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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460

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OFFICE OF
PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Terrachlor (PCNB). EPA Reg. No. 400-401.
Storage Stability Studies.
DEB No. 4751. MRID Nos. 409216-00, -01.

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THROUGH: Andrew R. Rathman, Section Head
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TO: Larry Schnaubelt, PM-21
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By letter of 12/2/88, Uniroyal Chemical Company, Inc. has submitted storage stability studies for pentachloronitrobenzene (PCNB) and its metabolites/impurities on wheat, corn, soybeans, kidney beans, peppers, tomatoes, catsup and dry tomato pomace.

Background

The PCNB Registration Standard, Residue Chemistry Chapter (6/20/86), noted that no data had been submitted concerning the storage stability of PCNB in or on raw agricultural commodities (racs) other than topically treated seed. Storage stability studies were required for residues of PCNB, per se, in or on the following commodities and their processed products: potatoes, brassica leafy vegetable, beans, peppers, tomatoes, cottonseed and peanuts. Also required were storage stability data for PCNB, pentachloroaniline (PCA), methylpentachlorophenyl sulfide (MPS), pentachlorobenzene (PCB) and hexachlorobenzene (HCB) "in or on the crop and animal R.A.C.S. for which tolerances are currently proposed" (page 29).

In its 90-Day Response to the Registration Standard, Uniroyal stated that storage stability studies would be done on peanuts, cabbage and potatoes. This change was accepted by EPA in a meeting on 4/27/87 (S. Hummel). However, the crops tested for this report are all different.

Conclusion

With two exceptions (wheat grain and kidney beans), residues declined at variable rates over a 6 month period. Recoveries at six months were 20 - 40% lower than at day 0. In general, PCNB and its metabolites/ impurities declined at about the same rate.

Recommendations

1. For those commodities whose residue decline has been studied, correction factors should be applied to residue values where decline at 6 months exceeds 20%.
2. Additional residue decline data should be required to support the residue levels on crops which have not been studied unless the crops are analyzed within two weeks after harvest. [Refer to our 8/87 document: "Effects of Storage (Storage Stability) on validity of Pesticide Residue Data". (Attachment)]

Detailed Considerations

Uniroyal's Report No. UR-1405 (MRID No. 409216-01) is entitled "Stability of Terraclor and Allied Metabolites in Frozen Wheat, Corn, Soybeans, Kidney Beans, Peppers, Tomatoes, Catsup, and Dry Tomato Pomace", 11/28/88. The author is J.O. Ball. Work was performed in two laboratories: Huntingdon Analytical Service (HAS) in Middleport, NY carried out studies on kidney beans, peppers, tomatoes, catsup and pomace. Hazleton Laboratories America (HLA) in Madison, WI carried out studies on wheat grain, corn and soybeans.

Wheat, Soybeans, Corn Grain

These commodities are grown from treated seeds, so low residues are anticipated in the harvested crop.

Stability studies were carried out by HLA (HLA Reports 6012-198A, B and C). Most of HLA's report consists of residue data on samples of wheat, corn and soybeans from studies done elsewhere and not described. These data will not be reviewed here.

Two samples of each of the crops were fortified with 0.025 ppm each (5x the reported method sensitivity) with PCNB, PCA, MPS, PCB and HCB and maintained under frozen conditions (-18°C - 20°C). In addition, two samples of each crop were fortified with PCNB alone at 0.025 ppm. Samples were analyzed at day 0 and 2, 3, 4, 6 and 8 months using Uniroyal Method CA-24-73, which involves extraction with hexane followed by injection into a GC equipped with an electron capture detector. The method is essentially that given in PAM II, Method I. Samples high in

lipid content were cleaned up by Florisil chromatography followed by gel permeation chromatography. Stability data were corrected by recoveries obtained by spiking samples on the day of analysis.

Wheat

Recoveries for parent and metabolites/impurities showed an initial decline over two months followed by an increase to initial levels. The two month decline is probably more reflective of the analyses than any actual residue decline. For example, recoveries of PCNB when spiked along with metabolites declined from 93% at day 0 to 62% at 3 months but were 98% at 4 months. Corresponding recoveries when PCNB was spiked alone were 80%, 86%, 96% and 102%. We conclude that PCNB residues are stable in wheat under frozen storage.

Corn

Again, the stability curves for parent and metabolites in the combined spike were similar. Recoveries declined over the first two months and then remained stable. For example, percent recovery of PCNB at day 0 was 93%. The average of 2,3,4,6 and 8 month recoveries was $72.6 \pm 11.1\%$ -- about a 21% decline. Corresponding HCB recoveries were 91% and $67 \pm 7.2\%$. The decline of PCNB when spiked alone was similar -- 98% at day 0, $74 \pm 12\%$ for the average of the other values.

Soybeans

Stability curves for parent/metabolites in the combined spike were similar. Recoveries declined from 95-100% at day 0 to 50-58 at 2 months. Recoveries at 8 months were 73-77%. Percent recovery of PCNB at day 0 was 98%. The average of the 2,3,4,6 and 8 month recoveries was $66 \pm 12\%$. Corresponding HCB recoveries were 100% and $66 \pm 9\%$. We conclude that residues decline by about 30% at two months and remain more or less constant to 8 months.

General Comment for Hazleton Studies

Individual chromatograms have not been submitted, although chromatograms of standards and spiked sample extracts suggest that peaks should be well resolvable at levels on the order of 0.025 ppm. All commodities except wheat showed significant residue decline over the 8 month period.

Kidney Beans, Peppers, Tomatoes, Catsup and Tomato Dry Pomace

Stability studies were conducted at Huntingdon Analytical Services (HAS report A026.0010). Duplicate matrices were fortified with a combined spike of 0.2 ppm each of PCNB, PCB, HCB, PCA and MPS for each time interval. Samples were held under frozen storage and analyzed at day 0, 2,4 and 6 months by

Uniroyal Method CAM-24-73. There were no cleanup steps. Stability data were corrected by recoveries obtained by spiking samples on the day of the analyses.

Kidney Beans

Stability curves for parents and metabolites in the combined spike were similar, declining slightly over the six month period. The average recovery for PCNB and metabolites at day 0 was $103.4 \pm 1.3\%$. The average recovery at 6 months was $90.2 \pm 5.7\%$. We conclude that PCNB residues in kidney beans are stable under frozen storage for at least six months.

Peppers

As in commodities analyzed by HLA, recoveries declined sharply at two months, then less noticeably through the remaining period. The average recovery at day 0 was $96 \pm 2.1\%$; the average recovery at 2, 4 and 6 months was $67 \pm 10\%$; and the average recovery at 6 months was $56.6 \pm 5.0\%$. PCNB declined from 97% at 0 day to 67% at 2 months and 57% at 6 months. Corresponding HCB recoveries were 96%, 71% and 58%.

Tomatoes

Recoveries averaged $88.6 \pm 1.7\%$ at day 0 and declined to $71.4 \pm 7.0\%$ (range 60-78%) at 6 months. The decline was slower than that for peppers. Recoveries at 4 and 6 months did not differ significantly. The PCNB recovery at day 0 was 89% and at 6 months 72%. The HCB recovery declined from 90% at day 0 to 71% at 6 months.

Catsup

Decline was the most pronounced of all matrices studied. Recoveries at day 0 varied from 91 to 96%. Recoveries at 6 months varied from 37% (PCB) to 66% (MPS). Recoveries at 2 months averaged $80 \pm 4\%$; at 4 months $63 \pm 7\%$; at 6 months $55 \pm 11\%$. This represents a 41% decline.

Tomato Pomace (Dry)

In contrast to all other commodities, the average PCA recovery in pomace was low at day 0 -- 58% -- and did not rise or fall appreciably during the remainder of the period. Recoveries of the other species declined from an average of $90.2 \pm 3\%$ at day 0 to $59.5 \pm 2\%$ at 6 months.

Comment

All commodities analyzed by HAS, except for kidney beans, showed significant decline over a six month period. Supporting

chromatograms show well resolved peaks. There is a significant background in the chromatogram for catsup, but there are no interferences at the retention times of interest.

General Conclusion

Residue decline cannot be predicted for a given commodity. For example, soybeans and kidney beans, in the same crop group in 40 CFR 180.34(e), exhibit different residue decline patterns. Kidney bean residues show little decline over 6 months; soybean residues decline by 30% in 2 months and then decline more slowly. Tomatoes and peppers, in the same crop group in §180.34(e), also show differing residue decline patterns. Tomato residues declined by an average of about 20% in six months; pepper residues declined by about 40%.

No data have been submitted for forage or fodder -- there are currently no PCNB registrations for such commodities -- or leafy vegetables.

We make the following recommendations:

1. For those commodities whose residue decline has been studied, correction factors should be applied to residue values where decline over six months exceeds 20%.
2. Additional residue decline data should be required to support the residue levels on crops which have not been studied unless the crops are analyzed within two weeks after harvest. (Refer to our 8/87 document: "Effects of Storage (Storage Stability) on Validity of Pesticide Residue Data".)

Attachment: "Effects of Storage (Storage Stability) on Validity of Pesticide Residue Data".

cc: RF, Circu., PCNB SF, PCNB Reg. Std. File, PMSD/ISB(Eldredge),
Reviewer (Mike Flood).

RDI:SectionHead:ARRathman:1/25/89:DeputyChief:RDSchmitt:1/25/89.
TS-769C:DEB:557-4362:MTF:mtf:CM#2:Rm810:1/26/89.