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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Alachlor(090501) - Processing/Cooking Studies
[Accession No. 264946, RCB No. 1443]

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[Signature]

Monsanto Agricultural Company has submitted protocols for peanut and legume processing studies, a request for a time extension for the peanut studies, and a request for a waiver from the requirement for processing studies on corn sugar. Processing/cooking studies were required for residues of alachlor and its metabolites in legumes, peanuts, and corn sugar in a 3(c)2(B) letter dated June 9, 1986. The 3(c)2(B) letter was subsequently discussed in a telephone conference between EPA and Monsanto personnel on July 23, 1986. The following personnel were present: Lois Rossi, Jane Talarico, Susan Hummel, and Edward Zager from EPA; and Lyle Gingerich, Sam Dubelman, and Stephen Muench, from Monsanto. The 3(c)2(B) letter required a protocol for the studies within three months, a progress report within six months, and a final report within 12 months. The purpose of these studies is to obtain a better estimate of actual exposure and possible reduction of residues when food is prepared for consumption.

The Processing/Cooking Studies were to be carried out as outlined in Subdivision O §174-4(c)(2)(iv) of the Pesticide Assessment Guidelines. Specifically, processing studies must simulate commercial practices as closely as possible. RAC samples used in processing and cooking studies must contain field-treated detectable residues, preferably at or near the tolerance level, so that concentration/reduction factors for the various processed/cooked commodities can be determined. This may require field treatment at

exaggerated application rates to obtain sufficient residue levels for processing studies. Processing/cooking studies utilizing spiked samples are not acceptable. The residue must be determined before and after processing/cooking. Raw data, including sample chromatograms, must be submitted. A description of the treatment program (location, rate, PHI) must be submitted, as well as a complete description of the processing/cooking.

The following Processing Studies were required.

- Fresh succulent peas, canned. These peas must be analyzed with and without the liquid in the can.
- Dry beans, processed into canned beans. These beans must be analyzed with and without the liquid in the can.
- Peanuts, dry roasted
- Peanuts, oil roasted
- Peanuts, processed into peanut butter
- Corn Sugar
- Corn Meal

The following Cooking Studies were required.

- Fresh succulent peas, cooked. Two batches are required. The first batch must be boiled in 1 inch of water for ten (10) minutes. A second batch of two (2) pounds of peas must be microwaved without water for 12-14 minutes on high. The cooked peas must be drained before analysis.
- Dried split peas, cooked. Cook one (1) pound peas in one (1) gallon water for 15 to 20 minutes.

Monsanto included a protocol for the peanut studies, Monsanto protocol #87-24-R-1, dated August 18, 1986. Monsanto proposes to process peanut nutmeat into dry roasted peanuts, oil roasted peanuts, and peanut butter. According to Monsanto, they do not have sufficient supplies of treated peanuts to conduct the processing studies. Therefore, they must grow additional peanuts. They propose to plant peanuts in April, 1987; and submit the processing study in September, 1988. This is reasonable, provided Monsanto submits progress reports in March and September, 1987, and in March, 1988.

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Monsanto included a protocol for the legume studies, Monsanto protocol #86-01-02-01, dated August 27, 1986. They indicate that legumes already grown will be processed. They propose to submit the processing studies in December, 1986, along with the residue studies on the legume crops.

Monsanto indicates that a corn processing study was submitted on September 9, 1986, which includes data on corn meal. Monsanto requests a waiver from the requirements for processing studies on corn sugar.

We will respond to each of the protocols and the waiver below.

Corn Processing

Monsanto requests a waiver from the requirements for processing studies on corn sugar for several reasons. They indicate that residues of alachlor, per se, have never been found in corn; that the highest residue of alachlor metabolites ever found in corn grain is <0.042 ppm; that the process for making corn sugar is proprietary, and that no plant or pilot plant could be found to do the study.

RCB Comment

The fact that alachlor, per se, has never been detected in corn is not relevant, when alachlor and its metabolites are the residue of concern. Residues of alachlor DEA and HEEA metabolites have been detected in corn. Additionally, no data reflecting analysis for DEA and HEEA metabolites have been submitted for the maximum treatment of alachlor on corn, the preplant or preemergence treatment, followed by late post-emergence layby treatment. This treatment would be expected to result in higher residues than other registered treatments. Secondly, Monsanto has not submitted any residue data where corn has been treated at the maximum allowable rate and the maximum number of applications. Thirdly, the process for making corn sugar (dextrose) from corn starch is discussed in the same Corn Refiner's Association publication referenced by Monsanto. Processing for production of high fructose corn sweeteners and other newly marketed corn sweeteners may be more difficult to obtain, and was not intended to be required. Lastly, availability of a commercial plant or pilot plant to perform the processing is not a valid reason for a data waiver. Processing for processing studies needs to simulate commercial practice as closely as possible.

Upon further consideration, we have determined that the data required on corn starch as part of the corn processed products from wet milling will be adequate. However, it may be in the registrant's best interest to

determine if residues of alachlor and its metabolites concentrates or decreases in the processing of corn starch to corn sugar. Additionally, we note that the corn processing data recently submitted by Monsanto (currently in review in RCB) does not appear to include data from the wet milling of corn grain. (Starch is a product of the wet milling of corn.) These data are required.

Peanut Processing

Monsanto plans to plant peanuts in April, 1987. Peanuts will be treated either preemergently, or at cracking, using either the EC or MT formulations. Two trials will be done in the southeast peanut growing area, and two trials will be done in the southwest peanut growing areas. One preemergent and one at cracking treatment will be done at each location. One check sample will come from each location. Monsanto SOP, RES-86-GSOP-071-0, "Instructions for Field Residue Plots," by S. Dubelman, dated January, 1986, will be followed. A copy of the protocol was enclosed.

To produce dry roasted peanuts, shelled peanuts will be batch roasted in an oven at 350F for 60 minutes. Oil roasted peanuts will be fried in food grade peanut oil at 290F for 10 minutes. Peanut butter will be produced by fine grinding shelled dry roasted peanuts and adding 1.5% pulverized table salt and 2% partially hydrogenated food grade soybean oil.

Samples will be analyzed by "Analytical Method for the Determination of 2,6-Diethylaniline (DEA) and 2-(1-Hydroxyethyl)-6-ethylaniline (HEEA) Yielding Alachlor Metabolites in peanut nutmeat, dry roasted peanuts, oil roasted peanuts and peanut butter," no author, no date. A copy of this method is included in the submission (Accession No. 264945). Briefly, the samples are extracted with 20% acetonitrile/water, hydrolyzed in base to produce DEA and HEEA, and the DEA and HEEA steam distilled into dilute acid using specially fabricated glassware. The distillate is made basic and partitioned into methylene chloride, and solvent exchanged into 0.02% TEA in isooctane. The sample is cleaned up using normal phase HPLC; separate fractions of DEA and HEEA are collected. DEA is derivitized with HFB for analysis. HEEA is derivitized with TFAA. The derivitized fractions are analyzed by GC/ECD. A standard curve is used for quantitation. Typical chromatograms from the analysis of peanut nutmeat were included with the method.

RCB Comments

Monsanto's proposal to submit peanut processing data in September, 1988, is appropriate, based on the need to plant additional peanuts in April, 1987.

We note that the SOP for field residue plots includes a four page form required from the field cooperators. The form includes records of sample history from planting to harvest, records of sample storage from harvest to shipping and records of time of receipt in the laboratory. This included time from sampling to freezing, and temperature and dates of storage. These storage conditions have typically been omitted from Monsanto submissions, along with dates and storage conditions from receipt in the laboratory until analysis, length of sample storage, and date of analysis. These data are needed for all residue data submissions.

We note that typical chromatograms (for peanut nutmeats) are included with the method. Typical chromatograms are needed from each time the method is used to gather residue data for EPA, not just once when the method is developed. These chromatograms have typically been omitted from Monsanto submissions, and are needed.

Monsanto proposes to treat peanuts either preemergent or at cracking. However, sequential treatments of alachlor are registered for use on peanuts. Peanuts may be treated both preplant or preemergent, and again at cracking. Additionally, a late postemergence layby treatment appears on 24(c) labels. Residue data must be submitted to reflect the maximum registered rate and the maximum number of treatments (and the minimum PHI).

For processing studies, the geographical representation is not important. However, the registrant should be reminded that processing studies must be done with samples bearing detectable residues, preferably at or near the tolerance level (or proposed tolerance level). This may require treatment at exaggerated rates.

According to our reference book; "Peanuts: Production, Processing, Products," Third Edition, edited by J. G. Woodruff, Avi Publishing Company, Westport, CT, 1983; peanuts are dry roasted by heating to 320F in an 800F oven for 40 to 60 min. Roasting in a 350F oven for 60 minutes should be comparable. Oil roasted peanuts are usually blanched before roasting (removes skin), however, blanching is not always done. Peanuts are oil roasted in coconut, cottonseed or peanut oil at 280-290F for 3 - 10 minutes, depending on the variety and desired doneness. Roasting at 280F for 5 minutes would be more reasonable than Monsanto's proposal. The process described by Monsanto for peanut butter is similar to commercial practice.

The analytical method should be adequate for the generation of the processing data required for the special review of alachlor. However, the registrant should be reminded that the analytical method has been considered to

be inappropriate for enforcement purposes (F.D. Griffith, 1/15/86, Results of MTO for Alachlor DEA Metabolites).

Valid storage stability data are also needed to support residue data. Deficiencies in Alachlor storage stability data are discussed in our memo of 5/12/86 (S. Hummel, RCB No. 448, Accession No. 260257).

Processing and Cooking of Legumes

Monsanto submitted Protocol #86-01-02-01, which is similar but not identical to the protocol outline, dated 12/20/85, reviewed in our memo of 4/18/86 (M. L. Loftus, RCB No. 478).

Monsanto proposes to plant the following legumes in the states listed.

<u>Legume</u>	<u>Location</u>
peas	MN, WA
lima beans	WI, CA
navy beans	MI
red kidney beans	IL, CA
snap beans	IN, WA
pinto beans	ND

Lasso or Lasso MT will be applied either preemergent or preplant incorporated. Monsanto SOP, RES-86-SOP-071-0, will be followed. This SOP is discussed above under peanuts. Forage, vine, and straw samples will be collected in addition to the beans and peas.

Peas and dry red kidney beans will be canned as follows. The peas and beans will be cleaned with air, washed, and the skin, etc. removed. They will be blanched at 205F for three minutes, cooled in water, and hand packed into cans with a brine tablet. The cans will be closed, and cooked in a steritort for 7.5 min at 260F. The cans will be cooled and stored at room temperature until analysis. The peas and red kidney beans will be analyzed with and without the canning liquid.

Succulent peas will be cooked in two ways. Two pounds of peas will be boiled in 1" water for 2 minutes, drained and analyzed. Two pounds of peas will be microwaved for 12 minutes, cooled in cold water, drained and frozen, then thawed and drained prior to analysis.

Dried split peas will be cooked by boiling one pound in one gallon water for 20 minutes. They will be drained before analysis.

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The analytical method to be used is, "Analytical Method for the Determination of 2,6-Diethylaniline (DEA) and 2-(1-Hydroxyethyl)-6-ethylaniline (HEEA) Yielding Alachlor Metabolites in Edible Beans and Peas by Gas Chromatography/Mass Spectrometry (GC/MS)," no author, no date. A copy of this method is included in the submission (Accession No. 264945). Briefly, the samples are extracted with 20% acetonitrile/water, hydrolyzed in base to produce DEA and HEEA, and the DEA and HEEA steam distilled into dilute acid using specially fabricated glassware. The distillate is washed with hexane, made basic, and partitioned into methylene chloride, and solvent exchanged into 0.02% TEA in isooctane. 4-Fluoro-2,6-diethylaniline (FDEA) is added at this time as an internal standard. DEA, HEEA, and FDEA are derivitized with HFB for analysis. GC/MS with selected ion monitoring (SIM) is used for analysis. A standard curve of ratios of analyte to internal standard is used for quantitation.

RCB Comments

In our review of the Monsanto protocol for the legume residue trials (M. L. Loftus, 4/18/86, RCB No. 478), we concluded that the geographical representation was inadequate; that data are required for each type of application at the maximum application rate; and that several trials at different locations within a geographic area are needed for each type of application.

Monsanto originally proposed to conduct trials for dry beans in ND, MI, WI, IL, and CA. We commented that studies are also needed in ID, CO, and NE. Monsanto has now deleted the proposed trials in WI. However, no trials in ID, CO, and NE were proposed. The deletion of trials in WI is acceptable. However, data are needed from ID, CO, and NE.

For lima beans, we concluded that trials in WI and CA would be adequate.

For peas, we concluded that to maintain registration in MN only, only field trials from MN were needed. However, to expand the use, trials were needed from OR/WA, and ID.

For snap beans (not currently registered), Monsanto proposed trials in MI and WA. For a crop group tolerance, field trials would be needed from NJ/NY, TN/NC/VA, CA and FL, in addition to MI and WA.

For a crop group tolerance for legumes, Monsanto also needs to satisfy the data gaps for soybeans (See M. L. Loftus, 10/29/86 review, S. Hummel reviews of 10/31/86, and 2/14/86). Additionally, residue data reflecting the maximum labeled use for alachlor on soybeans are needed, i.e., two sequential

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treatments at 4 lb ai/A. Alternatively, this deficiency may be resolved by removing the second treatment for soybeans from the label.

For the legume processing studies, geographic representation is not applicable. However, the registrant should be reminded that processing studies must be done with samples bearing detectable residues, preferably at or near the tolerance level (or proposed tolerance level). This may require treatment at exaggerated rates.

Additionally, complete sample history, as discussed above for peanuts, is needed, along with chromatograms from the analyses being submitted.

Monsanto proposes to cook peas for two minutes in boiling water. The 3(c)2(B) letter specified that the peas should be cooked for ten minutes in boiling water.

Monsanto proposes to cool microwaved peas in cold water. Microwaved peas should be cooled at room temperature without adding water.

Monsanto's proposals for canning dry beans and cooking dry peas are acceptable.

The analytical method submitted requires the use of custom made glassware and an internal standard. We will accept data generated by this method for the purposes of the Special Review. However, we have already concluded that the use of custom made glassware makes this method unsuitable for enforcement purposes (F. D. Griffith, 1/15/86). Additionally, RCB discourages the use of internal standards.

CONCLUSIONS AND RECOMMENDATIONS

The requested time extension for the peanut processing study and the waiver for the corn sugar study are appropriate. Our conclusions regarding the protocols are included in the body of this memo. The entire review should be sent to the registrant as comments on their protocol.

cc: R. F., circu, S. Hummel,alachlor S.F., Alachlor S.R.F.,
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RDI:EZ:12/22/86:RDS:12/22/86
TS-769:RCB:SVH:svh:RM810:CM#2:12/22/86