative quantities of P, P_1, P_2, and O_2 in potatoes, some samples with high P_t levels were selected from the 1972 and 1973 treatments for the determination of these residues individually.

The distribution of P_t residues in tubers was studied by determining the P_t residues in different parts (skin, outer part, and inner part) and sizes (small, medium, and large) of the tubers. From a 200-g fresh sample, 150 g of potato juice and 35 g of dry matter were obtained and the P_t residues in the juice were determined.

For studying the changes of P_t residues during storage, tubers from two plots of a treatment were analyzed immediately after harvest. The samples were stored in the dark at room temperature in paper boxes and analyzed at the 10th week for P_1 and P_2. Starting from the 11th week, sprouts began to emerge and one-half of the tubers were set out on a lab bench and exposed to standard fluorescent light for an average of 8 h per day. The remaining tubers were retained in the paper boxes. At the 20th week, both the tubers and sprouts were analyzed.

To study the thermostability of P in water and oil solutions, two test tubes (15 mm i.d. × 150 mm) containing 2 ml of water were set in water baths maintained at 45 and 100 °C. Approximately 25000 dpm of [^{14}C]P in 5 μl of 10^{-3} N HCl was mixed with the water in the tubes. After the mixture was allowed to stand for 60 min, the radioactivity was extracted with 2 × 20 ml of $CHCl_3$ for subsequent analysis by TLC (Holm et al., 1975). In a third test tube, the same amount of [^{14}C]P was mixed with 2 ml of vegetable oil maintained at 200 °C in an oil bath. After standing for 10 min, the radioactivity was extracted with 3 × 20 ml of 0.2 N HCl. Radioactive components in the aqueous extract were then extracted (3 × 20 ml of $CHCl_3$) for TLC analysis. The thermal influence on P under these

Diamond Shamrock Corporation, T. R. Evans Research Center, Painesville, Ohio 44077.

Table I. Determination of P_t in Potatoes Harvested from Treatments of Dacamox (3 lb of AI/Acre) (ppm)

Locations	1972	1973	1974
Hastings, Fla.		0.493	
Grand Forks, N.C.	0.024		
Painter, Va.	0.147	0.404	
Wooster, Ohio	0.074	<0.001[a]	0.139
Concord, Ohio	0.012		
East Lansing, Mich.	0.103	0.179	0.071
Entrican, Mich.	0.150		
Montealm, Mich.		0.028	
Parma, Idaho		0.012	
Aberdeen, Idaho		<0.001[a]	
Kinberly, Idaho			0.017
Arlington, Wis.	0.017		
Rosemount, Minn.		0.017	0.017
Presque Isle, Me.	0.270		
Ontario, Canada			0.187

[a] The sensitivity of the published procedures is 0.001 ppm. Those that cannot be detected by these procedures are considered <0.001 ppm.

conditions may serve as a model for studying the changes of P residues in potatoes during baking, frying, and boiling.

To prepare baked potatoes, whole fresh potatoes were tightly sealed with aluminum foil and placed in a home oven at 260 °C for 60 min. To prepare fried potatoes, the tubers were cut into average size for french fries and immersed in vegetable oil at 200 °C for 10 min. For the boiling test, potatoes were chopped in two forms: average size for french fries and 30–40 g cubes. A 200-g sample was boiled in 1 l. of boiling water for 10 min. Residues in the baked and boiled potatoes were analyzed using the published procedures for analyzing fresh potatoes. The fried potatoes were analyzed using the published procedures for cottonseeds, except 2 × 500 ml of acetone was used instead of dichloromethane (Chin et al., 1975).

RESULTS AND DISCUSSION

Routine Analysis of P_t. Starting from 1972, P_t residues in the tubers harvested from Dacamox-treated potato plants were analyzed. Data presented in Table I indicate that P_t levels in potatoes varied significantly in different locations, even at the same rate of treatment. Generally speaking, at 3 lb of active ingredient (AI) of thiofanox per acre, less than 0.5 ppm of P_t was determined in the U.S. and Canada.

Determination of P, P_1, P_2, and O_2. The residues of P, P_1, P_2, and O_2 in tubers were determined individually, as shown in Table II. These data indicate that in no case was P detected, and the residues of P_1 and P_2 were at approximately equal levels. The sums of P_1 and P_2 were close to the P_t residues determined in comprehensive analysis. The quantities of O_2 detected were in a level averaging one-tenth of P_t. These data indicate that the similar two-step oxidation of P to P_2 through P_1 and the subsequent hydrolysis of P_2 to O_2 which took place in pH 10 solutions (Chin et al., 1976) happened in potato tubers.

Distribution of P_t. Data shown in Table III indicate that the P_t quantities determined in the comprehensive samples and in skin, outer, and inner parts are nearly identical, indicating an even distribution of the P_t residues in potato tubers. This even distribution of P_t residues was supported by the fact that nearly all the P_t residues in potato tubers were found in the aqueous phase of the tubers. However, tubers with smaller sizes showed slightly higher P_t contents indicating effects of growth dilution.

Changes of P_t during Storage. Analyses of P_t residues before and after storage are presented in Table IV. The P_t residues decreased up to 48 and 97% after the 10 and 20 weeks of storage, respectively. These data indicate continued metabolic degradation of P_t taking place during these periods by forming conjugates with glucose and hydrolysis of P_2 followed by deoximation of O_2. Relatively greater metabolic activities were shown by the tubers exposed to light as these had more advanced sprouts and lesser P_t residues than those retained in the dark. The detection of small quantities of P_1 and P_2 in the sprouts themselves indicated that these residues were translocated from the tubers. Since the quantities of these cholinesterase-inhibiting P_1 and P_2 residues in both the tubers and sprouts became insignificant after storage for 20 weeks, no residue carry-over should be expected in succeeding crops planted from potatoes treated with this pesticide.

Table II. Determination of Metabolites of Thiofanox in Potatoes (ppm)

Samples (1972-1973)	Dacamox-10G applied, lb of AI/acre	P_t[a]	P	P_1	P_2	O_2
Presque Isle, Me.	3.0	0.270	<0.001	0.181	0.115	0.019
Entrican, Mich.	3.0	0.150	<0.001	0.085	0.034	0.029
Painter, Va.	3.0	0.147	<0.001	0.132	0.064	0.045
Painter, Va.	4.0	0.534	<0.001	0.272	0.320	
East Lansing, Mich.	3.0	0.179	<0.001	0.123	0.031	0.011
Hastings, Fla.	2.0	0.280	<0.001	0.154	0.196	0.027
Hastings, Fla.	3.0	0.493	<0.001	0.279	0.315	0.022
Painter, Va.	2.0	0.229	<0.001	0.113	0.152	0.040
Painter, Va.	3.0	0.404	<0.001	0.187	0.211	0.040

[a] P_t residues were determined for routine, comprehensive analysis. All other residues were determined individually.

Table III. Distribution of P_t in Potato Tubers (ppm)

Samples (1975)	Dacamox-10G applied, lb of AI/acre	P_t in representative samples	P_t in different parts of potatoes			P_t in potato juice[a] (150 g)	P_t in different sizes of tubers		
			Skin (20%)	Outer part (40%)	Inner part (40%)		Small (59-63 g)	Medium (154-165 g)	Large (373-431 g)
Ridgetown, Ont., Canada	2.00	0.082	0.093	0.090	0.093	0.109	0.124	0.103	0.083
Bloomfield, N.B. Canada	2.30	0.089	0.089	0.090	0.095	0.110	0.122	0.098	0.090

[a] For a 200-g fresh potato sample, 150 g of juice was obtained after macerating and centrifuging and the dry material weighed 35 g.

Table IV. Changes in P_t in Potatoes during Storage

Sample 1974 (Concord, Ohio)	Dacamox-10G applied, lb of AI/acre	P_t in fresh potatoes		P_t in tubers after 10 weeks storage in the dark		P_t in tubers after 20 weeks storage in the dark		P_t in tubers after 20 weeks storage lighted between 11 and 20 weeks		P_t in sprouts, ppm	
		ppm	%	ppm	Loss %	ppm	Loss %	ppm	Loss %	Produced in the dark	Produced under light
Plot 1	3.00	0.182	100.0	0.094	48.4	0.025	86.3	0.011	94.0	<0.001	<0.001
Plot 2	3.00	0.176	100.0	0.069	60.8	0.058	67.0	0.005	97.0	0.010	0.017

Table V. Temperature Influence on Thiofanox in Solutions

		% [^{14}C]P incubated at		
	R_f	45 °C	100 °C	200 °C
P	0.48	0.0	0.0	0.0
P_1	0.06	0.3	0.3	0.3
P_2	0.25	90.0	61.9	4.1
O	0.57	1.7	0.0	0.0
O_1	0.15	0.0	0.0	0.4
O_2	0.36	1.5	1.3	0.4
K_2	0.42	3.0	0.4	3.9
Recovery,[a] %		96.5	63.9	9.1
^{14}C loss		3.5	36.1	90.9

[a] For each test, theoretically 25 000 dpm of [^{14}C]P was used and was considered as 100% during spot countings.

Thermostability of P. Data on thermal degradation of P are given in Table V, from which the following changes are observed.

(1) 45 °C. All the applied [^{14}C]P underwent degradation mainly to P_2 with some minor products such as O, P_1, O_1, O_2, and K_2. Since only negligible amounts of P_1 were detected, both P and P_1 must be very sensitive to heat in aqueous solutions and the oxidation of P to P_2 through P_1 is a two-step spontaneous reaction. In addition, the 96.5% total recovery of the applied radioactivity, of which 90.0% was P_2, indicates that P, P_1, and P_2 are not volatile under these conditions.

(2) 100 °C. The pattern of degradation of [^{14}C]P at 100 °C was the same as at 45 °C. The recovery of total radioactivity, however, was reduced to 63.9%. The 36.1% loss of the residues may be due to volatilization of the degradation products of P_2, mainly O_2 and K_2.

(3) 200 °C. After 10 min incubation of [^{14}C]P at 200 °C, nearly 91% of the applied radioactivity was lost. The major residues in the remaining fraction were P_2 and K_2. Judging from the relative quantities of P_2 and percentage of loss of the applied radioactivity at these three temperatures shown in Table V, it is concluded that the hydrolysis of P_2 and the subsequent loss of O_2 and K_2 are increased with increased temperature.

Effects of Baking on P_t. Table VI indicates that in the noncooked, fresh potatoes, P_t was the major residue and O_2 was present in negligible amounts. These results are consistent with the data obtained in other locations, as shown in Table II. Using the P_t levels in fresh potatoes as standards, 46.7 to 68.4% of the P_t residues were hydrolyzed to O_2 during the 1-h baking at 260 °C. Since the sums of P_t and O_2 in the baked potatoes were very close to the P_t residues in the fresh potatoes, no significant residue losses took place during baking. However, these results are different from the data of the [^{14}C]P test at 100 °C given in Table V, which show that P_t was the major residue and O_2 was in negligible amounts. The higher quantities of O_2 accumulated in the baked potatoes may be due to two reasons: (1) additional hydrolysis of P_t to O_2 at a higher temperature, 260 °C; and (2) the O_2 residues produced were protected from volatilization by both the tubers themselves and aluminum foil.

Effects of Frying on P_t. The losses of P_t residues after frying (51.1 to 89.5%) were generally greater than after baking as shown in Table VI. This confirmed the [^{14}C]P test at 200 °C indicating a faster rate of hydrolysis of P_2 in the oil than in water. On the other hand, the O_2 residues in the fried potatoes were much lower than those in the baked potatoes. The low quantities of O_2 in the fried

Table VI. Effects of Baking and Frying on Residues of Thiofanox in Potatoes

Residues in fresh potatoes			Residues in baked potatoes			Residues in fried potatoes		
P_t		O_2,	P_t		O_2,	P_t		O_2,
ppm	%	ppm	ppm	Loss %	ppm	ppm	Loss %	ppm
0.075	100.0	0.003	0.032	57.3	0.035	0.025	66.7	0.008
0.091	100.0	0.004	0.029	68.1	0.060	0.036	60.4	0.013
0.057	100.0	0.003	0.018	68.4	0.041	0.006	89.5	0.004
0.058	100.0	0.003	0.022	62.1	0.023	0.007	87.9	0.004
0.090	100.0	0.004	0.048	46.7	0.045	0.044	51.1	0.022

Table VII. Effects of Boiling on Residues of Thiofanox in Potatoes

P_t in fresh tubers, ppm (%)	Potatoes chopped as fries				Potatoes chopped as cubes			
	P_t in boiled potatoes		P_t in boiled water, ppm (%)	Total P_t recovered, ppm (%)	P_t in boiled potatoes		P_t in boiled water, ppm (%)	Total P_t recovered, ppm (%)
	ppm (%)	Loss, %			ppm (%)	Loss, %		
0.044	0.017		0.024	0.041	0.032		0.018	0.050
(100.0)	(38.6)	61.4	(54.5)	(93.2)	(72.7)	27.3	(40.9)	(113.6)
0.047	0.019		0.028	0.047	0.028		0.001	0.040
(100.0)	(40.4)	59.6	(59.6)	(100.0)	(59.6)	40.4	(21.3)	(85.1)
0.044	0.015		0.024	0.039	0.033		0.013	0.047
(100.0)	(34.1)	65.9	(54.5)	(88.6)	(75.0)	25.0	(29.5)	(106.8)
Av 100.0%	(37.7)	62.3	(56.2)	93.9	(69.1)	30.9	(30.6)	101.8

potatoes may be attributed to the difference in sample thickness and lack of further protection by aluminum foil during frying, resulting in more volatilization of O_2 in this case.

Effects of Boiling on P_t. Determinations of P_t residues in both the boiled potatoes and boiled water are presented in Table VII. Taking the P_t quantities determined in fresh potatoes as 100.0%, the P_t in the boiled potatoes chopped in the form of fries reduced to an average of 37.7%, and in the boiled potato cubes, 69.1%. On the other hand, the P_t residues reduced in the boiled potatoes were found nearly quantitatively in the boiled water, indicating that water extraction is the major way for reducing the P_t residues in boiled potatoes. These data also show that in a given boiling period, the P_t residues extracted from potatoes chopped in smaller pieces, as in the form of fries, are more than those in larger pieces, as in the form of cubes. This is due to the fact that smaller pieces have a larger surface area to contact with water. The hydrolysis of P_t during the 10-min boiling was insignificant because the sum of P_t determined in the boiled potatoes and water was very close to the P_t levels in the original fresh potatoes.

Cooking Effects on P_t. Based on the results obtained, it is concluded that cooking potatoes may reduce or detoxify the anticholinesterase carbamate residues derived from thiofanox in two ways: (1) Baking and frying potatoes at or above 200 °C may reduce the anticholinesterase residues of thiofanox 50 to 90% through the chemical hydrolysis of P_2 to O_2 which is 386 times less toxic than P_2 (Chin et al., 1975). (2) Boiling potatoes at 100 °C may reduce the anticholinesterase residues of thiofanox 30 to 60% through physical extraction of P_2 from the boiled potatoes by the boiling water.

LITERATURE CITED

Chin, W. T., Duane, W. C., Ballee, D. L., Stallard, D. E., *J. Agric. Food Chem.*, **24**, 1071 (1976).
Chin, W. T., Duane, W. C., Szalkowski, M. B., Stallard, D. E., *J. Agric. Food Chem.*, **23**, 963 (1975).
Duane, W. C., Technical Bulletin, Diamond Shamrock Corporation, Cleveland, Ohio, 1974.
Holm, R. E., Chin, W. T., Wagner, D. H., Stallard, D. E., *J. Agric. Food Chem.* **23**, 1956 (1975).
Schauer, R. L., Technical Bulletin, "DACAMOX Systemic Insecticide—Acaricide", Diamond Shamrock Corporation, Cleveland, Ohio, 1976.
Tallant, M. J., Sullivan, L. J., 168th National Meeting of the American Chemical Society, Division of Pesticide Chemistry, Atlantic City, N.J., Sept 1974, PEST-56.
Whitten, C. J., Bull, D. L., *J. Agric. Food Chem.* **22**, 234 (1974).
Wolfe, A. L., Magee, T. A., Research Report No. 1611, Diamond Shamrock Corporation, Cleveland, Ohio, 1975.

Received for review March 12, 1976. Accepted June 9, 1976.

Fate of Chlorothalonil in Apple Foliage and Fruit

Mason Gilbert

Chlorothalonil, a fungicide that enhances the growth regulating activity of ethephon, was applied to apple foliage and fruit under field and laboratory conditions. No evidence of chemical breakdown products of chlorothalonil was obtained. In addition, chlorothalonil apparently did not alter ethephon metabolism when used in combination with the growth regulating chemical. It is theorized that the increased fruit maturation effects of ethephon in the presence of chlorothalonil may be related to increased foliar uptake of ethephon.

Chlorothalonil (tetrachloroisothalonitrile) is produced by the Diamond Shamrock Corporation under the trade name Bravo and is an effective fungicide against a broad spectrum of plant pathogens. Studies have recently demonstrated additional biological activities of this chemical in addition to its well-known fungicidal action. Thus, chlorothalonil can dramatically enhance the plant growth regulating action of ethephon (2-chloroethylphosphonic acid) resulting in more rapid apple fruit maturation expressed by such growth parameters as increased color and soluble solids and decreased pull force and fruit firmness in apples and cherries (Edgerton and Hatch, 1972; Holm and Edgerton, 1976). The present study is concerned with the possible translocation and degradation of chlorothalonil when used alone and in combination with ethephon on the fruit and foliage of apple, *Malus domestica*.

EXPERIMENTAL SECTION

Translocation Studies. The possible translocation of ring-labeled [^{14}C]chlorothalonil was studied using 4-month old McIntosh seedlings raised under greenhouse conditions. The top and bottom surfaces of selected leaves were liberally painted with a radioactive mixture (0.94 μCi/ml) containing 500 ppm of [^{14}C]chlorothalonil (formulation code DS-28052B, Diamond Shamrock Corporation) and 250 ppm of ethephon (Ethrel, Amchem Products, Inc.). Seedlings were harvested after 3 days and covered with Kodak Royal X-Omat medical x-ray film for 2 weeks at 4 °C in a dark room.

Fruit and Leaf Treatment. Leaves and fruit of mature McIntosh trees growing in the Cornell University orchard were analyzed for radioactive residues of chlorothalonil by a liquid scintillation counter (lsc) and by gas–liquid chromatography (GLC). Treatment consisted of applying either a 500-ppm radioactive chlorothalonil formulation (12 μCi/ml) or an aqueous mixture of 500 ppm of [^{14}C]chlorothalonil (195 μCi/ml) and 250 ppm of ethephon. The leaves and apples were painted to the point of run-off with the aid of a small brush.

In additional experiments, fruit bearing branches on orchard McIntosh trees were thoroughly covered with 250 ppm of [^{14}C]ethephon by applying the solution with a brush. Additional branches were painted to run-off with an aqueous formulation mixture of 250 ppm of radioactive ethephon (255 μCi/ml) and 500 ppm of chlorothalonil.

Pesticide Residue Laboratory, Department of Food Science, Cornell University, Ithaca, New York 14853.