9-2-97

MEMORANDUM

SUBJECT: Malathion Reregistration. Residue Chemistry: Magnitude of the Residue in Dates [860.1500 & .1520], Six-Months Storage Stability in Various Processed Commodities [.1380], & Analytical Methods for Determining Malathion and its Metabolite Malaoxon in/on Various RACs & Processed Commodities [.1340]. MRID Nos. 43684801, 43688701, & 43703401; RRB2 No. 15843; DP Barcode D217170; Rereg. Case No. 0248.

FROM: K. Dockter, Chemist
Reregistration Branch 2
Health Effects Division (7509C)

THRU: Alan Nielsen, Branch Senior Scientist
Reregistration Branch 2
Health Effects Division (7509C)

TO: Larry Schnaubelt / Susan Jennings, PM 72
Reregistration Branch
Special Review and Reregistration Division (7508W)

The three non-CBI studies provided in this data package are:

1. Determination of the Magnitude of Residues of Malathion and Malathion Oxygen Analog in Dates from Trees Treated with Malathion 5 Dust - Gown 95-01, 147-page report completed 5/10/95 to satisfy data requirements of Guidelines 860.1500 & .1520 **[a time extension was granted for .1520]** - analyses performed by Pacific Analytical of Carlsbad, CA - MRID No. 43688701.

2. Stability of Malathion and Malaoxon in Various Processed Commodities **[Cottonseed Meal, Hulls & Bleached & Deodorized Oil; Wheat Bran, Flour, Middlings & Shorts: Tomato Dried Pomace, catsup, & Juice]** During 6 Months of Frozen Storage EN-CAS 93-0038B 440-page report completed 6/12/95 to satisfy data requirements of Guideline 860.1380 **[the waiver requested was denied]** - performed at EN-CAS Analytical Labs. of Winston-Salem, NC - MRID No. 43684801.

3. Determination of Malathion and its Metabolite Malaoxon in/on Various **[i.e., 90]** Raw Agricultural and Processed Commodities - JSC JCode 2139 534-page report completed 6/30/95 to satisfy data requirements of Guideline 860.1340 performed at Jellinek, Schwartz & Connolly, Inc. of Arlington, VA.

The Tentative Residue Chemistry Data Summary through 5/14/93 indicates that all these studies are required. They are discussed below.

CONCLUSIONS:

Study No. **1:**

1. The analytical method is adequate for determining the magnitude of residues in/on dates from trees treated with malathion.

2. The highest levels of residues found, 3.3 ppm malathion and 0.3 ppm malaoxon, are below the established tolerance of 8 ppm in/on **dates** PRE-H.

3. A **date** processing study is not required.

4. The proposed use requires a label amendment to accommodate the 7th application on **date trees**, i.e., 40 lbs EP/A 7 days pre-harvest.

Study No. **2:**

1. The analytical methods are adequate for determining the stability of malathion residues in processed commodities from **cottonseed, wheat, and tomatoes** after 6 months frozen storage.

2. The residues are stable in **cottonseed** meal, hulls, bleached & deodorized oils, **wheat** bran, flour, middlings, & shorts, & **tomato** dried pomace, catsup, & juice stored frozen for 6 months.

Study No. **3:**

The analytical methods are adequate for determining the magnitude of residues of malathion in/on the following 90 commodities [**alfalfa** forage & hay, **avocado, bell pepper, blueberry, bulb onion, clover, cottonseed** RAC, meal, hulls, crude oil, refined oil, & bleached & deodorized [B & D] oil, **cucumber, dry bean, field corn** grain, forage, fodder, Wet milled [starch, crude oil, refined oil, B & D oil], Dry milled [medium grits, meal, flour, crude oil, refined oil, B & D oil], & grain dust, **grapes** RAC, raisin, wet pomace, dry pomace, raisin waste, & juice, **grass, pasture** forage & hay, **green onions, head lettuce, leaf lettuce, lima bean, oranges** RAC, peel, dried pulp, oil, molasses, & juice, potatoes RAC,

granules, chips, wet peel, dry peel, rice grain, straw, polished rice, hulls, bran, & grain dust, **sorghum grain**, **snap bean**, **spring wheat** grain, forage, straw, bran, patent flour, middlings, shorts, & grain dust, **strawberry**, **sweet cherry**, **sweet corn** K+CWHR & forage, **tart cherry**, **tomatoes** RAC, wet pomace, dry pomace, puree, catsup, & juice and **winter wheat** grain, forage, straw, bran, patent flour, middlings, shorts, & grain dust.

RECOMMENDATIONS:

1. We recommend that the information in these studies be added to the data base for malathion reregistration.

2. The registrant be required to submit a label amendment to accommodate the 7th application on **date trees**, i.e., 40 lbs EP/A 7 days pre-harvest.

Detailed Considerations

Study No. **1:** Malathion residues on dates.

In response to an Agency letter dated 9/30/93, Gown Co. has submitted this study of generic residue data on dates for the reregistration of malathion [Gown Malathion 5 Dust, EPA Reg. No. 10163-142]. In the cover letter to the transmittal document, the registrant stated that the previously submitted information, MRID Nos. 43269401 & 43269402 could also be used to satisfy data requirements of Guidelines 860.1500 & .1520.

An evaluation of the analytical method and residue data given in the current study follows below.

Tolerances are established for residues of the insecticide malathion [O,O-dimethyl dithiophosphate of diethyl mercaptosuccinate] in or on many racs including grapes [PRE-H] at 8 ppm.

MAGNITUDE OF RESIDUES - **FIELD TRIAL:**

Two Deglet Noor [semi-soft] variety date trees at Thermal, CA were treated with 6 applications at the maximum label rate of 85 lbs. EP/A/application from 8/26/94 to 9/30/94, which was 21 PHI. A 7th application of 40 lbs. was applied on 10/13/94 [7 PHI]. We note that this last application is not on the current label. Composite treated & untreated samples were placed-in coolers, delivered to the lab, frozen within 9 hrs., & stored at -20 C until extracted.

Previously, we had required field trials at two CA sites of a different registrant, which see F. Toghrol 3/11/93 review; CBRS 11364. Also required at that time, were residue data for the fresh fruit as well as a processing study for two varieties of dates [soft & semi-soft].

Gown argues that the data presented in the current study represent the worst case, and asks that the Agency accept this data to represent both the RAC and the processed commodity. As justification, Gown stated, "dates at harvest are at the lowest moisture percentage and consequently, the highest residue level". Also, "Information provided by date growers & shippers indicates":

1. Moisture content of Deglet Noor dates at harvest is 1421%; average about 16%.

2. After storage, cleaning & packing it is 21%.

3. Medjool [soft] dates average moisture content at harvest as well as after storage, cleaning and packing is 20%.

- ANALYSES:

On 11/11/94 & 1/18/95, samples including a matrix spiked sample were extracted and analyzed by GC/FPD[w/ phosphorus selective filters] for malathion and malaoxon.

Sample preparation entailed placing a 40 g aliquot of minced composite sample into a 32 oz. jar w/ a teflon lined lid. Then 1 mL of 10 ug/mL of tributyl phosphate, triethylphosphorthioate and triphenyl phosphate as surrogates was added. After the addition of 400 mL of chloroform, the jars were capped and shaken overnight. Then the shakeate was filtered thru glass wool into a flask containing 60 g of anhydrous sodium sulfate, the flask stoppered, shaken, and allowed to sit for 1 hr. A 100 mL portion of the sample was evaporated to dryness, the residue dissolved in 1 mL acetone, and placed in an autosampler vial at a final volume of 4 mL for analysis by GC/FPD w/ an LOD of 0.004 ppm. An additional 40 g aliquot of the sample was spiked with 320 ug of malathion & malaoxon, the "QC Sample", and treated as above. The instrument parameters were given; the data acquired by HP Chemstation.

- RESULTS:

Recoveries of surrogates ranged from 72 to 100%. Recoveries of

the target analytes were: malathion 76-138%; malaoxon 99-130%.

Residues in samples from treated plots were: malathion 1.4-3.3 ppm; malaoxon 0.2-0.3 ppm. Residues from untreated controls were below the LOD; 0.004 ppm. Gown concludes that these data support, "the proposed seasonal use pattern".

If approved, the proposed use would require a label amendment.

Study No. **2**: 6 months stability in processed commodities.

The study was designed using the combined crop group approach suggested by our Guidance dated 1/14/93.

The processed commodities [**cottonseed** meal, & **hulls; wheat bran**, flour, middlings, & shorts; **tomato** dried pomace, catsup, & juice] from various 1993 Cheminova Agro A/S field trials [controls & malathion treated] were sampled for this 6-month storage stability study. Bleached & deodorized **cottonseed** oil samples were obtained from a local grocer in 1994 and included in this study.

The samples were thoroughly mixed and 10-g subsamples were weighed into 8- or 16-oz amber bottles with caps. Samples were separately fortified with malathion or malaoxon at 0.5 ppm and stored at <-5 C. Control and recovery samples were also stored. To facilitate analyses, storage set up dates ranged from 2/23/94 to 11/29/94.

The samples were analyzed at 0, 1, 3, & 6 months for malathion and malaoxon.

The cottonseed oils were extracted with acetonitrile for 30 min. by shaking, filtered, partitioned with hexanes, and concentrated to 1-2 mL. The cottonseed meal & hulls and all wheat matrixes were blended with 80/20 acetonitrile/water for 2 min., filtered, partitioned with hexanes [cottonseed matrixes] and evaporated to aqueous. The tomato matrixes were soaked in water for 15 min., extracted with acetonitrile, filtered, and evaporated to aqueous. All aqueous extracts were mixed with deionized water and sodium chloride, partitioned with dichloromethane and evaporated to dryness.

All extracts were mixed with acetone and activated charcoal, filtered, evaporated to dryness, redissolved in acetone/dichloromethane and passed through a silica gel column. The extracts were then redissolved in polyethylene glycol/acetone and analyzed by GC/FPD selective for phosphorous. The LOQ for all matrices for each analyte was 0.05 ppm.

- RESULTS:

The concurrent procedural recoveries of malathion and malaoxon were 64-112% and 74-125%, respectively. The low and high values for both analytes were with cottonseed hulls and tomato dried pomace, respectively.

The mean recoveries of malathion and malaoxon after 6-months frozen storage were 87-112% and 84-124%, respectively. Also, analyte interconversions did not occur during frozen storaqe.

Study No **3:** "Malathion Master Analytical Method"

This study reads like a review; a description of many **analytical** methods for determining magnitude of residues of malathion on 39 plant commodities with tolerances.

The "general or master method is with minor modifications identical to American Cyanamid Method M-1886 entitled GC Method for the Determination of Malathion [CL 6,601] and Malaoxon [CL 28,967] Residues in Alfalfa [Green Forage and Hay] When Using Continuous Automated Sample Injections, **issued 3/7/89".** This method is described in detail in Appendix C. It is now termed EN-CAS Method No. ENC-19/94 entitled Analytical Method for the Gas Chromatoqraphic Determination of Malathion and Malaoxon Residues in/on Alfalfa When Using Continuous Automated Sample Injections, **issued 12/30/94;** AASI Study No. AA920101. This AASI study is cited as the first of 39 "Residue Reports". It is entitled Magnitude of Residue of Malathion and its Metabolite Malaoxon in/on Alfalfa Raw Agricultural Commodities Harvested After Ground and Aerial Treatment **[MRID #43546101], issued 2/10/95.**

Many of these "Residue Reports" have been reviewed. [See R. Perfetti 9/6/94 review; CBRS Nos. 13197, 13690, & 13784 on **sweet & tart cherries, oranges, & bell peppers,** & D. Hrdy 5/8/95 review; CBRS Nos. 14467, 14863, 14945, & 14949 on **lima & snap beans, field & sweet corn, cucumbers, head & leaf lettuce, potatoes, sorghum, strawberries, tomatoes, field corn commodities, snap bean processed commodities, & tomato processed commodities.]** Supporting storage stability data are required for all of these commodities. Also, a feed additive tolerance is required for tomato pomace.

The analytical method includes extraction with acetonitrile [or aqueous mixtures of it] & partitioning with hexanes &/or dichloromethane. Activated carbon and silica gel solid-phase extraction cartridges are used for cleanup. Analytes are quantitated by GC/FPD selective for phosphorous. Matrix-specific minor modifications are given. The LOQ is 0.01 ppm [or 0.05 ppm

for most feed commodities]. Recoveries of malathion and malaoxon averaged 89.6 & 98.2%, respectively. Over 3,000 analyses were performed by En-Cas Analytical Labs. Winston-Salem, NC. Validation was performed by Agvise Labs. Northwood, ND.

cc: Kd, Reg. Std. File, SF, & RF.

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