9-23-97

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

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Malathion.Reregistration; Chem No. 057701; Case No. 0248; Storage Stability Studies in Various Raw and Processed Commodities; GLN 860.1380; Cheminova Agro A/S; MRID 43910901. DP Barcode D223392.

FROM: William Smith, Chemist
Chemistry And Exposure Branch I (CEB-I)
Health Effects Division (7509C)

THROUGH: F. B. Suhre, Branch Senior Scientist
Chemistry And Exposure Branch I (CEB-I)
Health Effects Division (7509C)

TO: Larry Schnaubelt / Susan Jennings
Reregistration Branch 2
Special Review and Reregistration Division (7508W)

Attached please find a review of data depicting the storage stability of malathion and malaoxon on various raw agricultural and processed commodities. The submission was reviewed by Dynamac Corporation under the supervision of HED. This information has undergone secondary review in CEB-1 and is consistent with Agency policies.

The submitted storage stability data are acceptable. They indicate that residues of malathion and malaoxon are relatively stable under frozen storage conditions for at least 12 months in/on: cottonseed and cottonseed meal, hulls, and bleached and deodorized oils; wheat straw, bran, flour, middlings, and shorts; leaf lettuce; tomatoes and tomato catsup, juice, and dried pomace. The only significant declines in combined residues were observed in wheat grain and forage and potato tubers. These apparent residue declines will be taken into consideration during tolerance reassessment of these commodities.

No additional storage stability data are required for raw agricultural and processed commodities since most samples collected from recent studies pertaining to magnitude of the residue in plants were stored for less than one year.

(1)

Storage stability data are required for livestock commodities if the registrant wishes to maintain use of malathion involving direct animal (dermal) treatments.

Attachment - Dynamac review of Registrant's Response to Residue Chemistry Data Requirements (CB 16944; D223392)

cc: W. Smith (CEB-I), SF, Reg Std File, RF

7509C:CEB-I:WOS:wos:Rm805A:CM2:305-5353:09/15/97
RDI: ResChemTeam (09/23/97) FSuhre (09/23/97).

MALATHION
Shaughnessy No. 057701; Case 0248
(CBRS No. 16944; DP Barcode D223392)

Registrant's Response to Residue Chemistry Data Requirements

May 29, 1997

Contract No. 68-D4-0010

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA

Submitted by:
Dynamac Corporation
The Dynamac Building
2275 Research Boulevard
Rockville, MD 20850-3268

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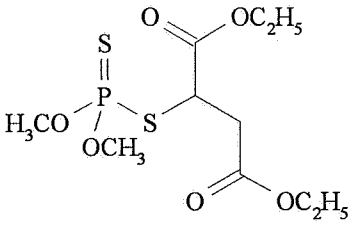
MALATHION



REGISTRANT'S RESPONSE TO RESIDUE CHEMISTRY DATA REQUIREMENTS

RESIDUE CHEMISTRY CONSIDERATIONS

Shaughnessy No. 057701; Case 0248

(CBRS No. 16944; DP Barcode D223392)

BACKGROUND

In response to the Malathion Reregistration Standard Guidance Document, dated 2/88, Cheminova Agro A/S, through its authorized representative Jellinek, Schwartz & Connolly, Inc. (JSC), submitted the final results of a study investigating the storage stability of malathion and malaoxon residues in/on various raw agricultural and processed commodities (1996; MRID 43910901). The preliminary results of the storage stability study indicated that residues of malathion and malaoxon are relatively stable under frozen storage conditions for up to 6 months in/on representative raw agricultural and processed commodities (DP Barcodes D213229 and D219313, 11/7/95, D. Miller; and DP Barcode D217170, 9/2/97, K. Dockter). The data from the current submission are reviewed herein to assess their adequacy in fulfilling residue chemistry data requirements for malathion reregistration.

The qualitative nature of malathion residues in plants is adequately understood based on acceptable metabolism studies involving alfalfa, lettuce, cotton, and wheat. The residues of concern are malathion and malaoxon. The qualitative nature of the residue resulting from oral dosing of ruminants and poultry is adequately understood; neither malathion nor malaoxon was detected in any tissue. If the direct livestock treatment uses of malathion are removed from all product labels, the tolerances for residues of malathion in animal commodities can be revoked. However, if the direct livestock treatment uses of malathion are supported, then appropriate dermal metabolism and magnitude of the residue in meat, milk, poultry, and egg studies are required.

Tolerances for residues in/on food/feed commodities are currently expressed in terms of malathion *per se* (*O,O*-dimethyl dithiophosphate of diethyl mercaptosuccinate) [40 CFR §180.111, §185.3850, §185.7000, and §186.3850]. The HED Metabolism

Committee has determined that the parent compound malathion and the metabolite malaoxon are the compounds to be regulated in plant commodities.

CONCLUSIONS AND RECOMMENDATIONS

1. The submitted storage stability data are acceptable. They indicate that residues of malathion and malaoxon are relatively stable under frozen storage conditions (-5 C) for at least 12 months in/on: cottonseed and cottonseed meal, hulls, and bleached and deodorized oils; wheat straw, bran, flour, middlings, and shorts; leaf lettuce; tomatoes and tomato catsup, juice, and dried pomace. The only significant declines in combined residues were observed in wheat grain and forage and potato tubers. Residues of malathion *per se* declined ~40% in/on wheat grain, ~32% in/on wheat forage, and ~35% in/on potato tubers following 12 months of storage. Residues of malaoxon declined ~26% in/on wheat grain, ~14% in/on wheat forage, and ~30% in/on potato tubers following 12 months of storage. These apparent residue declines should be taken into consideration during tolerance reassessment of these commodities.

2. The matrices chosen in the subject study sufficiently represent all types of raw agricultural and processed commodities for which malathion is registered. No additional storage stability data are required for raw agricultural and processed commodities since most samples collected from recent studies pertaining to magnitude of the residue in plants were stored for less than one year.

3. Storage stability data are required for livestock commodities if the registrant wishes to maintain use of malathion involving direct animal (dermal) treatments.

DETAILED CONSIDERATIONS

Residue Analytical Methods

Samples of raw agricultural and processed commodities from the submitted storage stability studies were analyzed using American Cyanamid Method M-1866 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," with individual matrix modifications. Method M-1866 is a GLC method with flame photometric detection (FPD) operating in the phosphorus mode. . Sample analyses were performed by EN-CAS Analytical Laboratories (Winston-Salem, NC). The limit of quantitation (LOQ) for each compound was 0.05 ppm in all matrices.

The registrant provided method validation data. Separate untreated samples were fortified with either malathion or malaoxon at 0.5 ppm each. The results of the method

validation are presented in Table 1. Sample calculations and chromatograms were also submitted. The method validation recoveries indicate that Method M-1866 is adequate for determining residues of malathion and the malaoxon metabolite in/on: cottonseed and meal, hulls, and bleached and deodorized oil; wheat grain, forage, straw, bran, flour, middlings, and shorts; leaf lettuce; potatoes; and tomatoes and tomato catsup, juice, and dry pomace.

Storage Stability Data

CBRS has previously evaluated (DP Barcodes D213229 and D219313, 11/7/95, D. Miller) the interim results of a study investigating the storage stability of malathion and malaoxon residues in/on various raw agricultural commodities (RACs). It was reported that residues of malathion and malaoxon are stable under frozen storage conditions for up to 6 months in/on representative RACs of: cottonseed; leaf lettuce; potato tubers; wheat grain, forage, and straw; and tomatoes. With respect to the storage stability of processed commodities, another CBRS review (DP Barcode D217170, 9/2/97, K. Dockter) reported that malathion residues of concern are stable under frozen storage conditions for up to 6 months in: cottonseed meal, hulls, and bleached and deodorized oils; wheat bran, flour, middlings, and shorts; and tomato dried pomace, catsup, and juice.

Table 1. Method validation of Method M-1866 using samples of various raw agricultural and processed commodities fortified separately with malathion and/or malaoxon at 0.5 ppm.

Crop Commodity	Percent Recovery [a]	
	Malathion	Malaoxon
Cottonseed	80, 83 (82)	95, 102 (99)
- Cottonseed meal	65, 72 (69)	92, 93 (93)
- Cottonseed hulls	83, 89 (86)	93, 99 (96)
- Bleached and deodorized oil	81, 84 (83)	92, 94 (93)
Wheat grain	89, 103 (96)	91, 97 (94)
Wheat forage	98, 99 (99)	109, 112 (111)
Wheat straw	92, 97 (95)	106, 112 (109)
- Wheat bran	104, 105 (105)	111, 111 (111)
- Wheat flour	85, 95 (90)	97, 98 (98)
- Wheat middlings	99, 101 (100)	104, 105 (105)
- Wheat shorts	91, 92 (92)	91, 93 (92)
Leaf lettuce	97, 100 (99)	100, 102 (101)
Potato tubers	91, 92 (92)	95, 97 (96)
Tomato fruit	81, 87 (84)	86, 96 (91)
- Tomato, dried pomace	83, 90 (87)	86, 96 (91)
- Tomato catsup	89, 94 (92)	98, 101 (100)
- Tomato juice	81, 86 (84)	99, 102 (101)

[a] Each recovery value represents a single sample; average recovery values are noted in parentheses.

Cheminova Agro A/S has now submitted (1996; MRID 43910901) the final results of the storage stability study initiated in 1992. The final report contains data reflecting 12-month storage interval for cottonseed (oilseed crop), wheat grain, forage, and straw (non-oily grain), leaf lettuce (leafy vegetable crop), potato tubers (root crop), and tomato fruit (fruiting vegetable crop), and processed commodities representative of the crop groupings. Descriptions of the study method (e.g., sample preparation and analyses) were provided and were similar to the initial report. To reiterate briefly, untreated samples were homogenized with dry ice, subsampled, and separately fortified with either 0.5 ppm of malathion or 0.5 ppm of malaoxon, and then stored frozen at -5 C. Replicate samples were removed from storage and analyzed after 12 months of frozen storage. Samples were analyzed using GLC/FPD method previously described. Quantitation limits for the analytical method were 0.05 ppm for each analyte.

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Apparent residues of the malathion and its malaoxon metabolite were each less than the LOQ (<0.05 ppm) in/on one unfortified sample each of cottonseed and meal, hulls, and bleached and deodorized oil; wheat grain, forage, straw, bran, flour, middlings, and shorts; leaf lettuce; potatoes; and tomatoes and tomato catsup, juice, and dry pomace. The storage stability recoveries of malathion and its malaoxon metabolite from fortified samples are presented in Table 2.

Table 2. Storage stability and concurrent method recovery (fresh fortification recovery) from samples of various RACs and processed commodities fortified separately with malathion and its malaoxon metabolite at 0.5 ppm and stored frozen at -5 C.

Storage Period (months)	Fortified Compound	Fortification Level (ppm)	Fresh Fortification Recovery (%) [a]	Storage Stability Recovery (%)	Corrected Storage Stability Recovery (%) [b]
Cottonseed					
12	malathion	0.50	80, 83 (82)	72, 78	88, 95
	malaoxon	0.50	95, 102 (99)	89, 89	90, 90
Cottonseed meal					
12	malathion	0.50	65, 72 (69)	72, 74	104, 107
	malaoxon	0.50	92, 93 (93)	82, 85	88, 91
Cottonseed hulls					
12	malathion	0.50	83, 89 (86)	78, 82	91, 95
	malaoxon	0.50	93, 99 (96)	82, 83	85, 86
Cottonseed bleached and deodorized oil					
12	malathion	0.50	81, 84 (83)	80, 81	96, 98
	malaoxon	0.50	92, 94 (93)	86, 91	92, 98
Wheat grain					
12	malathion	0.50	89, 103 (96)	56, 59	58, 61
	malaoxon	0.50	91, 97 (94)	66, 73	70, 78
Wheat forage					
12	malathion	0.50	98, 99 (99)	66, 68	67, 69
	malaoxon	0.50	109, 112 (111)	95, 95	86, 86
Wheat straw					
12	malathion	0.50	92, 97 (95)	74, 75	78, 79
	malaoxon	0.50	106, 112 (109)	78, 83	72, 74
Wheat bran					
12	malathion	0.50	104, 105 (105)	100, 101	95, 96
	malaoxon	0.50	111, 111 (111)	80, 85	72, 77
Wheat flour					
12	malathion	0.50	85, 95 (90)	91, 95	101, 106

(continued; footnotes follow)

Storage Period (months)	Fortified Compound	Fortification Level (ppm)	Fresh Fortification Recovery (%) [a]	Storage Stability Recovery (%)	Corrected Storage Stability Recovery (%) [b]
Wheat middlings					
12	malathion	0.50	99, 101 (100)	97, 98	97, 98
	malaoxon	0.50	104, 105 (105)	88, 93	84, 89
Wheat shorts					
12	malathion	0.50	91, 92 (92)	93, 95	101, 103
	malaoxon	0.50	91, 93 (92)	89, 90	97, 98
Leaf lettuce					
12	malathion	0.50	97, 100 (99)	92, 93	93, 94
	malaoxon	0.50	100, 102 (101)	106, 111	105, 110
Potato tubers					
12	malathion	0.50	91, 92 (92)	56, 64	61, 70
	malaoxon	0.50	95, 97 (96)	67, 67	70, 70
Tomato fruit					
12	malathion	0.50	81, 87 (84)	75, 77	89, 92
	malaoxon	0.50	86, 96 (91)	92, 93	101, 102
Tomato dried pomace					
12	malathion	0.50	83, 90 (87)	87, 88	100, 101
	malaoxon	0.50	86, 96 (91)	82, 102	90, 112
Tomato catsup					
12	malathion	0.50	89, 94 (92)	91, 96	99, 104
	malaoxon	0.50	98, 101 (100)	99, 107	99, 107
Tomato juice					
12	malathion	0.50	81, 86 (84)	84, 87	100, 104
	malaoxon	0.50	99, 102 (101)	100, 101	99, 100

[a] Average fresh fortification recovery values are noted in parentheses.
[b] Calculated by dividing the storage stability recovery by the average fresh fortification recovery.

Study summary: The submitted storage stability data are acceptable. They indicate that residues of malathion and malaoxon are relatively stable under frozen storage conditions (-5 C) for at least 12 months in/on: cottonseed and cottonseed meal, hulls, and bleached and deodorized oils; wheat straw, bran, flour, middlings, and shorts; leaf lettuce; tomatoes and tomato catsup, juice, and dried pomace.
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(continued; footnotes follow)

storage. Residues of malaoxon declined ~26% in/on wheat grain, ~14% in/on wheat forage, and ~30% in/on potato tubers following 12 months of storage. These apparent residue declines should be taken into consideration during tolerance reassessment of these commodities.

The matrices chosen in the subject study sufficiently represent all types of raw agricultural and processed commodities for which malathion is registered. No additional storage stability data are required for raw agricultural and processed commodities since most samples collected from recent studies pertaining to magnitude of the residue in plants were stored for less than one year.

Storage stability data are required for livestock commodities if the registrant wishes to maintain use of malathion involving direct animal (dermal) treatments.

EPA MEMORANDA CITED IN THIS REVIEW

CB No.:	15273 and 16257
DP Barcode:	D213229 and D219313
Subject:	Storage Stability Studies in Various Raw and Processed Commodities
From:	D. Miller
To:	S. Jennings
Dated:	11/7/95
MRID(s):	43549001 and 43684801

CB No.:	15843
DP Barcode	D217170
Subject:	Storage Stability Studies in Various Processed Commodities
From:	K. Dockter
To:	L Schnaubelt/S. Jennings
Dated:	9/2/97
MRID(s):	43684801, 43688701 & 43703401

MASTER RECORD IDENTIFICATION NUMBERS

The citations for the MRID documents referred to in this review are presented below.

43910901 Clayton, B. (1996) Stability of Malathion and Malaoxon in Various Raw Agricultural and Processed Commodities During Twelve Months of Frozen Storage: Lab Project Number: 93-0038C. Unpublished study prepared by Cheminova Agro A/S. 324 p.