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Date: 5/25/04

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Reregistration Branch 3  
Health Effects Division

Date: 5/26/04

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This DER was originally prepared under contract by Dynamac Corporation (20440 Century Boulevard, Suite 100; Germantown, MD 20874; submitted 04/05/2004). The DER has been reviewed by the HED and revised to reflect current OPP policies.

#### **STUDY REPORT:**

46151703 de Weerd, J. (2003) Magnitude of Residue of Chlorpropham in Potato Peel and Pulp after Post-Harvest Aerosol (145%) and Emulsifiable Concentrate Application. Study Number: DCLGLP03-003. Unpublished study submitted by PIN/NIP, Inc. 69 p.

#### **EXECUTIVE SUMMARY:**

Pin/Nip, Inc. has submitted data depicting the magnitude of chlorpropham residues in/on potato after postharvest fumigation in a storage facility and spray treatment at a packing facility. At a commercial storage facility containing approximately 3,000,000 lb of potatoes, chlorpropham was applied through the ventilation system at a rate of 0.0242 lb ai/1,000 lb of potatoes. Treatment was made with a 9.709 lb/gal RTU formulation applied as an aerosol using standard aerosol generating equipment. The ventilation system moved air through the storage facility, pushing air beneath the potato pile, which then flowed upward. Samples of whole potatoes were collected from the top, middle, and bottom portions of the storage facility at intervals of 3 days prior to treatment and 1, 13, 29, 62, and 90 days posttreatment.

In addition, after 98 days in storage, approximately 52,400 lb of treated potatoes were taken to a fresh packing plant, where the potatoes were washed and treated with an EC formulation of chlorpropham at 0.01 lb ai/1,000 lb of potatoes prior to packing. Samples of potatoes were collected at the beginning, in the middle, and near the end of the packing run.

Samples of potato peel and pulp were separately analyzed for residues of chlorpropham using an HPLC/UV method, and residues in whole potatoes were calculated by summing the actual residues quantitated in potato peel and pulp and dividing by the whole potato weight. The registrant reported the LOQ as 0.05 µg/mL of final extract volume; based on the varying weights of samples in the study, this corresponds to an LOQ of 0.01-0.06 ppm for pulp and 0.1-0.4 ppm



for peel. Adequate method recoveries were observed from potato samples fortified at 2 and 20 ppm.

Although samples were apparently not stored frozen prior to analysis, all samples were extracted within one week of collection. Certain extracts were stored for extended periods (up to 24 days) prior to analysis; however, the extracts of concurrent fortification samples were subjected to the same extended storage conditions. Adequate recoveries were observed in these samples, indicating stability during storage; therefore, HED will not require supporting storage stability data for this study.

Residues of chlorpropham in/on whole potatoes collected from the top, middle, and bottom portions of the storage facility following fumigation treatment at 0.0242 lb ai/1,000 lb of potatoes ranged 1.74-6.41 ppm, 2.73-8.44 ppm, and 2.02-11.20 ppm, respectively. Chlorpropham residues were primarily located in/on the peel, with maximum residues of 98.19 ppm at the 62-day sampling interval; maximum residues in the pulp (0.51 ppm) were observed at the 29-day sampling interval.

Residues of chlorpropham ranged 2.64-7.27 ppm in/on whole potatoes collected from the beginning, middle, and near the end of the packing run immediately following a spray application of a 2 lb/gal EC formulation at 0.01 lb ai/1,000 lb of potatoes made 98 days following fumigation treatment of potatoes (total application rate of 0.0342 lb ai/1,000 lb of potatoes). The majority of the residue were observed in/on the peel; maximum peel residues were 52.00 ppm, and maximum pulp residues were 1.31 ppm.

In general, residues of chlorpropham increased rapidly after fumigation treatment and appeared to level off within 13 days of treatment, with an average residue of 4-7 ppm in the whole tuber for the remainder of the storage period. Residues were typically highest in samples from the bottom of the storage pile and lowest in samples from the top of the storage pile; residues fluctuated the most in samples from the middle of the storage pile. Residue levels remained fairly constant in fumigated potatoes following the washing and EC spray application at the packing plant.

#### **STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:**

Under the conditions and parameters used in the study, the potato postharvest treatment data are classified as scientifically acceptable.

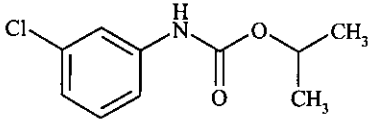
#### **COMPLIANCE:**

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were noted that would impact the study results or their interpretation.



## A. BACKGROUND INFORMATION

Chlorpropham is a plant growth regulator used to inhibit sprout formation on stored potatoes. The Chlorpropham RED was issued 10/96, and the Report of FQPA Tolerance Reassessment Progress and Interim Risk Management Decision (TRED) for chlorpropham was issued 9/02. Chlorpropham is formulated as an emulsifiable concentrate (EC) or ready-to-use solution (RTU).

Compound	
Common name	chlorpropham
Company experimental name	N/A
IUPAC name	isopropyl 3-chlorocarbamate
CAS name	1-methylethyl (3-chlorophenyl)carbamate
CAS registry number	101-21-3
End-use product	9.709 lb/gal RTU (Pin Nip 98.6% Chlorpropham, Aerosol Grade - Potato Sprout Inhibitor; EPA Reg. No. 65726-3); 2 lb/gal EC (Pin Nip 2 EC, Emulsifiable Concentrate - Potato Sprout Inhibitor; EPA Reg. No. 72790-1)

Parameter	Value	Reference
Melting point/range	38-40 °C	Chlorpropham RED, 10/96
pH	5.62-5.66	Chlorpropham RED, 10/96
Density	1.17 g/cm <sup>3</sup>	Chlorpropham RED, 10/96
Water solubility	89 ppm (25 °C)	Chlorpropham RED, 10/96
Solvent solubility	soluble in ethyl and isopropyl alcohols, ketones, and aromatic solvents	Chlorpropham RED, 10/96
Vapor pressure	2.46 x 10 <sup>-2</sup> Pa at 25 °C	Chlorpropham RED, 10/96
Dissociation constant, pK <sub>a</sub>	13.8 in 19% ethanol/water (v/v) at 20 °C	Chlorpropham RED, 10/96
Octanol/water partition coefficient, Log(K <sub>ow</sub> )	3.47 at 25 °C	Chlorpropham RED, 10/96
UV/visible absorption spectrum	not available	



## B. EXPERIMENTAL DESIGN

### B.1. Study Site Information

Trial Identification (City, State; Year)	Soil characteristics				Meteorological data	
	Type	%OM	pH	CEC	Overall monthly rainfall range (inches)	Monthly temperature range (°C)
Rosc, ID; 2003	Not applicable to postharvest storage treatments					

Storage facility temperatures were maintained at standard commercial temperatures ranging 4.5-8 °C.

Location (City, State; Year)	Application						
	EP <sup>1</sup>	Method; Timing	Appl. Rate (lb ai/1,000 lb of potatoes)	No. of Appl.	RTI <sup>2</sup> (days)	Total Rate (lb ai/1,000 lb of potatoes)	Tank Mix Adjuvants
Commercial storage facility in Rose, ID; 2003	9.71 lb/gal RTU	Postharvest via thermal aerosol fogger connected to the ventilation system <sup>3</sup>	0.0242	1	--	0.0342	None
Packing plant in Blackfoot, ID; 2003	2 lb/gal EC	Postharvest spray prior to packing	0.01	1	98		None

<sup>1</sup> EP = End-use Product.

<sup>2</sup> RTI = Retreatment interval.

<sup>3</sup> The ventilation system was closed to the outside during treatment and for 24 hours after treatment; fresh air ventilation was resumed 24 hours after treatment.



NAFTA Growing Region	Potato		
	Submitted	Requested	
		Canada	US
1			
1A			
2			
3			
4			
5			
5A			
5B			
6			
7			
7A			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
<b>Total</b>	<b>1</b>		

Geographic representation requirements are not applicable for a postharvest fumigation study.

## **B.2. Sample Handling and Preparation**

Single samples of potato tubers (10 potatoes per sample) from the top, middle, and bottom of the potato pile were collected 3 days prior to treatment (control) and 1, 13, 29, 62, and 90 days after treatment. At the packing plant, potatoes were placed in holding bins, washed with water using a flume spray, and graded prior to the EC spray treatment. Single samples (10 potatoes per sample) were collected at the start, during the middle, and near the end of the packing run. Collected samples were bagged and shipped within 24-48 hours of collection to DiChlor



Research Laboratory (Meridian, ID) for residue analysis. At the laboratory, samples were stored in mechanically cooled storage bins (temperature unspecified).

We note that the sampling intervals were calculated by the study reviewer based on the treatment and sampling dates provided by the registrant, and differ slightly from the sampling intervals reported by the registrant.

### **B.3. Analytical Methodology**

Potato peel and pulp samples were separately analyzed for residues of chlorpropham using an HPLC/UV method. Residues in whole potatoes were calculated by summing the actual residues quantitated in the potato peel and pulp and dividing by the whole potato weight. For a complete description of the method refer to the method validation study (DER for MRID 46151702). A brief description of the method follows.

To simulate consumer practices, whole potatoes were first washed with water to remove soil and debris, then peeled. Peel and pulp samples were blended with a reagent grade alcohol (90-91% ethanol denatured with 5% isopropyl alcohol and 4-5% methanol; 100% or 80% in water), warmed to 50 °C for 30 minutes in a water bath, and shaken for 20 minutes at ambient temperatures. The extract was filtered for HPLC/UV analysis. The reported limit of quantitation (LOQ) was 0.05 µg/mL of final extract volume (10x the noise level), and the limit of detection (LOD) was set at 3x the noise level (no actual value was specified). Because the method specifies that the entire potato sample is to be analyzed, there is no standard sample weight identified for analysis. Therefore, the LOQ in terms of ppm depends on the weight of pulp or peel analyzed. Based on the sample weights reported in the study, the LOQ for pulp ranged 0.01-0.06 ppm and the LOQ for peel ranged 0.1-0.4 ppm.

Untreated samples (collected prior to fumigation treatment) were spiked with chlorpropham for concurrent method recoveries, by trickling a chlorpropham solution onto the outer peel of the whole potato. After spiking, the whole potato was separated into peel and pulp for analysis, and chlorpropham recoveries from whole potato were calculated from the residues in the peel and pulp. Besides concurrent method validation, chlorpropham verification standards ranging 1-40 µg/mL were analyzed after every 10 samples to confirm the accuracy of the method. Average deviation from the expected concentration of chlorpropham in the verification standards ranged 1.2-7.7% (average of 3.2%).

## **C. RESULTS AND DISCUSSION**

Sample storage intervals are summarized in Table C.2; the registrant stated that samples were stored in mechanically cooled storage bins but did not report the storage temperatures. Although samples were apparently not stored frozen prior to analysis, all samples were extracted within one week of collection. Certain extracts were stored for extended periods (up to 24 days) prior to analysis. However, the extracts of concurrent fortification samples were subjected to the same extended storage conditions; adequate recoveries were observed in these samples, indicating



stability during storage. Therefore, HED will not require supporting storage stability data for this study.

Concurrent method recovery data are presented in Table C.1. Samples of potato peel and pulp samples were separately analyzed for residues of chlorpropham using an HPLC/UV method, and residues in whole potatoes were calculated by summing the actual residues in potato peel and pulp and dividing by the whole potato weight. The LOQs ranged 0.01-0.06 ppm for pulp and 0.1-0.4 ppm for peel. Adequate method recoveries were observed from whole potato samples fortified at 2 and 20 ppm. Although the fortification levels in this study bracketed the calculated residues in whole potatoes, actual residues quantitated in pulp ranged <LOQ-1.31 ppm, and residues in peel ranged 15.9-98.2 ppm. Based on the analytical data included in the submission, the fortification procedures used resulted in residues of <LOQ-0.35 ppm in pulp and 11.5-205 ppm in peel; therefore, HED will not require additional validation data to support this study. The registrant should note for future submissions that HED prefers validation data for each commodity as analyzed. Because peel and pulp were analyzed separately in this study, separate validation data should have been provided for peel and pulp, bracketing the expected residue levels in each commodity.

Apparent residues of chlorpropham were <0.05-0.24 ppm in/on the control whole tuber samples collected 3 days prior to treatment. The petitioner did not address the residues in the control samples, but did note that the storage facility had previously been used to store chlorpropham-treated potatoes. Because the residues in the treated samples were significantly higher than in the control samples, the observed residues in the control samples are not of concern for this study.

Residue data from the potato postharvest treatment study are reported in Table C.3. A summary of residue data for potato peel, pulp, and whole tubers is presented in Table C.4. Residues of chlorpropham in/on whole potatoes collected from the top, middle, and bottom portions of the storage facility following fumigation treatment at 0.0242 lb ai/1,000 lb of potatoes ranged 1.74-6.41 ppm, 2.73-8.44 ppm, and 2.02-11.20 ppm, respectively. Residues of chlorpropham ranged 2.64-7.27 ppm in/on whole potatoes collected from the beginning, middle, and near the end of the packing run immediately following a spray application of a 2 lb/gal EC formulation at 0.01 lb ai/1,000 lb of potatoes made 98 days following fumigation treatment of potatoes (total application rate of 0.0342 lb ai/1,000 lb of potatoes).

In general, residues of chlorpropham increased rapidly after fumigation treatment and appeared to level off within 13 days of treatment, with an average residue of 4-7 ppm in the whole tuber for the remainder of the storage period. A graph of the average residue levels in peel, pulp, and whole potato during storage is presented in Figure C.1. Residues were typically highest in samples from the bottom of the storage pile and lowest in samples from the top of the storage pile; residues fluctuated the most in samples from the middle of the storage pile. A graph of average residue levels in whole potatoes based on sampling location is presented in Figure C.2. Residue levels remained fairly constant in fumigated potatoes following the washing and EC spray application at the packing plant. Chlorpropham residues in whole potatoes were primarily located in the potato peel.



**TABLE C.1 Summary of Concurrent Recoveries of Chlorpropham from Potato.**

Matrix	Spiking level (ppm)	Sample size	Recoveries (%) <sup>1</sup>	Mean recovery ± SD
Potato, tuber <sup>2</sup>	2	35	84-111	97 ± 9
	20	35	71-104	93 ± 7

<sup>1</sup> Residues in fortified samples were corrected for average residues (0.07 ppm) in the samples collected 3 days prior to treatment.

<sup>2</sup> Whole potatoes were fortified and then separated into peel and pulp for separate analyses; residues in the whole potato tuber were calculated by the registrant by summing the actual residues in the peel and pulp (in µg) and dividing by the whole potato weight (in g).

**TABLE C.2. Summary of Freezer Storage Conditions**

Matrix	Storage Temperature	Actual Storage Duration	Limit of Demonstrated Storage Stability
Potato RAC	"Cool"; temperatures not specified	1-8 days	None provided.
Potato peel and pulp extracts	4 °C	0-24 days	None provided.

We note that peel and pulp extracts were analyzed within 3 days of extraction for all samples except those collected 62 days after treatment, which were analyzed 23-24 days after extraction, and those collected from the bottom of the bin 90 days after treatment, which were analyzed 8-12 days after extraction.

**TABLE C.3. Residue Data from a Potato Postharvest Treatment Study with Chlorpropham.**

Sampling location/timing	Potato Variety	Total Rate (lb ai/1,000 lb of potato)	PTI <sup>1</sup> (days)	Chlorpropham Residues (ppm) <sup>2</sup>		
				Peel	Pulp	Whole Potato <sup>3</sup>
<b>Potatoes sampled at storage facility<sup>4</sup></b>						
Top of storage bin	Russet Burbank	0.0242	-3	<LOQ-0.82 (0.40)	<LOQ-0.04 (0.03)	0.03-0.10 (0.07)
			1	15.92-34.38 (24.91)	<LOQ	2.31-3.36 (2.81)
			13	16.02- 53.61 (30.36)	0.03-0.08 (0.05)	1.74-5.20 (3.24)
			29	18.27-42.07 (33.57)	0.26-0.43 (0.35)	2.95-6.00 (4.36)
			62	27.51-42.50 (36.00)	<LOQ	4.22-6.41 (5.16)
			90	26.02-43.12 (33.92)	0.05-0.10 (0.07)	4.09-5.99 (4.74)
Middle of storage bin	Russet Burbank	0.0242	-3	<LOQ-1.58 (0.57)	<LOQ-0.06 (0.03)	0.04-0.24 (0.10)
			1	18.84-37.94 (27.24)	0.20-0.42 (0.31)	2.82-4.86 (3.75)
			13	36.83-62.74 (50.14)	<LOQ	4.32-7.51 (6.24)
			29	31.22-57.16 (42.86)	0.26-0.43 (0.35)	4.61-7.05 (5.84)
			62	20.27-52.90 (37.07)	<LOQ-0.03	2.73-6.25 (4.67)
			90	41.15-65.08 (54.02)	0.05-0.12 (0.08)	5.61-8.44 (7.28)





**TABLE C.3. Residue Data from a Potato Postharvest Treatment Study with Chlorpropham.**

Sampling location/timing	Potato Variety	Total Rate (lb ai/1,000 lb of potato)	PTI <sup>1</sup> (days)	Chlorpropham Residues (ppm) <sup>2</sup>		
				Peel	Pulp	Whole Potato <sup>3</sup>
Bottom of storage bin	Russet Burbank	0.0242	-3	<LOQ-0.35 (0.18)	<LOQ	0.03-0.06 (0.03)
			1	16.22-40.82 (27.08)	0.22-0.35 (0.27)	2.43-4.72 (3.44)
			13	23.47-74.40 (39.90)	<LOQ	3.49-8.14 (4.96)
			29	29.85-67.10 (46.98)	0.29-0.51 (0.42)	4.43-7.57 (6.00)
			62	13.89-98.19 (52.19)	0.06-0.16 (0.11)	2.02-11.20 (6.63)
			90	17.83-70.10 (48.81)	<LOQ	2.77-8.41 (6.40)
<b>Potatoes sampled at packing plant<sup>5</sup></b>						
Beginning of packing run	Russet Burbank	0.0342	0	23.12-47.47 (34.93)	0.12-1.06 (0.36)	3.65-6.78 (4.85)
Middle of packing run	Russet Burbank	0.0342	0	21.07-52.00 (31.27)	0.11-0.26 (0.19)	3.16-7.27 (4.41)
Near end of packing run	Russet Burbank	0.0342	0	17.17-43.25 (29.13)	0.12-1.31 (0.41)	2.64-5.28 (3.99)

<sup>1</sup> PTI = posttreatment interval

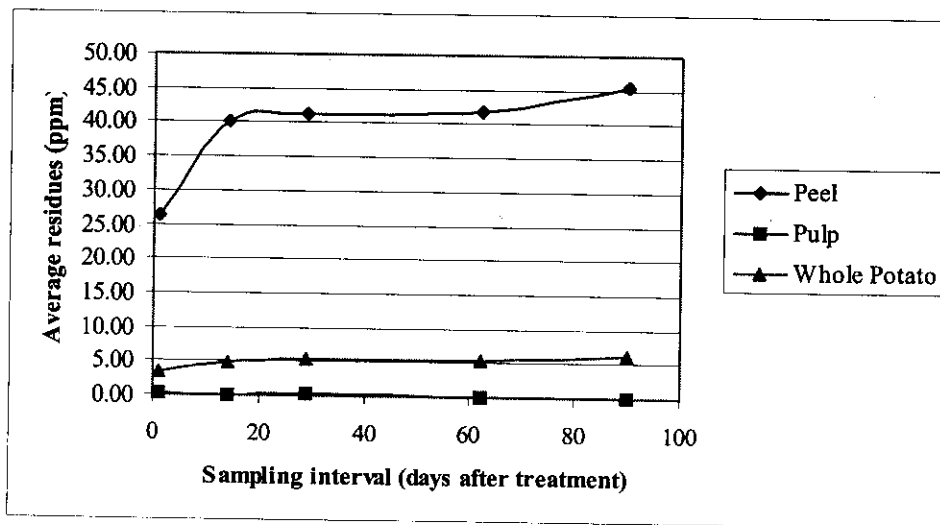
<sup>2</sup> Residue ranges are presented for 10 replicate samples from the single sample collected; averages, as reported by the petitioner, are presented in parentheses. The LOQ ranged 0.01-0.06 ppm for pulp and 0.1-0.4 ppm for peel, depending on sample weight.

<sup>3</sup> Residues in whole potato tubers were calculated by the registrant by summing the actual residues in the peel and pulp (in µg) and dividing by the whole potato weight (in g). A value of half the LOQ (0.025 µg/mL) was used in these calculations when residues were <LOQ.

<sup>4</sup> Potato tubers received a single postharvest fumigation treatment in a storage facility at 0.0242 lb ai/1,000 lb of potatoes.

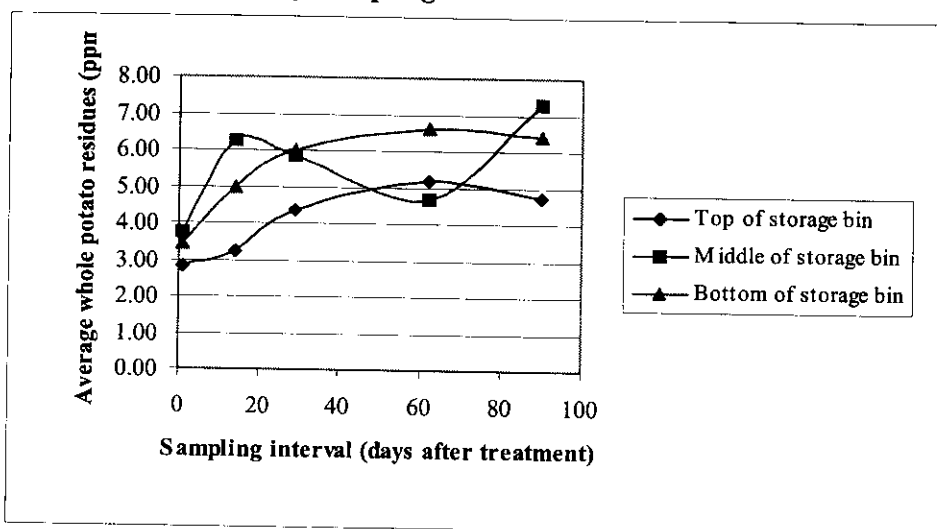
<sup>5</sup> Potatoes which had received postharvest fumigation treatment received a spray treatment at 0.01 lb ai/1,000 lb of potatoes at a packing plant, 98 after fumigation treatment.

**FIGURE C.1 Average Residues in Peel, Pulp, and Whole Potato Over the Course of the Study.**





**FIGURE C.2 Average Residues in Whole Potato Over the Course of the Study, by Sampling Location.**



**TABLE C.4. Summary of Residue Data for Potatoes from a Postharvest Storage Study with Chlorpropham.**

Potato Matrix	Total Applic. Rate (lb ai/1,000 lb of potatoes)	PTI (days)	Residue Levels (ppm) <sup>1</sup>						
			n	Min.	Max.	HAFT <sup>2</sup>	Median	Mean	Std. Dev.
Peel	0.0242	1	3	34.38	40.82	37.71	37.94	37.71	3.23
Pulp			3	<0.06	0.42	0.28	0.35	0.27	0.21
Whole tuber			3	3.36	4.86	4.31	4.72	4.31	0.83
Peel	0.0242	13	3	53.61	74.40	63.58	62.74	63.58	10.42
Pulp			3	<0.06	0.08	0.06	0.03	0.05	0.03
Whole tuber			3	5.20	8.14	6.95	7.51	6.95	1.55
Peel	0.0242	29	3	42.07	67.10	55.44	57.16	55.44	12.60
Pulp			3	0.43	0.51	0.46	0.43	0.46	0.05
Whole tuber			3	6.00	7.57	6.87	7.05	6.87	0.80
Peel	0.0242	62	3	42.50	98.19	64.53	52.90	64.53	29.61
Pulp			3	<0.06	0.16	0.08	0.03	0.07	0.08
Whole tuber			3	6.25	11.20	7.95	6.41	7.95	2.81
Peel	0.0242	90	3	43.12	70.10	59.43	65.08	59.43	14.35
Pulp			3	<0.06	0.12	0.09	0.10	0.08	0.05
Whole tuber			3	5.99	8.44	7.61	8.41	7.61	1.41



**TABLE C.4. Summary of Residue Data for Potatoes from a Postharvest Storage Study with Chlorpropham.**

Potato Matrix	Total Applic. Rate (lb ai/1,000 lb of potatoes)	PTI (days)	Residue Levels (ppm) <sup>1</sup>						
			n	Min.	Max.	HAFT <sup>2</sup>	Median	Mean	Std. Dev.
Peel	0.0342	0	3	43.25	52.00	47.57	47.47	47.57	4.38
Pulp			3	0.26	1.31	0.88	1.06	0.88	0.55
Whole tuber			3	5.28	7.27	6.44	6.78	6.44	1.04

<sup>1</sup> Maximum residues of potatoes (replicate samples) sampled at the top, middle, and bottom of the storage bin, or beginning, middle, and near the end of the packing run are reported for the summary table. For the determination of minimum, maximum, and HAFT values, the highest LOQ (0.06 ppm) was used for residues reported below the LOQ in Table C.3. Half the LOQ (0.03 ppm) was used for residues reported at levels less than half the LOQ in the determination of the median, mean, and standard deviation values.

<sup>2</sup> HAFT = Highest Average Field Trial.

#### D. CONCLUSION

The submitted potato postharvest storage treatment data reflect the use of chlorpropham as a fumigation treatment in a storage facility at 0.0242 lb ai/1,000 lb of potatoes. A portion of the samples were additionally treated with a spray application at a packing plant, 98 days after fumigation treatment, at 0.01 lb ai/1,000 lb of potatoes. The method used for sample analysis was determined to be adequate for the purposes of this study.

#### E. REFERENCES

None

#### F. DOCUMENT TRACKING

RDI: C. Eiden (5/26/04)  
 Petition Number(s): Not applicable  
 DP Barcode(s): D297635  
 PC Code: 018301

cc: Anthony Britton (SRRD), Michael Goodis (SRRD)