



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

OCT 18 1993

MEMORANDUM

Subject: Aldicarb Special Review and Reregistration (Chemical 098301, Case 0140, List A): Residues in/on Potatoes and in Processed and Prepared Potato Commodities. DP Barcode D192797. CBRS No. 12148. MRID Nos. 42827801 - 42827804.

From: Stephen Funk, Ph.D., Chemist *S. R. Funk*
Reregistration Section II
Chemistry Branch II - Reregistration Support
Health Effects Division (H7509C)

Through: Edward Zager, Branch Chief *E. Zager*
Chemistry Branch II - Reregistration Support
Health Effects Division (H7509C)

To: Dennis Edwards, Jr./PM 19
Insecticide-Rodenticide Branch
Registration Division (H7505)

A tolerance of 1 ppm exists for the combined residues of aldicarb and its aldicarb sulfoxide and aldicarb sulfone cholinesterase-inhibiting metabolites in/on white potatoes (40 CFR §180.269). There are no potato processed commodity tolerances. A DCI was issued 06/09/89 for data on potatoes and other crops. The presence of residues in excess of the tolerance level on individual potatoes led to a voluntary suspension of aldicarb for use on potatoes (04/18/90). Rhone-Poulenc Ag Company was subsequently granted an extension of the termination date for its registration on potatoes until 01/31/95. The registrant has now submitted several field trial, processing, and preparation studies for aldicarb on potatoes and seed potatoes. The studies are as follows:



Recycled/Recyclable
Printed with Soy/Canola Ink on paper that
contains at least 50% recycled fiber

Title	Date	MRID No.
Final Report: TEMIK® Magnitude of Aldicarb Residues in Processed Potatoes Potato Fractions. EC-92-211.	06/11/93	42827801
Final Report: Determination of Variation in Magnitude and Character of Aldicarb Residues in Potatoes from Temik-Treated Fields. EC-90-092 and EC-90-117.	02/05/93	42827802
Final Report: Temik®: Magnitude of Aldicarb Residue in Potatoes Grown from Seed Pieces Injected with Aldicarb Sulfoxide at 1.0 ppm. EC-92-208.	02/24/93	42827803
Final Report: Temik®: Magnitude of Aldicarb Residues in Potatoes Grown with Available Overhead Irrigation in 1992. EC-92-180.	06/21/93	428287804

Conclusions

1a. Total aldicarb residues do not concentrate in potato chips, potato fries, or wet potato peel. Residues do not concentrate significantly in potato flakes (average factor 1.1, range 0.07 to 1.4; Table 3). Based on the new data submitted, CBRS concludes that food additive tolerances are not required for potato granules and potato chips. Note that this reverses the position taken in the Registration Standard Update (R. D. Schmitt, 08/20/90). Residues do concentrate in dried potato peel (average factor 1.65, range 0.76 to 2.38). These results do not agree with a study reviewed previously and found deficient (J. Garbus, CBRS No. 10611, 08/19/93), where the concentration factor for dried peel was about 1.1. Therefore, a feed additive tolerance must be proposed for dried potato peel. A value of 2 ppm (2 X 1 ppm rac tolerance) would be appropriate for dried potato peel. This confirms the position of the Registration Standard Update.

1b. The values reported for the rac residue level from the Florida 10X trial and the rac residue level for the potatoes from this same location used for the processing study do not agree. The processing study rac values appear more in agreement with the residue levels found on the 5X Florida crop. This discrepancy must be addressed.

1c. The requirements of the 06/89 DCI for data on potato processing are satisfied (Section II-A.5).

2a. Baking whole potatoes (in conventional ovens) reduces the total aldicarb residue by an average of 60% (Table 1). Microwaving

whole potatoes does not have a definitive effect on total aldicarb residues (Table 2). DRES cannot distinguish consumption of microwave-prepared versus conventional oven-baked potatoes. Because no decrease in residue was seen for microwaving of potatoes, no decrease in residue level due to baking of potatoes should be incorporated into the dietary risk assessment.

2b. Preparing french fries results in a 40% decrease in total aldicarb residue from that found in the potato rac. All of the decrease occurs in the commercial preparation of the frozen fries. This may be considered when performing dietary risk assessments for aldicarb, if adequate consumption data are available.

2c. The requirements of the 06/89 DCI for data on potato preparation are satisfied (Section II-A.5).

3a. Potatoes grown from seed potatoes treated with aldicarb, i.e., second generation potatoes, do not contain aldicarb residues (<0.02 ppm total aldicarb plus aldicarb sulfone plus aldicarb sulfoxide). The seed potatoes contained about 1 ppm aldicarb (as aldicarb sulfone). This study shows that the primary route of entry of aldicarb into potatoes in the field is not via the treated seed.

3b. The analysis procedure for the injected seed potatoes/daughter potatoes was flawed. The laboratory failed to calibrate the gc at appropriate times. About 6 months elapsed from the creation of the calibration curve to the analysis of samples. Acceptable recoveries for fortified controls, including 0.02 ppm total aldicarb equivalents, show that the analysis was in control. Therefore, reanalysis will not be required.

4. The analysis of 918 individual tubers from 17 field trials (1X) in 1992 show that residues in excess of the established 1 ppm tolerance do occur, but only at the ends of rows. Parameters were application of Temik® 15G at the maximum label rate of 3 lbs. a.i./acre with gravity flow application equipment (except Texas). All applications were at planting; none were at crop emergence. Irrigation was overhead only. The end of row residue values exceeded the tolerance at locations in Colorado (1.11 ppm), Florida (1.04 ppm), Montana (1.75 ppm), and Michigan (1.16 ppm and 3.13 ppm). The data fully support the registrant's claim that residues in excess of tolerance arise from excessive application rates at the end of rows when gravity flow application equipment is used. The calculated amount of pesticide used (gravimetric determination) supports this claim for the Michigan trials only, where the amount of pesticide actually used corresponded to 6 lbs. a.i./acre. The registrant needs to demonstrate at several trial locations that the tolerance is not exceeded when positive displacement application equipment is used. Rhone-Poulenc in a letter of 06/25/93 (MRID 42827800) indicates that such a study is in progress (1993 season).

5a. The analysis of about 1000 individual tubers from 8 field

trials (1X) conducted in 1990 show that only 2 tubers contained residues in excess of the established 1 ppm tolerance, 1.30 ppm and 1.04 ppm in Washington (90-129). A second trial at the same Washington location (90-130) yielded all residues <1 ppm, 0.225 ppm maximum (Table 8). The only difference was a longer PHI, 123 days versus 97 days, for the second trial. The 8 trials contained a mixture of at-plant and at-emergence applications at the maximum label rate of 3 lbs. a.i. per acre (2 lbs. a.i. per acre in Maine). Geographic representation was adequate, with all major potato production regions represented, except California. Only overhead irrigation was used, and no attempt was made to segregate end-of-row samples from other tubers. At least 100 tubers were analyzed for each location. Average residues were <0.1 ppm for six locations and 0.14 ppm and 0.30 ppm for the other locations. In all cases 95% of residue values were within 2X of the mean.

5b. The analysis of tubers from individual plants from 7 field trials (1X) conducted in 1991 show substantial variation of aldicarb residue content for the tubers from a single plant. Residues varied by a factor of as much as 25X for tubers on a given plant (Table 9).

5c. Storage intervals and conditions must be reported for the tubers from each location. Intervals from harvest to analysis could not be correlated with the particular trial locations.

5d. The 1990 field trial studies partially fulfill the requirements of the 06/89 DCI, provided the information of 5c is supplied and found acceptable. Additional data are required on the effects of typical commercial storage on aldicarb, aldicarb sulfone, and aldicarb sulfoxide residues in/on potatoes (Section II-A.4). The present submission adequately demonstrates the variability of aldicarb levels among individual potatoes within fields (Section II-C.1).

Recommendation

CBRS recommends that Rhone-Poulenc (1) propose a feed additive tolerance for dried potato peel; (2) conduct side-by-side field trials at diverse locations comparing positive displacement application equipment with gravity feed applicators and using both at-plant and at-emergence applications and segregating end-of-row tubers from other tubers; (3) address the discrepancy in the values reported for the 10X Florida rac and the concentration of aldicarb residues on the potatoes processed; (4) provide information on the storage intervals for the tubers from the 1990 study; and, (5) provide the additional potato studies, e.g., degradation under commercial storage conditions, required by the 06/89 DCI.

CBRS further recommends that dietary risk assessment analyses be conducted using the individual tuber data from the 1990 and 1991

field trials. These assessments will be handled through HED/DRES.

Detailed Considerations

Magnitude of the Residue in Processed and Prepared Potato Fractions Field Phase

Temik® 15G aldicarb was applied at a rate of 30 lbs. a.i./acre (10X) to Atlantic potatoes in Florida. The plot size was 0.133 acre (218 ft. X 26.6 ft.) and was located in Hastings, St. John County, where the soil is Pamona fine sand. The potatoes were planted on 09/21/92. The aldicarb was applied 11 days after planting at crop emergence. The plants were 0 - 3 inches tall. The pesticide was applied with a Nobel applicator box with Gandy electric motor (positive displacement). The potato tubers were hand harvested 74 days after the treatment on 12/15/92. Samples (3 X 200 lbs.) for processing were shipped to Wm. J. Englar and Associates, Inc., Moses Lake, WA on 12/15/92. Samples (1 X 100 lbs.) from a control plot (0 X) were also shipped to the processor. Tubers for initial analysis were harvested and shipped directly to the analytical laboratory (CYAL, Inc., Morrisville, NC) on 12/03/92. Samples for individual tuber analyses and preparation studies were also sent to CYAL on 12/16/92..

Processing/Preparation

Processing studies were conducted from 01/11 - 01/15/93. Each lot of treated potatoes (3 X 200 lbs.) and the control lot (1 X 200 lbs.) was subdivided and processed into potato chips, potato flakes, and french fries. The processor noted that the potatoes were small and round, not the type typically used for the production of commercial frozen french fries. Chain of Custody records were maintained.

Potato chips were produced from one control and two treated batches of potatoes by a process that simulated commercial processing. Twenty pounds of potatoes were tub washed (5 - 10 minutes) and sorted. The washed potatoes were peeled in a Hobart Abrasive Peeler for 60 seconds. Damaged potatoes were discarded. The remaining potatoes were cut into 1/16" slices with a Lan Elec Food Cutter and washed (49 - 54° C). About 9 lbs. of slices were fried at 163 - 177° C for 90 seconds. The chips were drained and salted. Yield was about 3 lbs. of chips. Samples (2 lbs.) were frozen and dispatched to CYAL for analysis. Peel was dried (< 94° C), and samples sent to CYAL for analysis.

Potato flakes were produced from a process that simulated commercial processing. About 180 pounds (185 lbs. control, 215 lbs. treated rep 1, 190 lbs. rep 2, 222 lbs. rep 3) of potatoes were tub washed and sorted. The potatoes were steam peeled (45 seconds, 85

psi steam) and scrubbed/peeled using a Hobart Peeler. Damaged potatoes were discarded. About 20 lbs. were removed for french fry processing. The remaining potatoes (143 lbs. control, 134 lbs. treated rep 1, 116 lbs. treated rep 2, 142 lbs. treated rep 3) were cut into 1/2" slabs with a Lan Elec Food Cutter. The slabs were sprayed with cold tap water (30 seconds) to remove free starch and then precooked in a stainless steel kettle (71 - 74° C, 20 min.). The slabs were cooled (27 - 32° C, 20 min.) and steam cooked at atmospheric pressure (94 - 100° C, 35 - 45 min.). The slabs were mashed in a Hobart Meat Grinder and mixed (60 sec.) with food additives. The mash was placed in a drum dryer (5 - 20 rps, 80 - 100 psi steam, 62 - 170° C) to produce flakes. Samples of dried potato peel and flakes (2 lbs.) were frozen and sent to CYAL.

The 20 lb. samples from the initial steps of the potato flaking process (steam peeling) were processed into french fries. The potatoes were cut into 1/4" X 1/4" shoestrings with a commercial french fry cutter. The strips were blanched at 71° C for 10 minutes and then at 88° C for 3 minutes and dipped in 1% dextrose for 30 seconds. The strips were dried, fried in a restaurant style deep fat fryer (191° C, 60 sec.), drained, and frozen (-10 to -29° C). Samples of fries (5 lbs.) were sent frozen to CYAL.

Baked potatoes were prepared and analyzed by CYAL. One hundred individual tubers were randomly selected from the 10X treatment Florida lot. The potatoes were brushed (no washing) and were cut in half. One half of each tuber was extracted and analyzed. The other half was baked (190° C, 375° F) for about 30 minutes. The thirty baked potato halves corresponding to the 30 halves with highest aldicarb residues were extracted and analyzed. A similar process was conducted with an additional 100 potatoes, but using microwave cooking (5 minutes, full power (? watt)).

French fries were prepared at CYAL by cooking the processed commodity for 1.5 minutes in vegetable oil at 177° C (350° F). Prepared samples were stored frozen pending extraction and analysis.

Analysis

Analyses were conducted by CYAL, Inc. using analytical method #8, a modification of Rhone-Poulenc AG Company SOP 90015 (06/12/90). Briefly, finely ground potato product (10 g) is extracted with 1:1 acetonitrile:methylene chloride (75:25 methanol:water in the Rhone-Poulenc procedure). Interfering materials are removed by Florisil column chromatography. The residues (aldicarb, sulfoxide, sulfone) are determined by reverse phase hplc equipped with post-column derivatization and fluorescence detection. Post-column hydrolysis releases methylamine from each compound, and the methyl amine is reacted with o-phthalaldehyde and mercaptoethanol to yield a fluorescent compound, 1-(2-hydroxyethyl) thio-2-methyl isoindole.

The column is a Supelcosil LC-18, 25 cm. Gradient elution is used, going from 10% acetonitrile in water to 80% acetonitrile in water over 12.5 min at a flow of 1.0 ml/min. External standard calibration is used. The limit of quantitation is 0.02 ppm for each analyte. Approximate retention times are 7.7 minutes for aldicarb sulfoxide, 10.1 minutes for aldicarb sulfone, and 15.5 minutes for aldicarb.

Twenty pounds of brushed, unwashed rac (potato) were composited to yield a 10 g sample for analysis.

Fortified control samples (0.02 ppm and 0.10 ppm) were prepared and analyzed concurrent with treated samples to demonstrate method recovery. Control samples and reagent blanks were prepared and analyzed to show lack of contamination.

The method was verified by fortifying a matrix, presumably potatoes, with each analyte at concentrations of 0.02 ppm, 0.1 ppm, 0.5 ppm, and 1.0 ppm. Recoveries ranged from 68% - 83% at 0.02 ppm, from 80% - 98% at 0.1 ppm, from 70% to 99% at 0.5 ppm, and from 81% to 102% at 1.0 ppm.

Process potato fractions were analyzed within 8 weeks of processing. Incomplete data indicate that residues of aldicarb, aldicarb sulfoxide, and aldicarb sulfone are stable for at least 6 weeks in/on frozen potato commodities (R. B. Perfetti, CBRS Nos. 10186, 11468, and 10775, 04/06/93).

Results

The results for the 200 tuber halves individually analyzed ranged from 0.24 ppm total sulfone equivalents to 1.86 ppm. Results for 24 potato halves (12%) exceeded the established tolerance of 1 ppm. The potatoes were treated at 10X the label rate. Results for the 30 raw halves with greatest residues and the corresponding baked or microwaved halves are summarized in Tables 1 and 2. Baking reduced residues by an average of 62%; the minimum reduction was 27%. Microwaving had a variable effect and in a few cases actually increased the residue.

Table 1: Comparison of Raw Potato and Baked Potato Residues			
Sample ID	RAC Total Sulfone Equivalents ¹ (ppm)	Baked Total Sulfone Equivalents (ppm)	Residue Reduction ² (%)
7384-010	0.95	0.22	77
7384-015	1.0	0.39	-61
7384-018	1.2	0.41	64
7384-020	0.91	0.32	64
7384-024	0.91	0.29	68
7384-026	0.88	0.46	47
7384-028	0.70	0.21	70
7384-035	1.2	0.4	69
7384-039	1.2	0.37	69
7384-042	0.86	0.23	74
7384-043	1.0	0.46	54
7384-044	0.89	0.26	70
7384-045	0.73	0.22	30
7384-050	1.7	0.54	68
7384-053	0.82	0.60	27
7384-055	0.80	0.25	69
7384-059	0.75	0.29	62
7384-060	0.71	0.30	57
7384-062	0.70	0.32	54
7384-072	1.4	0.33	76
7384-074	0.74	0.34	54
7384-075	0.97	0.44	55
7384-076	1.0	0.23	78
7384-077	1.5	0.66	57
7384-079	1.3	0.42	66
7384-081	0.76	0.36	48
7384-086	0.83	0.23	72
7384-095	0.80	0.38	58
7384-096	0.80	0.33	59
7384-099	1.4	0.31	78
Range			27 - 78
Mean			62
S.D.			12.5
¹ Only 3 potatoes contained an aldicarb concentration ≥ 0.02 ppm (0.054, 0.025, 0.036 ppm).			
² $100\% - \left(\frac{\text{Total sulfone equivalents in baked}}{\text{Total sulfone equivalents in rac}} \right) \times 100$.			

Table 2: Comparison of Raw Potato and Microwaved Potato Residues			
Sample ID	RAC Total Sulfone Equivalents ¹ (ppm)	Microwaved Total Sulfone Equivalents (ppm)	Residue Reduction ² (%)
7384-111	1.1	1.4	-23
7384-112	1.2	0.91	-24
7384-113	0.85	0.87	-2.4
7384-114	1.4	0.88	36
7384-116	1.4	1.0	23
7384-126	0.84	0.57	32
7384-130	0.90	0.69	23
7384-132	0.90	1.2	-31
7384-137	1.2	1.1	5.5
7384-138	0.88	0.66	24
7384-144	1.8	1.2	33
7384-148	0.89	0.52	42
7384-162	1.5	1.7	-15
7384-165	1.2	0.66	44
7384-171	1.0	0.79	23
7384-173	1.0	0.88	16
7384-175	0.86	0.52	40
7384-176	1.9	0.95	49
7384-178	0.86	0.99	-16
7384-179	0.82	0.63	22
7384-180	0.94	0.89	5.5
7384-283	0.55	0.50	9.2
7384-186	0.88	0.82	6.8
7384-189	1.0	1.1	-4.9
7384-190	1.2	0.81	32
7384-191	0.93	0.89	5.1
7384-192	0.78	0.72	7.9
7384-195	0.91	0.81	12
7384-196	0.91	0.70	23
7384-198	1.0	0.67	34
Range			-31 - +41
Mean			16
S.D.			20

¹ Only 6 potatoes contained an aldicarb concentration ≥ 0.02 ppm (0.08, 0.05, 0.02, 0.07, 0.06 ppm).
² $100\% - \frac{[(\text{Total sulfone equivalents in microwaved}) + (\text{Total sulfone equivalents in rac}) \times 100]}{(\text{Total sulfone equivalents in microwaved})}$. A negative number indicates an increase in residue upon preparation.

Each of the processed fractions (flake, chip, wet peel, dry peel, processed fries, cooked processed fries) from each of three replicate processing studies were analyzed in triplicate. The rac corresponding to each replicate was analyzed once. Individual results and example chromatograms were presented. The results are summarized in Table 3. The total residue increased by as much as 36% in flakes. However, the registrant notes that potato flakes are normally hydrated before consumption, a process which would reduce the residue by 67% (relative to the rac), assuming potatoes contain about 75% water. Residues decreased in chips by an average of 28% and in processed fries by an average of 55%. Residues decreased by an average of 40% in cooked fries, relative to the rac.

Table 3: Summary of Potato Processing Data					
Fraction	Replicate #1 ^{1,2} (ppm/ % change)	Replicate #2 ^{1,2} (ppm)	Replicate #3 ^{1,2} (ppm)	Control (ppm)	Average Change ³ (%)
RAC ⁴	0.57	0.67	0.75	<0.06 ⁶	N/A
Potato Flakes ⁴	0.77 (-36)	0.76 (-13)	0.73 (3.2)	<0.06 ⁶	-15
Potato Chips ⁴	0.40 (30)	0.48 (28)	0.55 (27)	<0.06 ⁶	28
Fries ⁴	0.25 (56)	0.29 (56)	0.34 (55)	<0.06 ⁶	56
Cooked Fries ⁴	0.34 (40)	0.40 (40)	0.42 (44)	<0.06 ⁶	42
Wet Peel ⁴	0.42 (26)	0.33 (50)	0.40 (47)	<0.06 ⁶	41
Dried Peel ⁵	1.36 (-140)	0.51 (24)	1.36 (-81)	<0.06 ⁶	-65
¹ Average of three analyses, for all fractions except the potato (RAC). First entry is aldicarb sulfone equivalents concentration. Second entry is percent increase/decrease of residue relative to the RAC. ² % Change = $100 \times [1 - (\text{processed fraction} \div \text{RAC})]$. A negative value indicates an increase in concentration in the processed fraction relative to the RAC. ³ For the three replicates. ⁴ No aldicarb (<0.02 ppm) was found in any sample. ⁵ Replicate #1 contained aldicarb, 0.031 - 0.032 ppm. This was confirmed upon confirmation analysis. ⁶ 3 X 0.02 ppm, the stated limit of quantitation for each of the three analytes determined. The registrant used "N/D."					

Results are presented for fortification recoveries from control rac and processed fractions spiked at 0.10 ppm and 0.02 ppm with each of aldicarb, aldicarb sulfone, and aldicarb sulfoxide. The range of recoveries is indicated as follows:

Analyte	Minimum Recovery/Matrix/ Fortification	Maximum Recovery/Matrix /Fortification	Average/S.D. (n = 55)
Aldicarb	61%/chips/ 0.1 ppm	113%/potato/ 0.02 ppm	86/9.3
Aldicarb Sulfoxide	60%/potato/ 0.1 ppm	110%/potato/ 0.02	79/11
Aldicarb Sulfone	62%/potato/ 0.02	120%/potato/ 0.02	91/13

An apparent discrepancy exists as to the concentration of aldicarb sulfone equivalents in the potato rac. In order to select an appropriate field trial for the processing study, composite samples of potatoes from several trials conducted at different rates and in diverse geographical locations were analyzed. Ten potatoes were composited and 5 subsamples were analyzed for each trial. For trial 92-185 (Florida, 10X) residues ranged from 0.89 to 1.8 ppm. By comparison, the rac's (same field trial) used for the processing study ranged from 0.57 - 0.75 ppm. These latter values are in agreement with results obtained from the 5X Florida plot.

Magnitude of the Residue in Potatoes Grown from Aldicarb Treated (Injected) Seed Pieces

Field Phase

Both field and laboratory work was conducted by Agvise Laboratories, Inc., Northwood, ND. Weighed Norchip potato seed pieces (each >40 g) were injected with an aqueous solution of aldicarb sulfoxide, nominal concentration 5 mg/ml, to give seeds containing about 1 ppm aldicarb sulfoxide. About 40 injected pieces were selected randomly and stored at -12° C until analyzed 6 days later. Twenty-four fresh cut seed pieces, not injected, were also retained (-12° C). Four hundred seed pieces were planted in two separate plots, one on the Agvise research farm and the other on the Mutchler irrigated farm. Both plots were in Grand Forks County, North Dakota. Control plots were planted at both locations. The soil was loam at the research farm and sandy loam at Mutchler. Neither location had a history of aldicarb treatment.

The seed pieces were planted by hand in furrows on 06/05/92, 50 treated seed pieces 12 inches apart in each of four rows and forty control seed pieces in each of four rows at each location. The pieces were covered by hand raking the soil. Plants emerged 06/19/92. Irrigation water (amount ?) was applied at the Mutchler site on 07/31/92. Ambush (permethrin) was used at both locations to control Colorado Potato Beetle. Bravo 720 (chlorothalonil)

fungicide was used at the Mutchler farm only, 07/29/92. Potatoes were harvested at the Agvise location only with a spade fork on 09/10/92. Tuber quality was judged superior at the Agvise research farm. The potatoes were brushed, placed in labeled plastic bags, weighed, and immediately frozen. Thirty control tubers and 100 treated tubers were collected. Samples were stored frozen (-18° to -22° C) for less than 15 days prior to analysis.

Analysis

Rhone-Poulenc SOP Method 90001 was used to determine total aldicarb residues in seed potatoes and harvested potatoes. Residues are extracted by blending the sample with acetone/water (75/25) containing peracetic acid. The peracetic acid oxidizes aldicarb and aldicarb sulfoxide to aldicarb sulfone. The extract is purified on a Florisil column, and the residue is determined by gc with a flame photometric detector (sulfur mode) and a 3% FFAP or 5% SP-1000 6 ft, 4 mm (i.d.) glass column. An external calibration is used (0.10 µg/ml to 1.0 µg/ml aldicarb sulfone). The nominal limit of quantitation is 0.02 µg/g aldicarb sulfone equivalents.

The method was verified by the analysis on fortified tubers (0.02, 0.10, 0.50, and 1.0 ppm total aldicarb as aldicarb sulfone equivalents). The fortifications were equal concentrations (as aldicarb sulfone equivalents) of aldicarb, aldicarb sulfoxide, and aldicarb sulfone. Recovery (n = 8) ranged from 81% to 101%.

Results

The results of the analysis of untreated seed pieces, injected seed pieces, the injection solution, and the potato tubers are summarized in Table 4. Example chromatograms were supplied. It is noted that calibration was performed on 03/18/92, about 6 months before the potato analyses. There is no proof of calibration verification. A new calibration should have been performed at the time of analysis and certainly after changing from the FFAP to the SP-1000 column, as reported to have occurred during the analysis sequence.

Table 4: Aldicarb Sulfone Equivalents in Seed Potatoes and Daughter Potato Tubers			
Matrix	Number of Samples Analyzed	Aldicarb Sulfone Equivalents Mean/S.D. ($\mu\text{g/g}$)	Aldicarb Sulfone Equivalents Range ($\mu\text{g/g}$)
Potato Seed Pieces (Untreated)	24	<0.02	<0.02 -
Potato Seed Pieces (Injected)	20	1.00 $\pm$ 0.093	0.872 - 1.20
Injection Solution	4 ¹	42.7 $\pm$ 2.11 ²	40.4 - 45.5 ²
Daughter Tubers	100	<0.02	<0.02
Control Tubers	10	<0.02	<0.02
¹ Two each from different stock solutions.			
² $\mu\text{g/ml}$.			

Summary results were presented for concurrent fortified controls. The recovery of aldicarb sulfone equivalents in tubers ranged from 70.7% to 104.9% for fortifications of 0.020, 0.040, 0.50, 1.0 and 2.0 $\mu\text{g/g}$, $n = 10$. The recovery of aldicarb sulfone equivalents from untreated seed (0.020 $\mu\text{g/g}$ spike, $n = 3$) ranged from 93.2% to 115.6%. Recovery of aldicarb sulfone equivalents from treated seed (2.0 $\mu\text{g/g}$ spike, $n = 3$) ranged from 80.3% to 85.4%. Equal concentrations of aldicarb, aldicarb sulfone, and aldicarb sulfoxide were used to prepare the fortification solutions.

Magnitude of the Aldicarb Residues in Potatoes Grown with Overhead Irrigation in 1992

Field Phase

Seventeen field trials were conducted in 1992 in CA (1), CO (2), ID (2), MI (2), MN (2), MN (1), NB (1), ND (1), OR (2), TX (1), and WA (2). Additional trials were conducted in AZ, but the product was not marketable, and no analyses were conducted. Each trial consisted of two plots, one a control and the other treated at the maximum label rate of 3 lbs. a.i./acre at the time of planting. Gravity flow application was used in all trials except Texas, where positive displacement equipment was utilized. A single in-furrow application of Temik® 15G, assayed 14.2% a.i., was made at each location with actual rates varying from 2.79 to 3.12 lbs. a.i./acre. The registrant maintains that the use of gravity flow application equipment causes an excessive application of the granular material at the ends of rows. Overhead irrigation was utilized. Potatoes were collected at the normal harvest interval, 102 (FL) to 168 (OR) days after treatment.

At each treated plot 96 tubers were collected from the uniform application area, defined as the entire plot less five feet at each end and less the outside rows. Thirty of these tubers were randomly selected for analysis. Twelve tubers were collected from each row-end section (24/plot), and all were analyzed. Half of the row-end tubers were collected from the last plant in the row. Row-end tubers were combined for shipping and storage. Twenty-five tubers were collected from each control plot.

Samples were shipped at ambient temperature via overnight air to Rhone-Poulenc Ag Company, RTP, NC. There they were stored frozen (-20°C). Samples from one trial (MT) were shipped frozen via ground transport to RTP. All samples were shipped frozen over dry ice from RTP to Morse Laboratory in Sacramento, CA for analysis.

The registrant provided a summary table of application date, harvest date, extraction date, and total days in storage for each location. The storage interval, including field to Rhone Poulenc shipping and time in frozen storage prior to extraction, ranged from 17 days (MI) to 83 days (MT). Available data indicate that total aldicarb residues are stable in/on potatoes for at least six months.

Analysis

Individual potato tubers, not composites, were analyzed using the HPLC method (SOP 90015) described above for the potato processing studies. The nominal limit of quantitation is $0.02\text{ }\mu\text{g/g}$ of each of the three residues. The column was a DuPont Zorbax Phenyl, 5 micron particle size, 15 cm X $1/4$ " o.d. X 4.6 mm i.d. Example chromatograms were provided. Approximate retention times were 3.2 minutes for aldicarb sulfoxide, 5.2 minutes for aldicarb sulfone, and 9.4 minutes for aldicarb.

Results

A total of 918 individual tubers were analyzed. Twelve tubers had residues exceeding the 1.0 ppm tolerance, and all of these were end-of-row samples. The maximum residue found in any row-center sample was 0.91 ppm (MI). The registrant reports that the 95th percentile for all samples was 0.40 ppm aldicarb sulfone equivalents. For end-row samples it was 0.52 ppm, and for row center samples it was 0.34 ppm. The registrant assigned a value of $0.02\text{ }\mu\text{g/g}$ to analyte peaks detected that were less than the limit of quantitation ($0.02\text{ }\mu\text{g/g}$) and 0.000 to analytes with no detected peak (ND).

Some control samples were fortified with equal concentrations (0.02 to $1.0\text{ }\mu\text{g/g}$) of aldicarb, aldicarb sulfoxide, and aldicarb sulfone and extracted and analyzed concurrent with treated samples to demonstrate the method recovery. A total of 103

recovery samples were analyzed. The registrant defined acceptable recovery as 70% - 120% for concentrations ≥ 0.10 ppm and 60% - 120% for concentrations < 0.10 ppm. Samples were reanalyzed for any day in which the recovery criteria were not met. Data are presented for each fortified control, and summary statistical data (range, mean, standard deviation) are given. Overall recoveries are summarized as follows:

Analyte	Minimum Recovery (%)	Maximum Recovery (%)	Mean Recovery (%)	Standard Deviation of Mean	N
Aldicarb	60.7	93.6	77.8	6.5	103
Aldicarb Sulfoxide	69.5	112	94.6	7.1	103
Aldicarb Sulfone	82.1	102	93.4	4.9	103

All control samples, except two, contained no detectable quantities (ND) of aldicarb or the two metabolites. One Oregon control was reported to contain 0.006 ppm aldicarb sulfoxide. One California control was reported to contain 0.001 ppm aldicarb and 0.002 ppm aldicarb sulfoxide.

The field trial results are summarized in Table 5. The registrant contends that a few plants at the end of rows were subjected to an excessive application of aldicarb, and this is reflected in the amount of material actually applied (Table 5). This excessive application is attributed to spills and leaks from gravity flow application (GFA) equipment as the tractor stops or turns at the end of the row.

Table 5: Aldicarb Residues¹ in/on Potatoes from In-Furrow Application of Aldicarb at 3 lbs. a.i./acre

Trial Location	Application Rate (lbs. a.i./A) calc./wt. ²	Center Row Maximum Residue (ppm)	Center Row Average Residue ³ / Standard Deviation (ppm)	End Row Maximum Residue	End Row Average Residue ⁴ / Standard Deviation (ppm)
Colorado (92-112)	3.12/ 2.98	0.11	0.05 $\pm$ 0.02	1.11 ⁵	0.22 $\pm$ 0.31
Colorado (92-113)	2.83/ 2.98	0.15	0.06 $\pm$ 0.02	0.68	0.10 $\pm$ 0.14
Nebraska (92-114)	2.84/ 2.84	0.15	0.03 $\pm$ 0.03	0.09	0.04 $\pm$ 0.02
Florida (92-115)	2.87/?	0.57	0.21 $\pm$ 0.12	1.04 ⁶	0.25 $\pm$ 0.25
Minnesota (92-118)	3.00/ 2.84	0.40	0.17 $\pm$ 0.08	0.98 ⁷	0.18 $\pm$ 0.21
Oregon (92-119)	2.85/ 3.21	0.04	0.04 $\pm$ 0.01	0.06	0.03 $\pm$ 0.02
Oregon (92-120)	2.85/ 3.04	0.05	0.04 $\pm$ 0.00	0.06	0.03 $\pm$ 0.02
Montana (92-121)	2.79/?	0.26	0.10 $\pm$ 0.06	1.75 ⁸	0.23 $\pm$ 0.44
Michigan (92-122)	3.03/ 5.92	0.56	0.16 $\pm$ 0.11	1.16 ⁹	0.24 $\pm$ 0.37
Michigan (92-123)	3.02/ 5.92	0.91 ¹⁰	0.40 $\pm$ 0.21	3.13 ¹¹	0.53 $\pm$ 0.77
Washington (92-124)	2.86/?	0.2	0.00 $\pm$ 0.01	0.02	0.00 $\pm$ 0.01
Washington (92-125)	2.86/ 3.25	0.06	0.03 $\pm$ 0.02	0.04	0.03 $\pm$ 0.02
Idaho (92-126)	2.97/ 3.54	0.13	0.05 $\pm$ 0.03	0.30	0.07 $\pm$ 0.06
Idaho (92-127)	2.83/ 3.34	0.00	0.00	0.02	0.00 $\pm$ 0.01
California (92-128)	2.84/?	0.04	0.02 $\pm$ 0.01	0.06	0.01 $\pm$ 0.02
North Dakota (92-129)	3.01/ 3.09	0.15	0.08 $\pm$ 0.03	0.20	0.07 $\pm$ 0.08
Texas (92-130)	3.09/ 3.06	0.35	0.12 $\pm$ 0.08	0.57	0.12 $\pm$ 0.12

¹ Aldicarb sulfone equivalents. Analytes in a sample with no detector response were assigned 0.000 (ND); analytes with a response but < 0.02 ppm were assigned 0.02 ppm.

² First entry is by equipment calibration. Second entry is by amount used (weighed residual Temik) divided by plot area.

³ N = 30 tubers.

⁴ N = 24 tubers.

⁵ One sample $\geq$ 1.0; second highest, 0.88 ppm.

⁶ One sample $\geq$ 1.0; second highest, 0.72 ppm.

⁷ Second highest, 0.48 ppm.

⁸ Three samples $\geq$ 1.0: 1.19, 1.75, 1.02. Next highest, 0.24 ppm.

⁹ Three samples $\geq$ 1.0: 1.10, 1.15, 1.16. Next highest, 0.45 ppm.

¹⁰ Next highest, 0.78, 0.73 ppm..

¹¹ Four samples $\geq$ 1.0: 1.65, 1.57, 1.89, 3.13. Next highest, 0.77 ppm.

Variation in Magnitude and Character of Aldicarb Residues in Potatoes from Temik®-Treated Fields

Field Phase

Eight field trials were conducted in 1990 in Florida (1), Washington (2), Michigan (2), Maine (1), Pennsylvania (1), and Idaho (1). All plots were treated at the maximum label rate of 3 lbs.a.i./acre or 2 lbs. a.i./acre (Maine). Application was either at planting or at crop emergence. Control plots (0 X) were maintained at each location. Pertinent field trial information is summarized in Table 6.

A total of 1000 tubers were collected per each treated plot. Fifty sampling points were uniformly distributed throughout each plot and 20 potatoes were taken at each point. Additionally, 10 whole plants were taken at each location (except PA). Samples were boxed and sent overnight (ambient) to Rhone Poulenc Ag Company, RTP, NC. Samples were frozen and sent (presumably frozen) to one of four labs, as follows:

Location	Analytical Laboratory
Florida	Rhone-Poulenc Ag Co.: RTP, NC
Michigan (2)	McKenzie Laboratories, Inc.; Phoenix, Arizona
Maine, Pennsylvania	Morse Laboratories, Inc.; Sacramento, California
Washington (2), Idaho	CYAL, Inc.; Morrisville, NC

Table 6: 1990 Field Trials for the Application of Temik® 15G to Potatoes					
Location (Trial Number)	Application		Plot Size (ft.)	Irrigation	PHI (days)
	Rate (lbs. a.i./A)	Timing, Procedure			
Maine (90-107)	2.18	Top dress over row, 1" band, at emergence. Gravity flow.	1700 X 113.3, 40 rows	None	97
Washington (90-129)	2.96	Band- over row at emergence. Gravity flow.	489 X 92, 32 rows	Overhead (center pivot)	97
Washington (90-130)	2.95	9" band over row at emergence. Gravity flow.	100 X 170, 60 rows	Overhead (center pivot)	123
Idaho (90-146)	2.94	At planting, in furrow, soil incorporated. Gravity flow.	460 X 96, 32 rows	None	148
Pennsylvania (90- 191)	2.62	At planting, in furrow. Gravity flow.	500 X 220.7	Overhead	132
Florida (90-026)	3.03	At planting, in furrow soil incorporated. Gravity flow.	106 X 478	None	106
Michigan (90-095)	3.00	Soil incorporated band- at emergence. Gravity flow.	300 X 136, 48 rows	Overhead (center pivot)	100
Michigan (90-096)	3.14	At planting in furrow. Gravity flow.	300 X 136, 48 rows	Overhead (center pivot)	120

The registrant states that samples were stored for up to 18 months prior to analysis. From the information provided, the exact storage interval for the various samples from the various locations cannot be determined. For McKenzie Laboratories, Inc., samples were stored for at least 8.5 months before extraction. For Morse Laboratories, Inc. samples from Maine were stored for at least 13.4 months before extraction; samples from Pennsylvania were stored for at least 14.5 months before extraction.

Analysis

Samples were analyzed by the hplc procedure (SOP 900015) described above under potato processing. Some control samples were fortified by each laboratory with each of the three analytes at concentrations of 0.02 ppm, the nominal limit of quantitation, to

5.0 ppm and analyzed concurrent with the samples.

Results

Fortification recoveries are summarized in Table 7. The dates of analyses of most of the fortified controls are not given and are not correlated with the specific samples ran concurrently. The registrant notes that spike recoveries were outside the acceptable range of 70% - 120% for concentrations >0.10 ppm and 60% - 120% for concentrations ≤ 0.10 ppm on five occasions. The samples analyzed with the out-of-control spikes are not identified.

From each location, groups of 100 tubers were individually analyzed until the standard error for the total residues was < 0.01 ppm. This procedure required the analysis of 100 tubers only for all locations except Washington 90-129, where 300 analyses were required to achieve a standard error ($s.d./n^{1/2}$) ≤ 0.01 ppm. A total of 1000 tubers were analyzed for field variability. In addition, 761 tubers from individual plants were analyzed to establish variability within a plant. Results are presented, by participating laboratory, for all analyses for all field trials. Summary data are also presented for each location. Sample chromatograms are presented by each laboratory.

Table 7: Recoveries of Aldicarb and Its Metabolites from Fortified Controls				
Analyte	Spike Level ($\mu\text{g/g}$)	Laboratory	Recovery Range (%)	Mean Recovery/S.D. (%)
Aldicarb	0.1	Rhone-Poulenc	59 - 72	65 ± 4.6 (n = 10)
		CYAL	82 - 105	93 ± 3.7 (n = 120)
		Morse	75 - 88	81 ± 3.9 (n = 17)
	0.5	Rhone-Poulenc	54 - 76	66 ± 6.2 (n = 9)
	0.02	Rhone-Poulenc	60 - 87	74 ± 11 (n = 4)
		McKenzie	70 - 89	78 ± 4.7 (n = 34)
		Morse	69 - 88	80 ± 5.6 (n = 33)
	0.05	Rhone-Poulenc	57 - 63	n = 2
	0.20	Morse	77 - 87	83 ± 2.9 (n = 16)
		McKenzie	70 - 94	81 ± 6.0 (n = 37)
Aldicarb Sulfoxide	0.1	Rhone-Poulenc	87 - 114	96 ± 5.1 (n = 12)
		CYAL	63 - 103	85 ± 7.4 (n = 120)
		Morse	72 - 101	89 ± 7.2 (n = 17)
	0.5	Rhone-Poulenc	76 - 106	90 ± 8.1 (n = 9)
	0.02	Rhone-Poulenc	102 - 126	117 ± 11 (n = 4)
		McKenzie	76 - 122	96 ± 11 (n = 35)
		Morse	69 - 105	89 ± 9.2 (n = 32)
	0.05	Rhone-Poulenc	98 - 111	n = 2
	0.2	Morse	73 - 96	88 ± 7.8 (n = 16)
	1.0	McKenzie	81 - 109	95 ± 9.4 (n = 37)
Aldicarb Sulfone	0.1	Rhone-Poulenc	87 - 130	96 ± 13 (n = 10)
		CYAL	66 - 128	94 ± 11 (n = 120)
		Morse	84 - 97	89 ± 3.8 (n = 17)
	0.5	Rhone-Poulenc	66 - 94	83 ± 7.8 (n = 9)
	0.02	Rhone-Poulenc	87 - 114	101 ± 13 (n = 4)
		McKenzie	72 - 116	89 ± 9.1 (n = 35)
		Morse	73 - 100	89 ± 6.0 (n = 33)
	0.05	Rhone-Poulenc	87 - 88	n = 2
	0.2	Morse	81 - 100	90 ± 4.6 (n = 16)
	1.0	McKenzie	70 - 113	90 ± 8.6 (n = 37)

Results for the in-field portion of the study are summarized in Table 8.

Table 8: Summary of In-Field Individual Potato Tuber Analyses ^{1,2}				
Location	Number of Tubers	Range ($\mu\text{g/g}$)	Average/Standard Deviation ($\mu\text{g/g}$)	Relative Standard Deviation (%)
Florida (90-026)	100	<0.01 - 0.543	0.085 $\pm$ 0.076	89.4
Michigan (90-095)	100	<0.01 - 0.374	0.089 $\pm$ 0.060	67.4
Michigan (90-096)	100	<0.01 - 0.150	0.050 $\pm$ 0.030	60.0
Maine (90-107)	100	0.042 - 0.342	0.140 $\pm$ 0.073	52.1
Washington (90-129)	300	0.041 - 1.30 ³	0.295 $\pm$ 0.182	61.7
Washington (90-130)	100	0.021 - 0.225	0.057 $\pm$ 0.032	56.1
Idaho (90-146)	100	<0.01 - 0.065	0.019 $\pm$ 0.014	73.7
Pennsylvania (90-191)	100	<0.01 - 0.153	0.046 $\pm$ 0.019	41.3
¹ Potatoes harvested by hand from 50 equally spaced locations within the field. ² Results reported as aldicarb sulfone equivalents. N.D. values assigned by CBRS <0.01 ppm, the level of sensitivity (Rhone Poulenc SOP-90015). The registrant assigned 0.000 to N.D. Values between N.D. and the 0.02 ppm limit of quantitation were assigned 0.02 ppm and used in the calculation of the average. NOTE THAT AVERAGE VALUES ARE SOMEWHAT REDUCED BY USING 0.000 FOR N.D.'S. Values were not corrected for recoveries. ³ Two values exceeded the 1.0 ppm tolerance, 1.30 ppm and 1.04 ppm.				

Two potato tubers out of 1000 exceeded the 1 ppm tolerance. Both of these potatoes were from a WA trial. No potatoes had residues in excess of the tolerance from another WA trial. The only apparent difference in the two trials was the PHI, 26 days longer in the trial with no tubers having residues > 1 ppm.

The registrant concludes that the size of the relative standard deviations (40% - 90%) indicates a "significant variability in residues." The registrant further notes that 6 of the 8 trials had average residues below 0.1 ppm and that the highest average was 0.3 ppm. In all cases 95% of the residues were within about 2X of the mean. The maximum values are 4X to 6X the mean. Thus, the variability is attributed to "...a small percentage of tubers with residues much higher and atypical of the rest of the field."

The results of the analyses of the tubers from individual plants, 10 from each location, are summarized in Table 9.

Table 9: Variability of Total Aldicarb Residues Within Potato Plants¹

Location	Minimum Residue Range ² ($\mu\text{g/g}$)	Maximum Residue Range ³ ($\mu\text{g/g}$)	Average Residue Range ⁴ ($\mu\text{g/g}$)	Maximum Range In Plant ⁵ ($\mu\text{g/g}$)	Overall Average ⁶ ($\mu\text{g/g}$)	Relative Standard Deviation Range ⁷ (%)	Average Relative Standard Deviation ⁸ (%)
Florida (90-026)	0.042 - 0.141	0.056 - 0.326	0.050 - 0.206	0.371; 4.5	0.12	6.9 - 54.9	24
Michigan (90-095)	0.042 - 0.080	0.065 - 0.606	0.049 - 0.168	0.545; 9.9	0.10	17.0 - 121	46
Michigan (90-096)	0.022 - 0.077	0.042 - 0.187	0.042 - 0.117	0.110; 2.4	0.06	0.0 - 42.9	27
Maine (90-107)	0.042 - 0.102	0.083 - 0.176	0.054 - 0.123	0.134; 4.2	0.09	11.3 - 63.2	37
Washington (90-129)	0.041 - 0.187	0.336 - 1.036	0.128 - 0.995	0.995; 25	0.23	22.7 - 92.4	55
Washington (90-130)	0.000 - 0.042	0.042 - 0.338	0.035 - 0.142	0.296; 8.0	0.06	0.0 - 75.4	51
Idaho (90-146)	0.000 - 0.022	0.020 - 0.065	0.002 - 0.022	0.065; 6.5	0.06	0.0 - 350	109

¹ 10 plants per location. All tubers on each plant (4 - 21) were individually analyzed. Results are reported as aldicarb sulfone equivalents and are not corrected for recoveries. N.D. values were assigned 0.000 $\mu\text{g/g}$. Detectable values <0.02 $\mu\text{g/g}$ were assigned 0.02 $\mu\text{g/g}$. Use of 0.01 $\mu\text{g/g}$ (limit of sensitivity) for N.D. would yield somewhat higher results.

² Range of minimum residues across the ten plants.

³ Range of maximum residues across the ten plants.

⁴ Range of average residues across the ten plants.

⁵ Maximum range (maximum concentration less minimum concentration) found within a plant and maximum/minimum.

⁶ Average of average residues for each of the ten plants.

⁷ Range of standard deviations of the averages (See footnote no. 4).

⁸ Average of the standard deviations of the averages.

Substantial variability was found within the tubers of a given plant, among the plants of a given location, and among the plants of different locations. The residue levels on individual potatoes of one plant varied by as much as a factor of 25X. The average residue ranges show differences among the plants at a given location. For the plants at a given location, the average residue level (overall average) was about the same as the average for the in-field portion of the study. However, the average relative standard deviations (of the average of the ten plants) are consistently lower than those of the corresponding field samples.

cc: Aldicarb Subject File, RF, Aldicarb Registration Standard File, Sepehr Haddad (Special Review, SRRD), M. Clifford (SAB, HED), Karen Whitby (CCB, HED), S. Funk.

RDI:A. Rathman:10/12/93:M. Metzger:10/14/93:E. Zager:10/14/93:

H7509C:CBRS:S.Funk:305-5430:CM#2:RM803:Sf(0993.12):10/07/93.