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

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#1F2620/2H5331 Chlorpyrifos on apples. Evaluation of analytical method and residue data.

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Dow Chemical Co. proposes tolerances for residues of chlorpyrifos (which include the parent plus a metabolite, 3,5,6-trichloro-2-pyridinol (TCP)) on apples at 1 ppm and on dried apple pomace at 8 ppm.

Tolerances for chlorpyrifos on apples and apple pomace had been proposed with PP#OF2221. These proposals were withdrawn because questions concerning the metabolism of chlorpyrifos in apples were holding up the establishment of other tolerances (cucumbers, pumpkins seed and pod vegetables that were proposed with that petition).

Several chlorpyrifos tolerances are established ranging from 0.01 ppm for eggs and poultry to 15 for peanut hulls (40 CFR 180.342). Many petitions are pending.

Conclusions:

1. The nature of the residue in adequately understood. The residue of concern consists of chlorpyrifos and TCP.

2. Adequate analytical method are available for enforcement purposes.

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3a. The proposed tolerance for apples (1 ppm) is inadequate. A tolerance of 4 ppm would be adequate and should be proposed.

3b. Residues in dry apple pomace may be ca. 7.5 x that in apples. Therefore a tolerance of 30 ppm is needed and should be proposed for apple pomace. This would also accommodate expected residue in wet apple pomace.

4a. The pending tolerance (2 ppm) for the meat, fat, and meat by-products of cattle will accommodate any expected secondary residues in cattle tissue resulting from the proposed use.

4b. The pending tolerance (1 ppm) for the meat, fat, and meat by-products of goats, horses and sheep is inadequate. A tolerance of 1.5 ppm would be adequate and should be proposed.

4c. The pending tolerance for milk fat (0.5 ppm reflecting no more than 0.02 ppm in whole milk) will accommodate any chlorpyrifos residues expected in milk as a result of the proposed use.

4d. The pending tolerance (0.5 ppm) for the meat, fat, and meat by-products of hogs will accommodate any expected secondary residues in hog tissue that results from the proposed use.

4e. Since apples and the processed by products of apples are not normally used as poultry feed there will be no problem of secondary residues in poultry and eggs.

5. An International Residue Limit Status sheet is attached. The Codex MRL for chlorpyrifos on apples is 1 ppm. Since higher residues than this are expected from the proposed use the U.S. Tolerance cannot be made compatible with the Codex MRL. Also the Codex MRL does not include TCP.

Recommendation:

We recommend against the proposed tolerance. For a favorable recommendation we require a revised Section F in which the followings tolerances are proposed.

1.	apples	4 ppm
2.	apple pomace	30 ppm
3.	meat, fat and meat by-products of goats, horses and sheep	1.5 ppm

Also a favorable recommendation is contingent on the concurrent establishment of meat (cattle) and milk tolerances proposed with PP#0F2281.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

Detailed Considerations

Manufacture and formulation

The manufacturing process for chlorpyrifos was described in our review of PP#4F1445 (memo of 5/3/74 A. Smith). The technical material is, at minimum, 94% pure. The technical consists of [redacted] The remainder of the nonvolatiles consist of at least seven compounds. We do not expect these impurities to present a residue problem due to the dilution upon appliation.

The formulation proposed for use on apples is Lorsban 50W which contains 53.2% technical chlorpyrifos. A confidential statement of formula is included with this petition. The inert ingredients are cleared Section 180.1001.

Proposed Use

For control of various insects infesting the fruit and/or foliage of apple trees, Lorsban 50W is to be applied as a concentrate spray at the rate of 1.5 to 2.0 lbs a.i./A or as a dilute spray at the rate of 0.25-0.5 lb a.i./100 gallons spray at a rate not to exceed 2 lbs a.i./A.

No application is to be made within 14 days of harvest. No more than 8 applications of the maximum dosage level are allowed per season. Livestock are not to be grazed in treated areas.

Nature of the Residue

The metabolism of chlorpyifos has been studied in corn and bean plants (PP#3F306) and in apples and soybeans (PP#OF2281). These studies are most recently discussed in conjunction with PP#1F2475, chlorpyrifos on citrus (See memo of 3/4/82, K. Arne) and show that chlorpyrifos does not readily translocate, that it degrades in the presence of of UV light and that while several metabolites may be formed the only one formed in significant quantities is TCP. TOX has judged that unidentified metabolites uncovered in the apple and soybean studies are not of toxicological significance (See PP# OF 2281, memo of 10/21/81, W. Dykstra and Section 18 for chlorpyrifos on soybeans, memo of 8/11/81, A. Mafouz). We therefore reiterate our conclusion (made in conjunction with several petitions) that the nature of the residue in plants adequately understood. The residue of concern consists of parent plus TCP.

A summary of animal metabolism studies is available in our review of PP#F2575 (memo of 1/82, K. Arne). The metabolism of chlorpyrifos has been studied in rats and cows (PP#3F1306, See memo of F.D.R. Gee, 3/1/73) and in goats (PP#2281, See memo of 7/7/81 E. Leovey). In these studies the major metabolites uncovered were chlorpyrifos and TCP (plus conjugates of TCP). The nature of the residue in animals is adequately understood. The residue of concern consists of parent plus TCP.

Analytical Method

The following methods were used to determine chlorpyrifos and TCP in residue data submitted with #PP#9F2221.

Chlorpyrifos

Residues of chlorpyrifos in or on apple peels and apple pomace are extracted (method ACR 73.5.S1) by blending the sample with acetone, filtering and evaporating the acetone. The residue is partitioned into hexane and then from the hexane into acetonitrie. The combined acetonitrie extracts are concentrated to a residue which is dissolved in hexane and eluted through silica gel. The eluate is concentrated and dissolved in acetone for analyses by gas chromatography using a flame photometric detector. Apple juice samples are extracted with methanol. For whole apple and peeled apple samples, the residue after partitioning into hexane was not partitioned into acetonitrie but eluted directly through silica gel.

Apparent residues of chlorpyrifos in or on untreated samples (controls) ranged from non-detectable to 0.032 ppm for apples, apple juice and pomace. Controls were fortified with chlorpyrifos at 0.01-10 ppm (apples and pomace) and 0.01-1.0 ppm (apple juice). Recoveries of chlorpyrifos ranged from 72-111%.

3,5,6-Trichloro-2-pyridinol

Method ACR 71.19R is used to measure residues of TCP in or on apples (whole, washed, peeled, peels and pomace). The sample is heated with 10% sodium hydroxide in methanol. Residues of chlorpyrifos and chlorpyrifos intermediate hydrolytic metabolites are hydrolized to TCP. Actual TCP residues are determined by difference. The contribution from chlorpyrifos as determined by an independent method is subtracted.

After blending, the methanol is evaporated to a small volume which is diluted with water. With the addition of concentrated hydrochloric acid and sodium chloride, TCP is extracted into benzene and the benzene phase is chromatographed on an acidic alumina column which is eluted with diethyl ether/pH 6.5 buffer. TCP is then partitioned from the ether eluate into a sodium bicarbonate solution. After acidification, it is back-partitioned into benzene. An aliquot of the benzene phase is treated with N,O-bis (trimethylsilyl) acetamide to form the trimethylsilyl derivative which is determined by gas chromatography using an electron capture detector.

Apparent residues of TCP in or on untreated r.a.c.'s ranged from non-detectable to 0.04 ppm for apples, apple juice and pomace. Apple samples (whole, peeled apples, juice, and pomace) were fortified with 0.1-2-ppm chlorpyrifos. Recoveries ranged 77-109% This method will therefore hydrolyze chlorpyrifos and intermediate hydrolysis products formed by metabolism to TCP.

The tolerance is for combined residues of chlorpyrifos and TCP. combined control residues from non-detectable to 0.04 ppm (apple), 0.009-0.02 ppm (pomace), 0.001-0.009 ppm (apple juice).

Similar analytical methods were used for residue data collected for the present petition. These methods are in PAM II and are adequate for enforcement purposes.

Residue Data

Following is a summary of the residue data submitted with PP#9F2221:

Residue data was collected from California, Michigan, New York, North Carolina, Pennsylvania, Washington and Wisconsin. Chlorpyrifos was applied at 0.5 to 1.0 lb a.i./100 gallons and 400 to 800 gallons/A or 120 gal/A. Applications of concentrated solutions ranging from 7.5 lb to 2 lb a.i./100 gallons and 80 to 25 gallons/A were also applied. The number of applications ranged from 5 and PHI's extended from 0 to 35 days. Combined residues of chlorpyrifos and TCP for all studies ranged from 7.5 to 0.01 ppm. Residue data reflecting the proposed use was not submitted. (The use proposed with PP#9F2221 allowed up to 4 lbs a.i./A applied as a dilute spray and up to 3 lb a.i./A applied as a concentrated spray; the maximum proposed use is now 2 lb a.i./A for either dilute or concentrated spray; up to eight applications are allowed).

The highest residue found as the result of a dilute spray and at a 14 day or longer PHI was 1.9 ppm (9 applications of 8 oz/100 gal spray had been made). The highest residue found as the result of a high concentration spray and a PHI of 14 days or longer was 3.2 ppm (9 applications of 12 oz a.i./10 gal spray, at a rate of 2 lb a.i./A had been made; the PHI was 21 days; residues at 14 days were 1.0-20 ppm) These data are from slightly exaggerated applications (9 instead of the allowed 8).

Additional data submitted with the present petition are limited to one study from New York. Apples were treated with 12 applications of 2 lb a.i./A (8 oz a.i./100 gal spray; 400 gal/spray/A). The combined residues found at a 0 day PHI ranged up to 0.7 ppm (average = 0.57 ppm). No fruit were analyzed for residues at longer PHI's.

In our review of PP#9F2221 we concluded that the proposed tolerance of 1 ppm was inadequate and that a tolerance of 4 ppm would be needed, or, if this use were limited to dilute applications, a tolerance of 2 ppm would be adequate. The petitioner argues that the higher residue values are either anomalous (i.e., the New York studies, discussed above, in which residues as high as 3.2 ppm were realized as the result of some what exaggerated rate) or outliers (i.e., a North Carolina study in which residues of 1.26 ppm are reported).

The petitioner (See PP#9F2221) considers the New York data invalid because high control values were found and a decline plot indicates that contamination occured between days 14 and 21. We do not consider these to be sufficient reasons for dismissing these data (we have given this opinion earlier memo of 7/29/80, E. Leovey). Neither do the additional residue data submitted with this petition provide much support for the petitioners contention. These data are limited (it is actually a processing study) and the low volume application isn't represented. Finally we do not consider the high residue value from North Carolina to be an outlier especially when compared to the New York values. We therefore recommend that tolerance of 4 ppm be proposed for apples.

Two apple processing studies are available, one in PP#F2221 and one with the present petition. With PP#9F2221 one processing study with four replicate samples was reported. Whole apples were processed through a Hobart fruit juice extractor. The apple juice and wet pomace were analyzed (R.F. Bischoff, Dow Chemical, 8/4/79). Apples were processed on the day of the seventh and last treatment of a 2 lb a.i./A spray. Residues in or on the unwashed apples ranged from 4.67 to 2.4 ppm. Residues in or on juice and wet pomace ranging from 0.4 to 0.2 ppm and 9.4 to 8.0 ppm respectively. The concentration factor from apples to wet pomace was approximately 3.

For the processing study now submitted apples were treated with 12 applications of 2 lb a.i./A. The apples were found to carry residues of 0.57 ppm. These apples were processed into juice, wet pomace and dry pomace which were found to carry residues of 0.11, 0.97 and 4.15, ppm respectively.

These studies indicate that no concentration of residues is expected in the juice, that wet pomace is expected to carry 2-2.5 x the residues in apples and dry pomace is expected to carry ca 7.5x the residues in apples. We conclude that a tolerance of 30 ppm is needed for apple pomace. This would accomodate residues in both wet and dry apple pomace.

Meat, Milk, Poultry Eggs

Apples and the processed byproducts of apples can be used for livestock feed. A diet that would provide the maximum potential of chlorpyrifos to beef cattle would be:

	tolerance (ppm)	% in diet	ppm in diet
dried apple pomace	30	50	15.
alfalfa hay	15	25	3.75
corn grain	0.1	25	0.02

Cattle feeding studies were conducted at 3, 10, 30 and 100 ppm of the chlorpyrifos in the diet. Maximum residues at the 10 ppm level were 0.07, 0.52, 0.57 and 0.36 ppm for muscle, liver, kidney and fat respectively. At the 30 ppm level the maximum residues were 0.09, 1.68, 1.06 and 1.23 ppm for muscle, liver, kidney and fat, respectively.

Based on the 30 ppm (or 10 ppm) level feeding study we would expect 19 ppm in the diet to give levels of 0.06 (0.13), 1.05 (0.98) 0.66 (.02) and 0.77 (0.68) ppm in muscle, liver, kidney and fat, respectively. Another source of residues in cattle is a dermal treatment (a 0.025% spray not to be applied within 14 days of slaughter; see PP#3F1306) that can produce residues of up to ca 1 ppm in fat; other tissues do not contain residues of greater than 0.5 ppm as a result of this dermal treatment.

The dermal treatment gives a higher concentration in fat; ingestion tends to give higher concentration in the liver. The total residue in fat from both sources could be as high as 1.8 ppm; all other tissues would be expected to contain less. With PP#OF2281, a tolerance of 2 ppm is pending for the meat, fat, and meat byproducts of cattle; we conclude that this tolerance will accomodate the present use.

For the meat, fat and meat byproducts of sheep, horses and goat's a tolerance of 1.0 ppm is pending. For goats we estimate the potential ingestion of chlorpyrifos residues to be the same as that for cattle, 19 ppm, as discussed above. For horses the maximum potential for chlorpyrifos would be from feeding treated alfalfa hay (tolerance = 15 ppm, 70% in the diet) and apple pomace from treated apples (tolerance = 30 ppm, 30% of the diet. The maximum potential for chlorpyrifos in a sheeps diet is also 19.5 ppm from a diet of alfalfa hay (tolerance = 15 ppm, 30% of the diet), apple pomace (tolerance = 20 pm, 50% of the diet) and corn grain (tolerance = 0.01 ppm, 20% of the diet).

Based on the 30 ppm cattle feeding study we would expect 19 ppm chlorpyrifos in the diet of goats, horses or sheep to produce highest residues in the liver, up to 1.06 ppm. Based on the 10 ppm feeding study the highest residues would occur in the kidney, up to 1.03 ppm.

We therefore conclude that the pending tolerance of 1.0 ppm isn't adequate and that a tolerance of 1.5 ppm should be proposed for the meat, fat and meat byproducts of horses, sheep and goats.

For the meat, fat and meat byproducts of hogs a tolerance of 0.5 ppm is pending. Following is a hog's diet with the greatest potential for chlorpyrifos residues.

	tolerance (ppm)	% in diet	ppm in diet
dried apple pomace	30	30	9
alfalfa meal	4	50	2
corn grain	0.1	20	.02
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Hog feeding studies were conducted at 1, 3 and 10 ppm chlorpyrifos in the diet. Maximum combined residues at the 10 ppm feeding level were shown to be 0.3 ppm, 0.33 ppm, 0.16 ppm and 0.29 ppm for muscle, liver, kidney, and fat, respectively. We therefore would expect no residues greater than 0.5 ppm in the meat, fat and meat byproducts of hogs fed treated apple pomace and conclude that the pending 0.5 ppm tolerance is adequate.

For milk fat a tolerance of 0.5 ppm (reflecting no more than 0.02 ppm in whole milk) is pending. Following is a dairy cows diet with the greatest potential for chlorpyrifos residues.

	% in diet	tolerance	ppm in diet
dried apple pomace	25	30	7.5
alfalfa hay	60	15	9.0
corn grain	15	.1	.015
			1.65

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Dairy cow feeding studies were submitted with PP#3F1306. Dairy cows fed 30 ppm chlorpyrifos were found to have 0.03 ppm in whole milk. Therefore cows fed 17 ppm would produce milk containing 0.07 ppm chlorpyrifos residues; this means that residues in milkfat (assuming that the milk is 4% milkfat and that the residues partition to the fat) would be as 0.41 pm. We conclude that the pending tolerance (0.5 ppm) for milkfat is adequate.

Poultry and Eggs

Since apples and the processed byproducts of apples are not normally fed to chickens there will be no problem of secondary residues in poultry and eggs.

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cc:RF, Circ, Arne, Thompson, FDA, TOX, EEB, EFB, PP#1F2620/2H5331
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