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

FEB 19 1987

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Benomyl processing studies for several commodities submitted in response to a 3(c)(2)(B) letter. RCB No. 675 Accession No. 261596

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In response to the Agency's 3(c)(2)(B) letter of 5/14/85, du Pont has submitted results of benomyl processing studies for apples, peaches, rice, oranges, and tomatoes. The 3(c)(2)(B) letter required three additional studies: pineapples, milk, and soybeans. Du pont states in their cover letter that these three studies will be submitted shortly. The available studies are discussed below.

Analytical Method

The method used for all studies discussed below is a variation of the PAM II developed by Pease and Gardiner (see J. Ag. Food Chem., 17, 267 (1969). This method determines residues of benomyl, methyl benzimidazole carbamate (MBC), and 2-amino benzimidazole (2-AB). Benomyl and MBC are determined as MBC and reported as benomyl; 2-AB is determined and reported as 2-AB. Recovery and control data are included in the following discussions.

Apples

Apples trees were treated thirteen times with an exaggerated rate of benomyl (3 oz. a.i./A/application; the registered use is 1-3 oz. a. i. per 100 gallons of water for thorough cover sprays at 7 to 14 day intervals) and harvested 18 days after the last applications. The stage of maturity at harvest is described as "ripe (?) fruit."

It is not clear what this means. The apples were processed shortly after harvest, but analysis was not until three months later, and the conditions of storage are not stated. The processed products were analyzed for residues of benomyl and its metabolite 2-AB.

No residues of benomyl (<0.01 ppm) or 2-AB (<0.01 ppm) were uncovered in any control samples. Recoveries for benomyl at fortifications of 0.02 to 1 ppm were 55-110% (average = 97%) for apples and apple products. The recovery from apple jelly is listed as 0%, but du Pont has discounted this analysis, claiming that the sample was not spiked. The recovery from the prewash water was 280%.

Recoveries of 2-AB from apples and apple products were 71-200%. The 200% value was from a 0.02 ppm fortification. At higher fortifications (0.22-1.0 ppm) recovery from apples was 82-100%, and recoveries from processed apple products were 71-110%. Again, these data do not include apple jelly, which apparently was not spiked and also do not include the recovery value for prewash water, which was 190%.

No residues of benomyl or 2-AB were found in any control samples (<0.01 ppm), and 2-AB was not found in any treated samples (<0.01 ppm). The results for benomyl, per se, are summarized in the following table:

Benomyl Residues in Apple Byproducts

Sample	Benomyl (ppm)	Conc. Factor
Unwashed	1.06	--
Washed	0.89	0.84
Sliced	0.22	0.21
Blanched	0.18	0.17
Wet Pomace	1.3	1.2
Dry Pomace	2.9	2.7
Canned sliced	0.10	0.09
Applesauce	0.18	0.17
Precooked slices	0.15	0.14

Apple Jelly	0.11	0.10
Unclarified Juice	0.48	0.45
Clarified Juice	0.31	0.29
Prewash water	<0.01	--
Washwater	<0.01	--

These results suggest a considerable reduction of residues (3-10x) in processing apples into food items, and an increase of residues in dried pomace (3x).

RCB's Comments

The following questions need to be answered:

1. The harvested apples are described as being "ripe?." The petitioner should describe the stage of the fruit at harvest in more precise terms. If the fruit was harvested at a stage not normally harvested, an explanation should be provided, as well as a discussion of the effect this might have on the results.

2. The fruit was processed, then stored for about three months before analysis. The petitioner should describe the conditions of storage for this period.

3. Recovery of 2-AB from apples spiked at 0.02 ppm was as high as 200%. The petitioner should repeat the recovery study for apples at 0.02 ppm.

4. Recovery of both benomyl and 2-AB from apple jelly is reported as 0%, apparently because the sample was not spiked. Recovery data from spiked apple jelly is needed.

5. Benomyl is also registered for use as a post harvest fungicide for apples. The experiments did not incorporate this use. The petitioner either repeat the study and use the maximum possible use of benomyl on apples in both the field and after harvest. If it can be established that apples intended for processing would not be treated post-harvest with benomyl, then this additional study would not be needed.

Peaches

Peach trees were treated with benomyl five times at a rate of 2 lb a.i. per acre per treatment. The peaches were havested 17 days after the final treatment and processed into canned and baked peaches. The petitioner claims that "a large percent of fruit from both controls and treated lots were in very poor condition due to bruising and being overripe (see slides)." The slides were not submitted.

Recovery from samples of baked peaches spiked with benomyl at 1.3 ppm and 2-AB at 1.1 ppm was 120% and 110%, respectively. Lye-peeled peaches spiked with 0.44 ppm benomyl and 0.36 ppm 2-AB gave recoveries of 82% and 69%, respectively.

Analysis of each fraction gave the following results:

Benomyl in Processed Products of Peaches

Sample	Benomyl (ppm)		2-AB (ppm)		Concentration Factor
	control	treated	control	treated	
Raw	0.43	5.6	<0.02	0.04	--
Washed	0.07	1.5	<0.02	<0.02	0.27
Lye Peeled	<0.02	0.42	<0.02	0.15	0.10
Canned	<0.02	<0.02	<0.02	<0.02	0.007
Baked	<0.02	0.20	<0.02	<0.02	0.04

Du pont claims that the 0.43 ppm benomyl found in untreated peaches is due to drift. Benomyl residues in the treated smples were reduced by washing and peeling by a factor of 4x upon washing and 8x upon peeling. The residues in the treated peaches were also reduced by baking by a factor of 25X.

Benomyl did not concentrate in canned peaches (<0.02 ppm).

RCB's Comments

The following questions need to be answered:

1. Recovery studies were completed for only baked and lyepeeled peaches, and these were spiked at levels considerably higher than the limit of detection. The petitioner should repeat this recovery study with raw, canned, and baked peaches fortified at the limit of detection and a higher level.

2. The petitioner claims that "a large percent of fruit from both controls and treated lots were in very poor condition due to bruising and being overripe (see slides)." The slides were not submitted. The petitioner should submit the slides that have been referenced and explain what precautions were taken to ensure that the condition of the peaches did not invalidate the study.

Rice

Rice fields were treated three times with benomyl at a rate of 2 lbs a.i./A/treatment and harvested twenty-one days after the final treatment. The following recovery data have been submitted:

Substrate	Spike (ppm)	Compound	Percent Recovery
cooked rice	0.02	benomyl	100
	0.02	2-AB	0*
unmilled rice	0.42	benomyl	133
	0.42	2-AB	45
spanish rice	0.42	benomyl	131
	0.42	2-AB	102
rice hulls	1.0	benomyl	102
	1.0	2-AB	80

*This sample was apparently not spiked with 2-AB

The rice samples were received on 10/8/85, then processed on 10/8, 10/9, and 11/1/85. Analysis was on 10/3011/13/85. The following fractions were analyzed for residues of benomyl and 2-AB:

Benomyl in Processed Products of Rice

Sample	Benomyl (ppm)		2-AB (ppm)		Concentration
	control	treated	control	treated	Factor
Unmilled Rice	<0.01	3.0	0.66	0.56	--
Rice Hulls	<0.01	13	<0.01	0.55	3.4
Rice Bran	<0.01	3.2	0.95	1.04	1.3
Uncooked Rice	<0.01	0.05	<0.01	0.01	0.02
Cooked Rice	0.01	0.04	0.01	0.04	0.03
Canned (Spanish Rice)	0.06	0.05	0.28	0.29	0.16

Benomyl concentrates in rice hulls and bran by a factor of 3.4 and 1.3X, respectively. Benomyl does not concentrate in other milled products which are: uncooked rice, cooked rice, and Spanish rice.

RCB's Comments

The following questions should be answered:

1. The petitioner should describe the storage conditions between harvest and analysis.

2. Control values for 2-AB are high for unmilled rice, rice bran and Spanish rice. The petitioner claims that this is due to interference. This should be established by using a confirmatory method.

3. The recovery studies for unmilled rice, and rice hulls are at levels considerable higher than the claimed sensitivity of the method. These studies should be repeated to include fortifications at the sensitiviy of the method. This will also afford an opportunity to spike cooked rice with 2-AB.

Additional Comments: A feed additive tolerance of 10 ppm for residues of benomyl in/on rice bran is needed (a concentration factor of 1.3X x a tolerance of 5 ppm for rice established under 40CFR§180.295).

Previously, RCB has concluded that a feed additive tolerance for residues of benomyl in/on rice bran is not needed since benomyl residues in/on rice bran did not exceed those in the r.a.c., rice (PP#5F1612/FAP#5H5084, memo of Dr. M. Nelson, 9/9/75). It should be noted, however, that the processing study included in PP# 5F1612/FAP#5H5084, was conducted on rice samples fortified at 1 and 4 ppm, whereas, those in this petition were from field samples that received label rates.

Oranges

Orange groves were treated six times with benomyl at a rate of 3 lb a.i./A/application on a seven day schedule over five week period with last application at harvest. After harvest (6/14/85) the fruit was dipped in a 2 lb a.i. benomyl/100 gallon solution, then dried.

Samples of orange juice, peel oil emulsion, unwashed oranges, prewash water, orange oil, finisher pulp, and peel oil were fortifed at 0.02 to 1 ppm with benomyl and 2-AB. Recoveries ranged from 45 to 132% for benomyl and from 80 to 173% for 2-AB. The recovery of benomyl from orange juice was 0%, apparently because of failure to spike the sample.

The oranges were processed on 6/14-6/27/85 and were received in the lab on 9/19/85. The processed fractions were analyzed in December, 1985. Storage conditions were not described. Results are given in the following table.

Benomyl in Processed Products of Oranges

Sample	Benomyl (ppm)		2-AB (ppm)		Concentration Factor
	control	treated	control	treated	
Unwashed Orange	<0.06	3.3	<0.01	0.01	--
Prewash water	0.10	16	0.01	0.09	--
Afterwash Water	0.10	8.3	<0.01	0.05	--
Washed Oranges	<0.01	0.75	<0.01	0.17	0.34
Orange Juice	<0.01	0.07	<0.01	<0.01	0.03
Pressed Liquor	<0.01	0.37	<0.01	0.11	0.12
Peeled Oil Emulsion	<0.01	0.03	<0.01	<0.01	0.02
Orange Oil	0.06	2.5	<0.01	0.01	0.76
Molasses	<0.01	0.34	<0.01	0.03	0.12
Finisher Pulp	<0.01	0.09	<0.01	<0.01	0.03
Chopped Peel	0.01	1.9	<0.01	0.02	0.58
Dry Peel	<0.01	0.56	0.23	0.26	0.34
Peel frit	0.01	1.8	<0.01	0.10	0.61

Benomyl does not concentrate in any of the processed fractions of oranges.

RCB's Commments

The following questions should be addressed.

1. The conditions of storage should be provided.

2. The recovery study for benomyl in orange juice should be repeated. Orange juice should be spiked at 0.01 ppm and a higher level, then subjected to the method.

3. The recovery studies were carried out at levels considerably higher than the claimed sensitivity of the method. These studies should be repeated to include fortifications at or near the sensitiviy of the method.

4. The 0.23 ppm 2-AB that was uncovered in the dry peel of the control sample should be confirmed by a second, confirmatory, method. If this peak results from an interference, the treated dry peel should also be subjected to a confirmatory method.

Tomatoes

Tomato plants were treated seven times with benomyl at a rate of 1 lb ai.i/A. Tomatoes were harvested on the day of the last application. The tomatoes were processed shortly after analysis. Samples not canned were frozen until analysis, except for dry pomace, which was kept in a plastic bag.

Tomatoes were spiked with benomyl at 0.11, 0.25, 0.62, and 1.02 ppm and subjected to the method; recoveries were 76-120%. Recovery of 2-AB at spiking levels of 0.03, 0.09, 0.21, 0.55, and 0.91 ppm were 67-110%.

Each fraction was analyzed with the following results:

Benomyl in Processed Products of Tomatoes

Sample	Benomyl (ppm)		2-AB (ppm)		Concentration
	control	treated	control	treated	Factor
Raw	<0.02	2.7	<0.02	<0.02	--
Raw Washed	<0.02	0.47	<0.02	<0.02	0.17
Hot Break	<0.02	<0.02	<0.02	<0.02	--
Wet Pomace	<0.02	2.9	<0.02	<0.02	1.07
Dry Pomace	<0.02	1.0	<0.02	<0.02	0.37
Uncanned Juice	<0.02	<0.02	<0.02	<0.02	----
Canned Juice	<0.02	0.38	<0.02	<0.02	0.14
Puree	<0.02	0.03	<0.02	<0.02	0.01
Paste	<0.02	0.87	<0.02	<0.02	0.32
Catsup	<0.02	0.05	<0.02	<0.02	0.02
Reconstituted Juice	<0.02	0.05	<0.02	<0.02	0.02

Benomyl does not concentrate in any of the processed fractions of tomatoes.

RCB's Comments

The following questions should be answered:

1. Recovery studies were carried out only for tomatoes, not any of the processed products, and spiking levels did not reflect the sensitivity of the method. The petitioner should carry out recovery studies on tomatoes, tomato juice, and puree at the claimed sensitivity of the method and at at least one higher fortification.

Conclusions and Recommendations

RCB has raised several questions with these studies as given in our comments. Once the petitioner has responded to these, RCB will be able to make conclusions as to the level of benomyl and metabolites in the processed products of the subject crops. Furthermore, a feed additive tolerance of 10 ppm for residues of benomyl in/on rice bran is needed (a concentration factor of 1.3X x a tolerance of 5 ppm for rice established under 40CFR§180.295).

cc: RF, Circu, SF (benomyl), Registration Standard File (benomyl), K. Arne, S. Malak, and PMSD/ISB.
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TS-769:RCB/HED:CM#2:RM814A:X557-4379:2/12/87