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D-7689 / Linuron IR

PP#1E2486. Linuron in or on lettuce. Evaluation of analytical methodology and residue data.

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IR-4, on behalf of the IR-4 Technical Committee and the Agricultural Experiment Stations of Florida and Wisconsin, proposes the establishment of a tolerance for residues of the herbicide linuron (Lorox®; 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea) in or on the raw agricultural commodity lettuce at 0.25 ppm.

Tolerances for linuron residues in or on a variety of commodities are established (40 CFR 180.184; 21 CFR 561.265) at levels of 0.25-1.0 ppm. Included among these are tolerances at 1.0 ppm for residues in meat, fat, and meat by-products of cattle, goats, hogs, horses, and sheep.

This petition contains a letter from E.I. duPont de Nemours and Co. authorizing EPA to refer to the DuPont data on linuron in the Agency's files when considering this tolerance proposal.

This petition is being reviewed within the mandate and provisions of the OPP Minor Use Policy dated 9/30/80.

Conclusions

1. The nature of the residue is adequately understood. "Sound" residues are not expected to present a problem.
2. Adequate analytical methodology is available to enforce the proposed tolerance.
3. Based upon the results of the submitted residue studies, it is unlikely that, when used as proposed, residues of linuron in or on lettuce will exceed the proposed tolerance. In fact, detectable residues (0.05 ppm) are not anticipated.
4. There are no recognized feed items associated with lettuce. There is thus no reasonable expectation of any transfer of secondary residues to meat, milk, poultry, or eggs from the proposed use.
5. There will be no problem with residues of 2,3',4,4'-tetrachloroazobenzene, chlorinated asymmetrical azobenzenes, azoxybenzenes, or triazene compounds from the proposed use.

Formulation information deleted from page 2.

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6. An International Residue Limit (IRL) Status sheet for Linuron is attached. There are no Mexican or Canadian IRL's for Linuron. There are some Canadian IRL's for Linuron at 0.1 ppm, but not for lettuce.
7. The proposed tolerance, if and when established, will be based on the submission of residue data from a specific geographical area (East of the Mississippi River). This will be consistent with the OPP Minor Use Policy dated 6/20/80, but contrary to our usual requirements. RSC feels, therefore, that such tolerances should be identified in the C/P. (See attached sheet for our suggestion for accomplishing this.)
8. There is a label restriction, "Do not replant to crops other than celery, carrots, or lettuce within 4 months after application." While this seems consistent with the registered label, we defer to EPA to adjudicate the acceptability of this restriction.

Recommendations

EPA (see Conclusion 5) and TOI considerations permitting, we recommend that the proposed tolerance be established.

P.S., please note Conclusion 7.

DETAILS CONSIDERATIONS

Manufacture and Formulation

Technical Linuron may be prepared by reaction of 2,4-dichlorophenyl isocyanate and 5-methyl hydroxylamine ("Guide to the Chemicals Used in Crop Protection", Publication 1893, Canada Dept. of Agriculture, 5th edition, 1958).

The technical product contains 95% Linuron. The remaining 5% consists

These impurities are not expected to present a residue problem.

The formulation to be used is "Lerex" Linuron Weed Killer, a 50% wettable powder (EPA Reg. No. 352-273). The Inerts (listed in E.J. Gooder/E.J. Gausch review of 5/13/71, PP41F1146) are all cleared under Sec. 136.1001.

Proposed Use

For weed control in the cultivation of lettuce, apply 1.5 lb of Lerex Weed Killer (0.5 lb a.i.) per acre as a single, directed, shielded, post-emergent application approximately two weeks after germination of weeds, using a spray volume (minimum of 25 gals/A) for thorough coverage of weed foliage.

Limitations: Do not use within 35 days of harvest. Use only east of the Mississippi River. Use only on lettuce grown on rock or bent soils. Do not replant to crops other than celery, carrots, or lettuce within 4 months after application. (There are established tolerances of 0.1 and 1.0 ppm for celery and carrots, respectively.)

Nature of the Residue

It has been reported in the literature that linuron is absorbed from soil, metabolized, and translocated by plants. The work of Hasted and Illich, Weed Sci. 19:35, 1970 (which dealt with linuron absorption, distribution, and metabolism in corn, soybeans, and crabgrass) showed that degradation proceeds via demethylation to 3-(3,4-dichlorophenyl)-1-methoxyurea followed by demethoxylation and hydrolysis to yield 3,4-dichloroaniline. (These metabolites will be detected by the analytical method for enforcement use.) These findings parallel results of earlier work on related substituted urea herbicides (e.g., diuron and monuron) with a number of crops; those compounds are also demethylated and further degraded to aniline derivatives.

Hasted and Illich also noted that 15-25% of the linuron absorbed in the aforementioned root-uptake study was present at intervals up to 14 days in the form of a "bound" residue. The data showed the bound residue levels tended to increase with time. This does not present an enforcement methodology problem, however, since the rigorous caustic digestion (hydrolysis) employed in the residue method to be used would be expected to release these "bound" residues.

No metabolism data was submitted for lettuce. However, it seems reasonable to assume that the nature of linuron residues in lettuce will be similar to those in the aforementioned crops.

We conclude that the degradation of linuron is sufficiently defined.

Analytical Methodology

The WI field trial residue data was reportedly assayed by the procedure of H.L. Gleidner, J. Agric. Food Chem. 2, 532 (1954). This is enforcement method I of FAO II for linuron residues and has a product sensitivity of 0.05 ppm. The petitioner modified the determinative step to use a GLC equipped with a nitrogen-specific detector.

The FL field trial residue data was reportedly assayed by the procedure of H.L. Pease, J. Agric. Food Chem. 10, 278 (1962). That procedure, developed for diuron residue analyses, was modified to use a conversion factor of 1.54 (for dichloroaniline to linuron) in the calculations to make it applicable to linuron. Analytical sensitivity is also reported as being 0.05 ppm.

The principle of both procedures entails digestion-extraction of the residue from the crop sample under reflux conditions in a strongly alkaline medium, which quantitatively hydrolyzes the linuron residue to 3,4-dichloroaniline (DCA). DCA is then either (1) diazotized and coupled with diethylamine and measured colorimetrically at 580 mμ (Pease), or (2) steam-distilled into benzene and quantitated by GLC (Gleidner, as modified by the petitioner).

Both monuron and diuron, if present, will reportedly interfere with the Pease procedure, and diuron with the modified Fleidner procedure. An additional step, entailing cellulose powder column clean-up, is available to separate dichloroaniline from p-chloroaniline in cases where residues of both linuron and monuron may be present (an unlikely situation since all monuron tolerances and registrations have been revoked).

The paper chromatographic procedure of A. Major, JAOAC 45, 387 (1962) (enforcement Method II, Part II, for linuron), can be utilized to distinguish linuron residues from those of diuron.

Recovery values submitted by the petitioner on escarole and 2 varieties of lettuce to validate the basic procedure ranged from 96-110% following fortification with linuron at a level of 0.1-1.0 ppm. Control values were all reported as being <0.05 ppm.

We conclude that adequate analytical methodology exists to enforce the proposed tolerance.

Residue Data

Field trials were conducted in FL and MI in 1979 to provide data on the level of linuron residues in or on lettuce grown in muck or peat (high organic matter content) soils East of the Mississippi River.

In addition to iceberg lettuce and romaine lettuce, the FL field trials included escarole. (Note: this petition is not proposing that a tolerance for residues of linuron be established for escarole; the escarole data is included merely as a supplementary source of information.) The type(s) of lettuce grown in the MI field trials was/were not identified.

Linuron application rates ranged from 0.25-2.0 lbs a.i. (0.5-4.0 lbs Lorox 50W) per acre in the single treatment which was given; 45 gpa of spray mix was used in the FL field trials and an unspecified amount in the MI field trials.

In all field trials involving the 0.5 and 1.0 lb a.i./A rates (=1X and 2X, respectively, the proposed use rate), residues of linuron exceeding the sensitivity of the analytical methodology (0.05 ppm) were not detected in lettuce samples taken either at harvest (35-42 days after treatment) or prior to normal harvest (20-25 days after treatment). In fact, in only one instance (FL, 4X rate, 42-day PH) was a "real" (i.e., detectable) residue, 0.07 ppm, reported from any of the field trials on lettuce or escarole.

Based upon the results of these residue studies, it is unlikely that when used as proposed, residues of linuron in or on lettuce will exceed the proposed tolerance (0.25 ppm). (In fact, it is doubtful that detectable (0.05 ppm) residues will be found.)

Note: Since residue data from East of the Mississippi River reporting no detectable residues were provided for head (iceberg), loose head (romaine) and leaf (escarole) types of lettuce/escarole from exaggerated rates (up to 4X) ~~and shortened~~ PHI's, and since the proposed use (single, directed, shielded spray to ~~and foliage~~) does not involve direct application to the crop, we feel the limited ~~data~~ is adequate to support the proposed tolerance and to forego our usual need for clarification re the number of wrapper leaves included in the analyses of head-type lettuce. This is consistent with the OPP Minor Use Policy dated 9/30/80, which requires no more data than are absolutely necessary to assess the risks of a minor use chemical.

Residues in Meat, Milk, Poultry, and Eggs

There are no recognized feed items associated with lettuce. Thus, there is no reasonable expectation of any transfer of secondary residues to meat, milk, poultry, or eggs from the proposed use.

Other Considerations

Concern has been expressed in the past over whether use of phenylurea herbicides or other compounds (e.g., propanil) yielding 3,4-dichloroaniline on hydrolysis would lead to problems with residues of 3,3',4,4'-tetrachloroazobenzene (TCAB), perhaps followed by formation of chlorinated asymmetrical azobenzenes, azoxybenzenes, and triazene compounds.

We reiterate our conclusion (see reviews of PP#OF0932 and PP#E1148) that there will be no problem with residues of these compounds from the proposed use.

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An International Residue Limit (IRL) Status sheet for linuron is attached. According to it, there are no Mexican or Codex IRL's for linuron. There are Canadian IRL's for linuron on various vegetable, grain, and orchard crops at 0.1 ppm, but lettuce is not among them.

* * *

The proposed tolerance, if and when established, will be based on the submission of residue data from a specific geographical area (East of the Mississippi River). This will be consistent with the OPP Minor Use Policy dated 9/30/80, but contrary to our usual requirements. RCB feels, therefore, that such tolerances should be identified in the CFR. Our suggestion for accomplishing this is detailed ~~as an attachment~~ hereto.

Attachments (2)

TS-769:RCB:MMelson:gs:X77377:CM#2:PM:810:5/22/81
cc: RF, Circ.(3), MMelson, Watts, FDA, TOX, EEB, EFB, PP#E2486
PHI: Quick, 4/17/81: Schmitt, 4/17/81

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Linuron*

PETITION NO. 1E2486

CCPR NO. None

Codex Status

Proposed U.S. Tolerances

☒ No Codex Proposal Step
6 or above

Residue (if Step 9): None

Residue: Linuron

Crop(s)	Limit (mg/kg)
NONE	

Crop(s)	Tol. (ppm)
Lettuce	0.25

CANADIAN LIMIT

Residue: Linuron

MEXICAN TOLERANCIA

Residue: None

Crop	Limit (ppm)
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None on this particular commodity

Crop	Tolerancia (ppm)
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None

asparagus	wheat	} 0.1 ppm
barley	apples	
carrots	cherries	
corn	peaches	
dill	pears	
parsnips	plums	
potatoes	soybeans	

Notes: * (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea)

Minor Use Tolerances

Mr. Edwin L. Johnson, Office of Pesticide Programs, Deputy Assistant Administration, has issued a minor use policy dated 9/30/80. One of the issues addressed in the statement is the setting of minor use tolerances based on the submission of residue data from specific geographical areas. A tolerance is normally set on a national basis and is supported by residue data from the major growing areas for the individual crops.

In order to enable users of 40 CFR Section 180. to be able to distinguish these minor use tolerances for specific areas from other tolerances which are supported by the full complement of residue data, we recommend that these tolerances be identified in the CFR.

We suggest a system whereby the minor use tolerances be asterisked in the CFR and be accompanied by an explanatory footnote. An appropriate footnote would be, "This minor use tolerance is based on residue data from specific geographical areas. In order to expand the area of usage on this crop, additional residue chemistry data for these areas will need to be submitted."