9/16/94

MEMORANDUM

SUBJECT: **Metolachlor.** Addendum to RED. Magnitude of Residue in Legumes (Succulent and Dried). DP Barcode: D206103; CBRS No. 14160; MRID No.: 432957-01; Case No. 0001.

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Metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide] is a List A chemical which is registered for use as a preemergence herbicide for selective control of grassy weeds in corn, cotton, non-bearing citrus fruit, nonbearing grapes, peanuts, pod crops, potatoes, safflowers, grain or forage sorghum, woody ornamentals, stone fruits, and tree nuts. Data supporting the preemergent or preplant incorporated use of metolachlor had been previously submitted to the Agency. These data were reviewed and accepted by the Agency and on the basis of those residue data the registration was granted and tolerances were set. The EPA since determined that these data may be considered suspect because they were generated by Craven Laboratories of Austin TX. Subsequent to this, Ciba-Geigy agreed to supply new data to supplement any data previously generated by Craven Laboratories.

The present study fulfills this agreement. The study (1994; 43295701) depicts residues of metalochlor and its metabolites [regulated as the acid-hydrolyzed derivatives 2-(2-ethyl-6-methylphenyl)amino-1-propanol and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone, expressed in terms of parent metolachlor] in/on the two legume commodities. Specifically, data are provided from eight field trial studies conducted in major commercial legume production areas to determine the magnitude of metolachlor residues remaining in or on peas (dried peas, hay, pods, and vines) and beans (vines, hay, dried, pods), and snap beans (vines and pods). These data are evaluated herein to determine their adequacy in fulfilling residue chemistry data requirements for reregistration.

The qualitative nature of the residue in plants is adequately understood; the Metolachlor

Reregistation Eligibility Document (dated June 28 1993) and the Metolachlor Registration Standard (dated March 1980) concluded that the qualitative nature of the residue is adequately understood in corn and soybean. Metabolism of metolachlor involves conjugation with glutathione, breakage of this bond to form the mercaptan, conjugation of the mercaptan with glucuronic acid, hydrolysis of the methyl ether, and conjugation of the resultant alcohol with a neutral sugar. Residues of concern in corn and soybeans are metolachlor and its metabolites, and are determined as the acid-hydrolyzed derivatives CGA-37913 (the propanol derivative) and CGA-49751 (the morpholinone derivative).

Tolerances have been established for residues of metolachlor in/on a variety of raw agricultural and in animal commodities [40 CFR §180.368 (a), (b), and (c)]. The tolerances listed in 40 CFR §180.368 are expressed in terms of the combined residues (free and bound) of metolachlor and its metabolites, determined as the 2-(2-ethyl-6-methylphenyl)amino-1-propanol and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone acid-hydrolyzed metabolites (calculated as parent metolachlor). As there are no Codex MRLs for residues of metolachlor, there are no questions with respect to Codex/U.S. tolerance compatibility.

Adequate methods are available for enforcement of tolerances. Methods for determining the combined residues os metolachlor and its metabolites (as the derivatives) are described in PAM, Vol II as Method I (plants: GC-NPD) and Method II (animals:GC-MS).

CONCLUSIONS

The available data support the following tolerances for pre-emergent or pre-plant incorporated usage of metolachlor:

Peas

- 0.5 ppm on *peas, succulent*
- 0.1 ppm on *peas, dried*
- 15 ppm on *pea vines*
- 2 ppm on *pea hay*

Beans

- 0.5 ppm on *beans, succulent*
- 0.1 ppm on *beans, dried*
- 3 ppm on *bean forage*

- 3 ppm on *bean straw/hay*

RECOMMENDATIONS

The registrant should propose tolerances consistent with the above findings. CBRS has updated the RED to incorporate these recommendations: the updated RED is present as an attachment to this review.

DETAILED CONSIDERATIONS

Metolachlor is a preemergence herbicide registered for use on a variety of crops for selective control of grassy weeds. Emulsifiable concentrate formulation of metolachlor are registered as Dual® 8E (EPA Reg. No. 100-597), Medal® (EPA Reg. No. 100-688), Dual® (EPA Reg. No. 100-673), and Dual® II (EPA Reg. No. 100-711). These products are currently registered for use on pod crops as a preemergent (pre) or preplant incorporated (PPI) treatment, with a maximum use rate of 3.0 lbs ai/A. Dual® 8E was chosen as a representative formulation for use in this study; Dual® 25G (EPA Reg. No. 100-638) and Dual® IIG (EPA Reg. No. 100-712) are granular formulations, but are not currently registered for use on seed and pod vegetables.

Pesticide Application and Sample Harvest/Preparation

Ciba-Geigy submitted data (1994; MRID 43295701) from eight field studies conducted in WA(2), CA, CO, KS, MI, TN, and WI depicting residues of metolachlor in various legume crops. At each test site, legume plots were treated PPI with the Dual 8E formulation at 3.0 lbs ai/A (1x rate for soils with at least 3% organic matter).

Legumes were grown under normal agricultural conditions. Residue samples were collected at random from within the plots at maturity. The samples were not trimmed, cleaned, or washed, with any surface soil removed only by knocking or shaking the substrate.

After collection, legume vines and hay and dried and succulent pod and seed vegetables were frozen and shipped with dry ice to Ciba-Geigy in Greensboro, NC. Upon arrival, samples were stored frozen at $< -15^{\circ}$ C for 8 to 27 months until preparation for analysis.

Sample preparation was performed according to FDA Pesticide Analytical manual, Vol. I and Ciba SOP No. 7.20. After preparation, the samples were stored in polyethylene bags and maintained frozen until analysis.

Analytical Methods

Analytical Method AG-338 (with minor modifications) was used to determine residues of metolachlor as CGA-37913 and CGA-49751 in legume vines and hay, and dried and succulent pod and seed vegetables. Briefly, metolachlor residues are converted to CGA-37913 and CGA-49751 by refluxing overnight with 6 N hydrochloric acid. Filtered extracts are then analyzed for CGA-37913 and CGA-49751 as follows:

> CGA-37913: An aliquot of the acid extract is made basic with sodium hydroxide solution and partitioned with hexane. The hexane phase is chromatographed on a alumina column

followed by a silica Sep-Pak. Analysis is performed on a NPD-equipped GC in nitrogen-specific mode. Residues of CGA-37913 are reported as the parent metolachlor equivalent using a molecular weight conversion factor of 1.47. The limit of detection is reported as 0.03 ppm as the metolachlor equivalent.

CGA-49751: An aliquot of the acid extract is partitioned into dichloromethane which is washed with a sodium carbonate solution and chromatographed on an alumina column to remove interfering materials. The CGA-49751 is then converted to the chloroethyl derivative by reaction with boron trichloride and 2-chloroethanol at 90° C for 30 minutes. The product is partitioned into hexane and chromatographed on an alumina column. CGA-49751 is determined on a GC equipped with a NPD in the nitrogen specific mode. Residues of CGA-49751 are reported as the parent metolachlor equivalent using a molecular weight conversion factor of 1.14. The limit of detection is 0.05 ppm as the metolachlor equivalent.

The results of field trials are reported in Table 1. The residue values reported in these tables were not corrected for method recoveries.

CBRS makes the following observations and comments with respect to the values appearing in this table:

- procedural (or fresh fortification) recoveries were less than ideal, ranging from 67% to 163% (mean of 115%) for CGA-37913 and from 79% to 190% (mean of 117%) for CGA-49751. Nevertheless, CBRS concludes that these recoveries are acceptable.[1]

- Residues of metolachlor were detected in 16 of 45 control samples in the study, and ranged up to ca. 0.2 ppm. The field researcher stated that during the sampling of the pea vines from the field test in KS, he believes he may have mistakenly placed

[1] CBRS recognizes that good percentage recoveries of metolachlor may be difficult to achieve due to the severity of the extraction procedure (overnight refluxing with 6 N HCl). The method used by the registrant is similar to that previously approved by the Agency which currently appears in the PAM. In addition, CBRS recently concluded that the method was adequate following a submission in which recoveries of 70% to 197% were observed (see 6/13/86 Metolachlor FRSTR, the 6/28/93 Reregistration Eligibility Document, and the 6/23/94 Metolachlor Addendum to RED (S. Hummel, CB No. 13482).

the treated samples into the sampling bag for the control samples.[2] Additionally, the field researcher has observed that windblown topsoil

[2] After evaluating the results and noting that residue values in the control were several times higher than those in the treated samples, CBRS has corrected the data to account for this switch.

Table 1.	Residues of Metolachlor (and its derivitized metabolites) in/on Various Legume Vegetables, Legume Forage, and Legume Hay Crops Following Application of the 8E Formulation at 3.0 lbs ai/A (1x).				
Commodity	**Location**	**PHI [a] (Days)**	**Residues in ppm**		
			CGA-37913	**CGA-49751**	**Metolachlor equivalents**
Hay, pea	WA	121	0.64[b] 0.74	0.25 0.37	0.90 1.1
	KS (reprep)	100	0.46 0.44	0.17 0.14	0.63 0.58
Hay, bean	WA	120	0.54 (0.40)[c] 0.46 (0.34)	0.51 (0.34) 0.44 (0.36)	1.0 (0.75) 0.89 (0.69)
	CO	102	0.87 0.61	1.3 1.0	2.2 1.6
	CO	122	0.89 0.81	0.55 0.61	1.4 1.4
	CA	119	0.54 0.82	0.66 1.3	1.2 2.2
	MI	120	0.32 0.22	0.10 0.09	0.41 0.31
Vines, Pea	KS[d]	61	0.82 (0.57, 0.53)	0.14 (0.29, 0.18)	0.97 (0.85, 0.70)
	WI	57	0.15 (0.18) 0.16 (0.19)	<0.05 (<0.05) <0.05 (0.06)	0.15 (0.18) 0.16 (0.24)
	CA	52	6.1 (7.5) 4.5 (4.8)	3.5 (4.0) 3.0 (3.0)	9.6 (12.0) 7.4 (7.8)
Peas, dried	KS	100	0.04 (0.04) 0.03 (<0.03)	<0.05 (<0.05) 0.05 (<0.05)	0.04 (0.04) 0.03 (<0.08)
	WA	121	<0.03 <0.03	<0.05 <0.05	<0.08 <0.08
Pods, pea	WI	57	0.05 0.06	<0.05 <0.05	0.05 0.06
	CA	52	0.31 0.29	0.13 0.11	0.44 0.39
Vines, snap bean	WI	57	0.32 0.36	0.22 0.28	0.54 0.64
	CA	71	2.2 2.1	0.49 0.58	2.7 2.7
	TN	60	1.2 1.5	0.23 0.32	1.5 1.8
	MI	63	0.47 0.42	0.15 0.15	0.62 0.58
Vines, bean	WA	60	0.47 (0.42) 0.56 (0.35)	0.45 (0.85) 0.39 (0.63)	0.91 (0.85) 0.96 (0.63)
	CO	62	0.18 0.31	0.26 0.32	0.44 0.63

Table 1. Residues of Metolachlor (and its derivitized metabolites) in/on Various Legume Vegetables, Legume Forage, and Legume Hay Crops Following Application of the 8E Formulation at 3.0 lbs ai/A (1x).

Commodity	Location	PHI [a] (Days)	Residues in ppm		
			CGA-37913	CGA-49751	Metolachlor equivalents
Vines, bean (cont'd)	CA	57	0.88 0.86	0.44 0.50	1.3 1.4
	TN	60	0.70 0.81	0.15 0.17	0.85 0.98
	MI	60	0.71 (0.77) 0.60 (0.65)	0.39 (0.32) 0.36 (0.37)	1.1 (1.1) 0.96 (1.0)
Beans, dried	WA	120	<0.03 <0.03	<0.05 <0.05	<0.08 <0.08
	CO	102	<0.03 (0.03) <0.03 (<0.03)	<0.05 (<0.05) <0.05 (<0.05)	<0.08 (0.03) <0.08 (<0.08)
	CA	119	0.03 <0.03	<0.05 <0.05	0.03 <0.08
	TN	65	0.06 0.04	<0.05 <0.05	0.06 0.04
	MI	95	0.04 (<0.03) 0.04 (<0.03)	<0.05 (<0.05) <0.05 (<0.05)	0.04 (<0.08) 0.04 (<0.08)
Bean pods	WI	57	<0.03 0.03	<0.05 <0.05	<0.08 0.03
Pods, snap bean	CA	71	0.17 (0.24) 0.13 (0.29)	0.07 (0.07) 0.08 (0.09)	0.24 (0.31) 0.20 (0.37)
	MI	63	0.11 0.09	<0.05 <0.05	0.11 0.09
	TN	60	0.36 0.27	0.06 0.06	0.42 0.32

[a] Pre-harvest interval
[b] Values represent replicate analysis
[c] Parenthetical values represent subsequent re-analysis (confirmation of previous analyses)
[d] These samples represent the putative switch of the control (check) and treated samples, and have been corrected in this table.

between the treated and untreated plots may have contributed to the detections.

Geographic representation is adequate. The available data indicate that following PPI application of the Dual® 8E formulation to various cultivars of pea and bean crops, the CBRS-proposed tolerances appearing in Table 2 are appropriate.

Table 2. Summary of Maximum Detected Field Trial Residue Values and CBRS-recommended Tolerances.

Crop	RAC Item	Maximum Detected Field Trial Residue, ppm (at days PHI)	CBRS recommended tolerance
Peas	succulent	0.44 (52 dys.)	0.5
	seed	0.04 (100 dys.)	0.1
	vine	12 (52 dys.)	15
	hay	1.1 (121 dys.)	2
Bean	succulent	0.42 (60 dys.)	0.5
	seed	0.06 (65 dys.)	0.1
	forage	2.7 (71 dys.)	3
	straw/hay	2.2 (102 dys)	3

Storage Stability Data

Previously reviewed storage stability studies indicated that metolachlor metabolite hydrolysates CGA-37913 and CGA-49751 were stable during storage at -15 C for up to two years in/on peanut nutmeats, potatoes, corn grain, and corn forage (B. Cropp-Kohlligian, CBRS No. 8317, 4/16/92). Samples discussed in the present submission were analyzed after 19 to 27 months of freezer storage. Although the existing database for storage stability of CGA-37913 and CGA-49751 extends to 24 months, CBRS believes that the reported residues for pod and seed vegetables, vines, and hay are not expected to be adversely affected by freezer storage for up to 27 months. There are thus no storage stability concerns associated with the present study.

RDI: FSuhre:9/12/94;MMetzger:9/13/94;EZager:9/13/94.
cc: w/Attachment: SF, Rereg. Std. File.
w/o Attachment: RF, Circ., DJM.

METOLACHLOR
(Shaughnessy No. 108801)
(Case No. 0001)

TASK 2B

Reregistration Eligibility Document: Residue Chemistry Considerations

June 28, 1993

Contract No. 68-DO-0142

Submitted to:

U.S. Environmental Protection Agency
Arlington, VA 22202

Submitted by:

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NOTE: This Document is attached to the 10/4/94 Memo; Subject: Metolachlor (108801) Addendum to RED.

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