Atrazine/Review #38/3.3.81/6 pages

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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MEMORANDUM

PP#OE2398 Atrazine Use on Guava. Evaluation of Analytical and Residue Data.

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IR-4 Associate Coordinator G. M. Markle and Dr. R. H. Kupelian, National Director, State Agricultural Experiment Station, Rutgers University, New Brunswick, New Jersey, on behalf of the IR-4 Technical Committee and the Agricultural Experiment Station of Hawaii, have submitted a request for a 0.25 ppm tolerance for the combined residues of atrazine and its metabolites in/on the r.a.c. guava.

Presently, there are established tolerances of 0.02 to 5 ppm on a number of r.a.c.'s including meat, milk, poultry and eggs. These tolerances have been established for residues of atrazine only. Range grass is the only r.a.c. with an established tolerance of 4 ppm for combined residues of atrazine and its metabolites.

Conclusions:

1. This tolerance for atrazine on guavas is proposed in terms of atrazine and its metabolite, as has been done in Sec. 180.220(b) for grass. All other tolerances for atrazine have been established in terms of atrazine alone. Based on this proposed use to the soil

Formulation information deleted from page 2.

surface under guava, we believe that residues, if any, on guava will be as a result of contamination and will be parent compound. We suggest that Section F be revised to propose the tolerance in terms of atrazine per se.

2. Adequate analytical methodology is available for enforcement purposes.

3. In light of our conclusion above regarding the expression of the tolerance, we conclude that a tolerance level of 0.05 ppm on guava would be more appropriate than the 0.25 ppm proposed. Section F should be revised.

4. Because guavas are not normally a part of the livestock diet, we expect no problem of secondary residues in meat, milk, poultry and eggs.

5. Presently, there are no Codex tolerances established for atrazine in/on guava.

Recommendations:

We recommend against the proposed tolerance for the reasons cited above in Conclusions 1 and 3.

The manufacturer of atrazine (Ciba-Geigy) has been advised previously of the need to revise the established atrazine tolerances. Because guavas are a minor crop and because residues, if any, would be expected to be contaminative in nature and be comprised of parent compound, we see no need to hold up this petition on guava to obtain the type of data needed to revise the tolerances. However, when the manufacturer does revise the already established atrazine tolerances to include metabolites, this tolerance on atrazine should also be revised.

Detailed Considerations

Formulation:

Aatrex 80W is formulated as a wettable powder containing 76% active ingredient. There is an additional 4.85% related products which are considered active. From the manufacturing process these related products [redacted] We expect no residue problems for these impruities.

Inert ingredients are cleared under Section 180.1001.

Formulation information deleted.

Proposed Use:

For preemergence or early postemergence control of annual broadleaf and grass weeds in guava orchards, direct spray 2 to 4 lbs. A.I./acre of atrazine in 20 to 50 gallons of spray. When applying postemergence, the use of a surfactant and greater spray volume (80 to 100 gallons of spray mix per acre) is recommended to enhance weed control. Application is restricted to 4 month intervals and no more than 8 pounds, active ingredient, per year.

Do not allow spray to contact foliage or fruit. A surfactant, as specified in the Aatrex 80W label, is recommended for the spray mix if weeds have emerged.

Nature of the Residue:

No metabolism studies were submitted with this petition. However, studies have been previously submitted and have been reviewed in PP#7F0620 (S. Williams, 9/21/67), PP#4F1425 (D. Reed, 2/7/74) and PP#8E2076 (T. McLaughlin, 12/13/78).

Tolerances for atrazine were all established in 1967-68 and do not include metabolites; these metabolites were not included as they were thought to be more transitory than later studies would indicate.

Numerous studies were subsequently published on the metabolism of atrazine (R. H. Shimabukuro, R. E. Kadunce and D. S. Frear, J. Agr. Food Chem. 14, 392, 1966; R. H. Shimabukuro, J. Agr. Food Chem. 15, 557, 1967; R. H. Shimabukuro, Plant Physiol., 43, 1925, 1968; F. W. Roeth and T. L. Lavy, Weed Sci., 19, 98, 1971). Atrazine is absorbed through the roots of plants. The major metabolites, depending on the plant species and stage of growth, consist of hydroxylation and/or N-dealkylation of the parent and conjugate formation with glutathione and gamma-glutamyl-cysteine. Formation of both deethylated and deisopropylated atrazine and deethylated-deisopropylated atrazine has been noted in references above.

The petitioner has already been requested to update his residue data requirements with respect to atrazine metabolites in the raw agricultural commodities with established tolerances (D. Reed, PP#4F1420, 2/7/74; J. Mayes, RD, 2/20/74).

For the above reason and because this is a ground application (trunk, leaves and fruit would not be directly exposed to atrazine), the only significant residue of concern is expected to be contaminative in nature and to be comprised of the parent compound, atrazine.

Analytical Method:

The analytical method used for residue data in this petition is the same as referenced for triazine herbicides under Simazine in Pam II. This microcoulometric gas chromatography method determines the parent compound, atrazine, and its metabolites, 2-amino-4-chloro-6-ethylamino-S-triazine and 2-amino-4-chloro-6-isopropylamino-S-triazine (Mattson, A. M. et al., J. Agr. Food Chem. 13, 120 (1965)). A method is also available to determine the diamine metabolite,2-chloro-4,6-diamine-s-triazine (J. Worthington, PP#4F1425, 3/31/75).

For the determination of atrazine and its two monodealkylated chlorometabolites, sample is blended with chloroform, vacuum filtered, and the extract is dried with anhydrous sodium sulphate. After evaporating to dryness, the residue is partitioned between acetonitrile and hexane. The acetonitrile fraction is chromatographed in an aluminum oxide column with atrazine and its monodealkylated chlorometabolites eluted separately using mixtures of ethyl ether and carbon tetrachloride at various concentrations (the petitioner eluted atrazine with 1:1 mixture of toluene:hexane). After evaporating the respective eluates to appropriate volumes, residues are determined by GLC with a chlorine specific microcoulometric detector.

Method AG-232A determines 2-chloro-4,6-diamine-S-triazine. Samples are extracted with methanol and the extract cleaned up using liquid-liquid chromatography with a pH 7 buffered stationary phase and hexane as the mobile phase. Quantitation is accomplished using a GLC equipped with a microcoulometric detector or a quadrupole mass spectrometer.

Because no atrazine was detected at 1 day PHI, the petitioner decided there was no reason to analyze for other metabolites. Validation data indicate the per cent recovery as 85 to 106% for 0.05 to 0.2 ppm atrazine. Control values for guava were reported as none detectible (< 0.002 ppm) to 0.006 ppm. We have no argument with their reasoning about the absence of atrazine metabolites, if the proposed use and residue data of 1 day PHI indicate little (0.005 ppm) or no presence (<0.002 ppm) of parent compound.

The above analytical methods for atrazine and its dealkylated and diamino chlorometabolites have been accepted for inclusion in Pam II.

A U. V. spectrophotometric enforcement method is also available for atrazine determination and is described in Pam II under Simazine.

Residue Data:

Samples of guava for analysis were collected from orchards in Waimanalo and Malama-Ki, Hawaii. These studies reflect multiple applications and cover periods of 1-2 years. Residues of atrazine reported for both locations ranged from None Detectible to 0.011 ppm at PHI's of 1,14 and 28 days.

As stated above under Analytical Method, little or no residues of the parent compound were reported at 1 day PHI. Therefore, no metabolites (the dealkylated and diamino chlorometabolites) are expected to be residues of concern. Keeping in mind this is a ground application, the above interpolation, with respect to other metabolites of concern, is reasonable.

In addition, the residue data indicate the requested tolerance of 0.25 ppm atrazine is too large for the proposed use. The requested tolerance should be lowered. An adequate requested tolerance supported by the data would be 0.05 ppm atrazine.

Meat, Milk, Poultry and Eggs:

Guava are not normally considered as an animal feed item. Therefore there will be no problem of secondary residues in meat, milk, poultry and eggs.

INTERNATIONAL RESIDUE LIMIT STATUS

Chemical Atrazine

PETITION NO. OE2398

CCPR NO. _____

Codex Status

Proposed U. S. Tolerances

[ ] No Codex Proposal
[ ] Step 6 or above

Residue (if Step 9): _____

None

Crop(s)	Limit (mk/kg
None	

Residue: Atrazine

Crop(s)	Tol. (ppm)
Guava	0.25 ppm

CANADIAN LIMIT

Residue: _____

Atrazine

Crop	Limit (ppm)
None on this commodity	

MEXICAN TOLERANCIA

Residue: _____

Atrazine

Crop(s)	Tolerancia (ppm)
None on this commodity	

Notes: