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

JAN 24 1986

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#6E3325 (RCB#310). Benomyl on Watercress. Evaluation of Analytical Methods and Residue Data (Accession No. 074014).

FROM: Michael P. Firestone, Ph.D., Chemist
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and

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THRU: John H. Onley, Ph.D., Section Head
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John H. Onley

Interregional Research Project No. 4 (IR-4) Assistant Coordinator Dr. W.L. Biehn, and National Director Dr. R.H. Kupelian, on behalf of IR-4 and the Agricultural Experiment Station of Florida, request the establishment of a tolerance for residues of the fungicide benomyl (methyl-1-(butylcarbamoyl)-2-benzimidazole carbamate) and its metabolites containing the benzimidazole moiety (calculated as benomyl) in or on the raw agricultural commodity (RAC) watercress at 10 parts per million (ppm). In conjunction with this tolerance proposal, IR-4 is also requesting a regional registration for benomyl use in Florida only (note: Watercress has been identified by the Agency as a minor use commodity - see EPA Draft Policy Statement on Minor Use Pesticides [OPP-30099]).

Benomyl tolerances are established on a wide variety of RAC's at levels ranging from 0.1 to 50 ppm (see 40 CFR 180.294); food additive tolerances are established as high as 125 ppm (see 21 CFR 193.30 and 561.50).

Data gaps involving animal metabolism and feeding studies have been identified in a Residue Chemistry Branch (RCB) memorandum re: Benomyl 3(c)(2)(B) Letter to Support Tolerances on Various Raw Agricultural Products and Feed Items (see C. Trichilo memorandum of May 9, 1984); these data gaps would not apply to the subject petition since watercress is not considered an animal feed item.

Benomyl has not yet been the subject of a Registration Standard.

E. I. du Pont de Nemours & Company (the registrant of benomyl) has written a letter dated October 23, 1985, authorizing EPA to refer to previously submitted data the Agency may have on file in support of the benomyl on watercress petition.

Conclusions

1. The nature of the residue in plants is adequately understood for the purposes of supporting the proposed benomyl use on watercress. The residues of concern consist of benomyl and its metabolites containing the benzimidazole moiety (i.e., MBC and 2-AB).

2. Adequate analytical methodology is available for enforcement of the proposed benomyl tolerance of 10 ppm on watercress.

3. RCB concludes that residues of total benomyl (including MBC and 2-AB) are not likely to exceed the proposed 10 ppm tolerance as a result of the proposed use on watercress grown in Florida only.

4. Since watercress is not considered an animal feed item, RCB does not anticipate a problem of secondary residues in meat, milk, poultry, and eggs resulting from the proposed use of benomyl on watercress.

5. An International Residue Limit Status sheet is included with this review as Attachment 1. Since Codex, Canada, and Mexico have not established any tolerance/limit covering residues of benomyl in/on watercress, there is no compatibility problem.

Recommendation

At this time, RCB recommends for the proposed 10 ppm benomyl tolerance on watercress, Toxicology Branch and Exposure Assessment Branch considerations permitting.

DETAILED CONSIDERATIONS

Manufacture and Formulation

The manufacturing process for technical benomyl is discussed in RCB's review of PP#4F1466 (see R. Quick memorandum of July 24, 1974). The only possible contaminant of concern, methyl 2-benzimidazole carbamate (MBC), is detected by the available enforcement methodology and, thus, is included in the tolerance expression for benomyl (note: MBC is also a major plant metabolite of benomyl). No other impurities in the technical material are expected to result in a residue problem.

The formulation proposed for use on watercress is Benlate® Fungicide (EPA Registration No. 352-354), a wettable powder which contains 50 percent active ingredient (ai) by weight. All inerts in this formulation are cleared under 40 CFR 180.1001.

Proposed Use on Watercress

For control of white mold (Sclerotinia) on watercress, apply 0.25 to 0.5 lb ai/A. Begin treatment when the disease first appears and repeat at 5- to 7-day intervals as needed. Label restrictions include the following:

> Apply by ground equipment using at least 25 gallons of water per acre;
>
> Do not apply more than four applications per fresh market crop;
>
> Do not apply within 5 days of harvest;
>
> For use in Florida only.

Nature of the Residue

The metabolism of benomyl in a wide variety of plants (beans, cotton, apples, oranges, and cucumbers) is discussed in RCB's review of PP#0G0936 (see W. Boodee memorandum of February 20, 1970). The major metabolites of benomyl in these crops were found to be methyl-2-benzimidazole carbamate (MBC) and 2-amino-benzimidazole (2-AB). These metabolites in turn break down to carbon dioxide and other small organic fragments. Based on the consistency of the metabolic profile in the aforementioned crops, RCB now concludes that the nature of the residue in/on plants is adequately understood for the purposes of the proposed use of benomyl on watercress. The residues of concern include benomyl, MBC, and 2-AB (i.e., benomyl and its metabolites containing the benzimidazole moiety).

Analytical Methodology

The analytical method used to quantitate residues of benomyl, MBC, and 2-AB in watercress and water is titled "Determination of Benomyl and its Metabolites by Cation Exchange HPLC" (T. Spittler, R. Marafioti, and L. Lahr, J. Chromatography, 317:527-31, 1984). The submitted Minor Use Residue Form also cites the method of Kirkland, Holt, and Pease (J. Agric. and Food Chem., 21:368, 1973) as a reference.

The second method is described in the Pesticide Analytical Manual - Volume II (PAM-II), and has previously been reviewed by RCB in conjunction with PP#6E1812 and PP#3F2924. This method involves acid hydrolysis to convert benomyl to MBC and to free conjugated metabolites, extraction with ethyl acetate, and cleanup by liquid-liquid partitioning.

The residues are determined by HPLC using a strong cation exchange resin (Zipax) and a mobile carrier of 0.025N HNO_3 and 0.025N tetramethyl ammonium nitrate and a UV detector at 280 nm. The reported method sensitivity is 0.02 ppm benomyl and 0.05 ppm 2-AB in watercress and 0.006 ppm benomyl and 0.02 ppm 2-AB in water. All control values are reportedly at or below the level of sensitivity, except for one water sample (benomyl/MBC = 0.03 ppm).

At fortifications of 0.2 ppm benomyl and 2-AB, recoveries of 105 percent benomyl/77 percent 2-AB in watercress and 111 percent benomyl/111 percent 2-AB in water are reported.

A fluorometric procedure, described in PAM-II, is also available for regulatory purposes.

RCB concludes that adequate analytical methodologies are available to enforce the proposed 10 ppm benomyl in/on watercress tolerance.

Residue Data

Watercress and water samples were stored frozen for approximately 4 months prior to analysis. A sample of watercress fortified with 0.2 ppm benomyl contained 0.19 ppm after 2 months' storage.

RCB concludes that adequate storage stability data are available to support the available watercress residue data.

A single residue field study was conducted in Altamonte Springs, Florida. Benomyl was applied at either 0.5 lb ai/A (the maximum proposed rate) or 1.0 lb ai/A (2X rate). Watercress

beds received a total of four applications; 5-day intervals were used between each application and a 5-day PHI was observed.

The petitioner analyzed four samples of watercress treated at each application rate, as well as three samples of water for both application rates sampled at 0, 1, and 24 hours after treatment (note: Benomyl was applied when water was flowing through watercress beds and samples were reportedly taken approximately 1000 ft downstream).

The following watercress residue data are reported:

Application Rate (lb ai/A)	PHI (days)	Residue Levels (ppm) Benomyl*	2-AB
0.5 (1X)	5	3.9-6.2	0.05-0.08
1.0 (2X)	5	10.0-13.0	0.14-0.16

*Residues of MBC are reported as benomyl equivalents.

Residue levels of benomyl and 2-AB in all (0-, 1-, and 24-hr PHI's) water samples were reportedly < 0.006 and < 0.02 ppm, respectively.

RCB concludes that residues of total benomyl (parent, MBC, and 2-AB) are not likely to exceed the proposed 10 ppm tolerance as a result of treatment according to the proposed use on watercress grown in Florida only.

Residues in Meat, Fat, Milk, Poultry, and Eggs

Since watercress is not considered a livestock feed item, RCB does not anticipate a problem of secondary residues in meat, fat, milk, poultry, and eggs resulting from the proposed benomyl use on watercress.

Other Considerations

An International Residue Limit Status sheet is included with this review as Attachment 1. Since Codex, Canada, and Mexico have not established any tolerance/limit covering residues of benomyl in/on watercress, there is no compatibility problem.

Attachment 1: International Residue Limit Status sheet

cc:R.F., Circu., MPFirestone, EAB, EEB, PMSD/ISB, FDA, PP#6E3325
RDI:JHOnley- 1/15/86 :RDSchmitt- 1/16/86
RCB:TS-769:MPFirestone:CM#2:Rm800b:557-1991
Typed by KENCO - 1/23/86

Attachment 1:

F. Stoes 12/31/85

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL: Benomyl

PETITION NO.: 6E3325

CCPR NO.:

REVIEWER: Michael P. Firestone

Codex Status

☐ No Codex Proposal Step 6 or above

Residue (if Step 9):

Crop(s)	Limit (mg/kg)
none (on watercress)	

Proposed U.S. Tolerances

Residue: benomyl and its metabolites containing the benzimidazole moiety (calculated as benomyl)

Crop(s)	Tol. (ppm)
watercress	10

CANADIAN LIMIT

Residue:

Crop(s)	Limit (ppm)
none (on watercress)	

MEXICAN TOLERANCIA

Residue:

Crop(s)	Tolerancia (ppm)
none (on watercress)	

Notes:

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