Petitions Control Branch and
Division of Toxic gical Evaluation

Division of Food Standards and Additives

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File: PP# 5F0426

PP #5F0426 and PP #5F0427 combined; Inorganic bromide tolerance for residues of "Trizone." Evaluation of analytical methods and residue data.

The Dow Chemical Company proposes in PP #5F0426 for residues of 3-bromopropyne, and in PP #5F0427 for residues of methyl bromide, the following inorganic bromide tolerances for residues of the soil fumigant "Trizone." The latter is a mixture of 61% methyl bromide, 30% chloropicrin, and 9% propargyl bromide (6.8% 3-bromopropyne and 2.2% related brominated C_3-hydrocarbons).

Crop	Inorganic Bromide Tolerances (ppm) from 3-bromopropyne	from methyl bromide
Broccoli	5	15
Peppers	5	15
Pineapples	5	15
Strawberries	5	15
Cauliflower	15	25
Muskmelons	15	25
Tomatoes	15	25
Eggplant	20	40

200
.61
120 lbs methyl Br-

A 50 ppm tolerance for inorganic bromide residues has been established on all of these commodities, except strawberries, from soil fumigation with 1,2-dibromo-3-chloropropane. A 30 ppm tolerance for inorganic bromide residues has been established on strawberries for post-harvest fumigation with methyl bromide.

Conclusions

1. The inorganic bromide residues from 3-bromopropyne on strawberries and tomatoes may exceed the proposed tolerances. This is rather academic, as there is no practical way to distinguish between residues from 3-bromopropyne and those from methyl bromide.

2. Two crops in the group with proposed tolerances of 5 and 15 ppm, i.e., peppers and pineapples, could have methyl bromide residues in excess of 15 ppm and combined residues in excess of 20 ppm--but less than 25 ppm.

3. Cauliflower, with proposed tolerances of 15 and 25 ppm, would have combined residues of less than 25 ppm, i.e., less than 5 from 3-bromopropyne and less than 20 from methyl bromide.

4. The proposed use would not result in residues of the fumigant components per se.

5. The feeding of bran from pineapples grown in fumigated soil would not result in bromide residues in meat (the bran is not used for beef cattle) and would increase the background bromide level in milk by less than 5 ppm. (Nine ppm is the maximum expected from pineapples grown in Nemagon treated soil.)

6. The proposed use would not cause a build-up of bromide residues in the soil.

Recommendations

The tolerances proposed for broccoli, muskmelons, and eggplant are adequate. If toxicological considerations permit, we recommend that they be established.

For strawberries and tomatoes, 10 and 20 ppm respectively, would be more suitable tolerances for residues from 3-bromopropyne than the 5 and 15 ppm proposed.

For peppers and pineapples, 20 ppm would be a more suitable tolerance for residues from methyl bromide than the 15 ppm proposed.

For cauliflower, 5 and 20 ppm respectively, would be more suitable tolerances for residues from 3-bromopropyne and methyl bromide than the 15 and 25 ppm proposed.

Since there is no means of distinguishing the individual sources of the residue, it would seem appropriate that any ensuing regulation be based on the combined residues from the bromide containing components of "Trizone." If this were to be done, the following tolerances would be adequate:

25 ppm--broccoli*, cauliflower, peppers, pineapples, and strawberries*

40 ppm--muskmelons and tomatoes

60 ppm--eggplant

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*Although 20 ppm would be adequate for these crops, we recommend their inclusion in this group for administrative conveniences.

Were the petitioner to propose these tolerances, toxicological considerations permitting, we would recommend their adoption.

Detailed Considerations

Use

Preplant applications are made by soil injection at a rate of 160-200 lbs "Trizone"/A. Treated areas are covered with film for 48 hours or more. The soil is then aerated for 2-3 weeks prior to planting or transplanting.

Residue Methods

Inorganic Bromide--Some of the data were obtained by the X-ray fluorescence procedure. This method, which was reviewed in our recent memo in PP #345, has a sensitivity of 5 ppm. We consider it adequate for obtaining the combined residues from "Trizone."

Most of the data were obtained by the method of Shrader, et al (Ind. Eng. Chem., 14, 1 (1942). This method also was reviewed in the aforementioned memo. It is sensitive to a few ppm although in the case of pineapples, blanks range up to 7 ppm. The last presumably is due to background bromide in the soil. This method is similar to our current enforcement procedure.

Chloropicrin--The petitioner's method involves acidifying and heating the macerated sample to release the fumigant, which is trapped in an isopropyl alcohol-water solution of sodium peroxide. On refluxing the chloropicrin is converted to nitrite, which is determined colorimetrically after a Bratton-Marshall reaction. Blanks on three crops range from 0.00-0.12 ppm and average 0.08 for sweet potatoes, 0.05 for white potatoes and 0.02 for strawberries. Recoveries range from 75-107% and average respectively 92, 85, and 88%.

We consider this procedure adequate for the determination of chloropicrin residues. In the unlikely event that an enforcement problem should arise, the polarographic method of Berk (see Anal. Chem., 34, 514 (1962) and J. Ag. Food Chem., 10, 158 (1962) could be applied to residues of chloropicrin--and methyl bromide as well.

3-Bromopropyne--The petitioner's method involves blending the macerated sample with water and extracting an aliquot with benzene. A portion of the extract is injected into a gas chromatograph, with an electron capture detector. The petitioner states that the method has a sensitivity of 0.1 ppm, the lowest fortification used. Since this level gave a 20% scale deflection on peppers (vs 1.7% for the crop blank) where the ratio of benzene to sample was twice that in some other studies, we feel that 0.05 is a more reasonable, and still conservative, estimate of the sensitivity. Recoveries on all crops range from 83-101% and average about 90%.

Check analyses on samples which indicated possible residues were made by a modified procedure using an eight-fold increase in instrument sensitivity. Here we believe 0.01 ppm would be a conservative estimate of the method's sensitivity. Recoveries by the modified procedure on three crops range from 70-90 (av.83)%.

We consider both versions of the procedure adequate for the determination of 3-bromopropyne residues.

Residue Data

Broccoli--In the one study on this crop, residues from "Trizone" range from 5-15 ppm. Residues from 3-bromopropyne range from 1-2 ppm. This is within the proposed tolerances, but for administrative convenience, we suggest that this crop be included in the group with a combined tolerance of 25 ppm (5 ppm from 3-bromopropyne and 20 ppm from methyl bromide).

Peppers--Residue values from 3 studies in two states range from 6-20 ppm (uncorrected for blanks of 0 to >5 ppm) for "Trizone." Residues from 3-bromopropyne range from 0-2 ppm. Since the maximum value for the residue from methyl bromide is close to the proposed tolerance, here too we feel that 20 rather than 15 ppm would be a more suitable tolerance for methyl bromide or 25 ppm combined.

Pineapples--Most of the data in eight studies involve plants treated with "Brozone" (a similar soil fumigant containing methyl bromide) or 3-bromopropyne alone. Residues from 3-bromopropyne alone range up to 4 ppm, adjusted for exaggerated dosages. In the three studies with "Trizone," residues range from 7-21 ppm, uncorrected for blanks of 4-7 ppm. Since the last two values are right at the combined proposed tolerance level, and in view of the high blanks, here too we feel that 20 ppm would be a more suitable tolerance for residues from methyl bromide or 25 ppm combined.

Strawberries--Residues from 3-bromopropyne were 5 ppm in two studies but ranged from 2-9 (av. 5.5) ppm in a third study. This indicates that the 5 ppm tolerance for 3-bromopropyne may be inadequate. As noted above, this is rather academic. Data in 11 studies from four states show residues from "Trizone" ranging from 1-18 ppm. While the combined 20 ppm tolerance proposed seems adequate, for administrative convenience, we suggest that this crop be included in the group with a 25 ppm tolerance.

Cauliflower--Four residues from 3-bromopropyne range from 0-3 ppm; one value is 24 ppm. We agree with the petitioner that the 24 ppm value is aberrant and that residues from 3-bromopropyne would not exceed 5 ppm. The one available "Trizone" study contains six residue values for "Trizone" ranging from 12-24 ppm. Half of this range is due to the difference between 24 ppm and the next highest value of 18 ppm. This leads us to conclude that

this value too is probably aberrant. Omitting the 24 ppm value from "Trizone," the average residue is 16 ppm (17 if it is included). Therefore, we conclude that tolerances of 5 and 20 ppm (or 25 ppm combined) rather than the 15 and 25 ppm proposed would be adequate for cauliflower.

Muskmelons--Three studies from two states are reported. Residues from 3-bromopropyne range from 3-10 ppm. Residues from "Trizone" range from 11-35 ppm. In the study with the highest residues, the range is 21-35 (av.31) ppm uncorrected for a 1 ppm blank. The 15 and 25 ppm tolerances (or 40 ppm combined) proposed are adequate.

Tomatoes--Four studies from three states are reported. Residues from 3-bromopropyne range from 0-4 ppm in three studies and 1-15 ppm in another. The last is right at the proposed tolerance level. Residues from "Trizone" range from 3-37 ppm. In the study with the highest residues, the range is 18-37 (av.28) ppm uncorrected for a 1 ppm blank. The 15 and 25 ppm tolerances (or 40 ppm combined) proposed for tomatoes are adequate.

Eggplant--Two studies from two states are reported. Residues from 3-bromopropyne range from 1-11 ppm. In one study, residues from "Trizone" range from 13-27 (av.22) ppm. In the other study, the range is 38-55 (av.46) ppm. The 20 and 40 ppm tolerances (or 60 ppm combined) proposed for eggplant are adequate.

Organic Residues

Methyl Bromide--The high volatility and reactivity of this fumigant component renders the persistence of its residues extremely unlikely.

Chloropicrin--In a supplemental study submitted by the petitioner, white potatoes from soil treated with 70-210 lbs/A (vs. about 60 lbs/A in "Trizone") showed no residues. The crop was harvested 3½ months after treatment. Similarly in two studies with sweet potatoes, application rates were 140-315 and 175-265 lbs/A, respectively. The crops harvested in less than nine months in one case, and after about seven months in the other, showed no residues. Strawberry studies in two states involved 480 lbs/A treatments. No residues were found after 9 and 14 months, respectively.

On the basis of these data, we conclude that the proposed "Trizone" usage will yield no residues of chloropicrin in food crops.

3-Bromopropyne--Residue analyses for this fumigant component were made at the same time that inorganic bromides were determined. No residues of 3-bromopropyne *per se* were detected on broccoli, cauliflower, pineapples, or tomatoes. In one study on strawberries, seven samples showed no residues; in another study, three samples out of 17 showed apparent residues of 0.02 ppm. In one pepper study, 12 samples showed no residues; but in another study five samples out of nine showed residues of 0.01-0.02 ppm. On muskmelons, one sample out of 14 showed residues of 0.01 ppm and

on eggplant two studies out of nine showed residues of 0.02-0.05 ppm. All of these residue values are within the estimated 0.05 ppm sensitivity of the method used.

An investigation of the source of these apparent residues was undertaken using a method of higher sensitivity. The petitioner claims that the residues were due to contamination from 3-bromopropyne stored in the same freezer as the samples. In support of this claim, he shows that in the check analyses both control and treated samples show residues, with greater residues in the outer part than in the cores of eggplants and muskmelons. In addition, air samples taken from the freezer showed 3-bromopropyne and stored bottles of benzene picked up the equivalent of 0.08 µg/ml. While the data do indicate higher residues on treated than on control samples in three cases and lower in a fourth case, this could be due to chance.

Considering the above, we agree that the residues were due to contamination. Based on evidence with similar fumigants (see Chloropicrin above), we would not expect this material to persist in the soil, get into young plants, and remain there until the crops are ripe. However, if such residues were to be present, they would be present at levels below 0.05 ppm.

Residues in Meat and Milk

The possible increase in background bromide levels in meat and milk from the feeding of pineapple bran was discussed in detail in the FSA (J.Alpert) memo in PP #294 (Nemagon). We reaffirm the finding made there that the feeding of pineapple bran would not yield residues in meat--this commodity is not fed to beef cattle--and would increase the bromide levels in milk by less than 5 ppm. The last is based on an estimated 9 ppm maximum increase due to the use of Nemagon treated pineapple where the inorganic bromide tolerance is 50 ppm vs the 25 ppm contemplated here.

Soil Residues

Naturally occuring bromides are believed to be tightly held by the anion exchange capacity of soils. Thus some bromide persists through leaching by rain. The addition of bromide beyond the anion exchange capacity of the soil would make it available for plant pick-up and leaching.

One soil study is given in PP #34. There soil was treated with "Dowfume W-85" (85% ethylene dibromide). The amount of bromide potentially available from the treatment used would exceed that from the use of 200 lbs/A of "Trizone." In addition the lower volatility of ethylene dibromide as compared to methyl bromide would tend to keep it in the soil longer. Overall, we would expect the residues from "Dowfume W-85" to exceed those from "Trizone."

In the study, four plots 30' x 28' were treated with 12 gals of "Dowfume W-85"/A. After 45 days samples were taken by compositing 12 soil cores (3/4" x 8") collected criss-cross of the plots. Blanks ranged from 10-30 (av.16) ppm and treated samples ranged from 12-19 (av.15) ppm. These results indicate no buildup of soil residues. However, in PP #5F0429, currently being reviewed, there is some indication of a slight increase in soil residues from ethylene dibromide treatments.

While the data are meager and conclusions must be based on analogy--we consider this a reasonable showing that the proposed use of "Trizone" would not cause bromide residues to become additive in the soil.

Other Considerations

There is a 50 ppm tolerance on all of these commodities, except strawberries, for inorganic bromide residues resulting from soil fumigations with Nemagon. Thus the proposed use would contribute lower bromide residues to all of these commodities except strawberries and eggplant. The former, however, has a 30 ppm tolerance (higher than the 25 contemplated here) for residues from post-harvest fumigation with methyl bromide. While the 60 ppm proposed for eggplant exceeds the present 50 ppm tolerance, this food is a very minor part of the diet.

The bromide level in concentrated tomato products might exceed the 40 ppm tolerance on the raw commodity. However, a 250 ppm tolerance has been established on concentrated tomato products in connection with the 50 ppm tolerance on raw tomatoes from Nemagon (FAP #782). The proposed use would thus yield lower residues and probably not require a modification of the Food Additives Regulations.

In the petitioner's method for the determination of 3-bromopropyne, an aqueous macerate is extracted with benzene. To ensure complete extraction of fumigant from the substrate, isopropyl alcohol should have been used as a bridge between the organic and inorganic phases. Since the recoveries were satisfactory, and since most of the fumigant would be extracted under the conditions used, we have no serious reservations about the method--for the purpose of showing the absence of residues.

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FSA/PB (PP #5F0426; #5F0427; #5F0429; #345; #294; #34)
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