FQPA-related Pesticide Residue Study, 1999

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Over the past several years, Members of the UMass Fruit Team have endeavored to provide information to Massachusetts fruit, vegetable, and berry growers as well as other pesticide applicators on developments associated with implementation of the Food Quality Protection Act of 1996 (FQPA). For fruit growers, this role has taken the form of multiple slide presentations at twilight meetings and annual updates in the March Message to Massachusetts fruit growers. These activities have also benefitted from close cooperation with Glenn Morin and Robin Spitko (NEFCON) who have been closely involved through membership on the national Tolerance Reassessment Advisory Committee (TRAC) and the National Alliance of Independent Crop Consultants.

In 1999, at the request of leading Massachusetts fruit growers, the Fruit Team designed two studies to generate data on mitigating uses of the key organophosphate (OP) insecticides azinphosmethyl and phosmet for submission to EPA. The studies were conducted at nine commercial fruit farms in Massachusetts and two in New Hampshire. Pesticide residue analyses were conducted by the Massachusetts Pesticide Analytical lab (MPAL) at UMass, Amherst. Studies were designed to show the effects on residues at harvest of restricting azinphosmethyl use only to the early season against plum curculio (Residue Decline Study), or of using various rates (full rate, half rate, one quarter rate) of azinphosmethyl or phosmet later in the season against apple maggot (Bridging Study). A residue-decline study seeks to establish a relationship between residue levels at the time of application and those detected over time, including at the pre-harvest interval specified on the label. A bridging study is intended to establish a relationship among residues from field trials conducted at the maximum application scenario (e.g., maximum application rate, highest application frequency, and shortest pre-harvest interval) and residues which occur from more typical applications.

Materials & Methods

Treatments. Seven orchards agreed to participate in the Azinphosmethyl Residue Decline Study (ARDS). Each test block consisted primarily of well-pruned, mature, semi-dwarf McIntosh trees. Applications were conducted by cooperating growers using their own calibrated sprayers and the 50WSP formulation, at per-acre rates ranging from 0.75 to 1.5 lbs. formulated product per acre (depending on tree row-volume). Timing and need for applications were determined by the grower, but no azinphosmethyl applications were planned after the last spray for plum curculio. Fungicides were applied by the grower on an as-needed basis and were not part of the residue analysis.

Three orchards agreed to participate in the Phosmet Bridging Study (PBS). Each test block consisted primarily of well-pruned mature McIntosh trees. With the understanding that one grower planned to switch from early-season azinphosmethyl use to later-season use of phosmet, in that case, the PBS was overlain on trees also sampled for the ARDS. In the other two orchards, phosmet was the insecticide primarily used throughout the season, so no ARDS was conducted. Pesticide applications were conducted by cooperating growers using their own calibrated sprayers and either the 70WP or 70WSB formulation, at per acre rates ranging from 0.8 to 3 lbs. formulated product per acre (depending on tree-row volume). Timing and need for applications were once again determined by the grower, and fungicides were applied as needed.

At the request of the growers, one orchard was the site of an Azinphosmethyl Bridging Study (ABS), using three rates of the 50 WSP formulation: 10 oz., 5 oz., and 2.5 oz. per 100 gallons, and a second was the site of an ABS using two rates of the 50 WSP formulation: 8 oz. and 4 oz. per 100 gallons. Cultivar mix and tree size in these two blocks were the same as other blocks described above. Timing and need for applications were once again determined by the grower, and fungicides were applied as needed.

Sample collection. At the study's onset, the authors met to discuss the protocol for collecting and storing samples. It was decided initially to collect composite samples of up to 20 fruit (depending on size) from each treatment block in collaborating orchards approximately monthly through the season. Fruit were collected by snipping the stem with a hand pruners (so as to not contaminate individual fruit by handling) and dropping the fruit into previously-labeled foil-lined Zip-Loc™ bags. Once fruit were collected, bags were placed immediately into a cooler with ice packs and returned to campus. After recording the specimens into a chain of custody form at the MPAL, samples were frozen and stored

Table 1. Sample dates and azinphosmethyl residues found on pooled samples of McIntosh apple. Also included are the dates of the last azinphosmethyl application. 1999 Azinphosmethyl Residue Decline Study.

Orchard	Date of last azinphos-methyl application	Sample collection dates (residues of azinphosmethyl in µg/g)				
A	May 27	6/23 (0.074)	7/27 (1 N.D.)[1]	8/23 (6 N.D.)	8/31 (6 N.D.)[2]	9/7 (7 N.D., 0.12, 0.11)
B	June 2	6/23 (0.307)	7/27 (0.05)	8/26 (3 N.D.)	9/1 (2 N.D., 0.12)[2]	No Sample
C	May 27	6/23 (0.167)	7/28 (1 N.D.)	8/23 (3 N.D.)[2]	No Sample	No Sample
D	May 30	6/24 (0.136)	7/27 (1 N.D.)	8/23 (3 N.D.)	9/1 (N.D.)[2]	No Sample
E	May 29	6/23 (0.13)	7/27 (1 N.D.)	8/23 (3 N.D.)	9/1 (3 N.D.)	9/7 (3 N.D.)[2]
F	May 28	6/23 (0.082)	7/28 (1 N.D.)	8/23 (3 N.D.)	9/1 (3 N.D.)[2]	No Sample
G	May 22	6/28 (0.106)	7/29 (0.05)	8/26 (3 N.D.)	9/2 (3 N.D.)[2]	No Sample

1. N.D.: no residues were detected on a specified number of pooled samples collected on that date.
2. Samples taken at the 14-day pre-harvest interval prior to estimated harvest date.

Table 2. Sample dates and phosmet residues found on pooled samples of McIntosh apple. Also included are the dates of the last phosmet application. 1999 Phosmet Bridging Study.

Orchard	Date of last phosmet application	Rate (oz./ 100 gal.)	Sample collection dates (residues of phosmet in µg/g)		
A	July 10	16	6/23 (1 N.D.)[1]	8/27 (2 N.D., 0.05)	9/7 (0.067)[2]
		8	6/23 (1 N.D.)	8/27 (3 N.D.)	9/7 (0.0933)
		4	6/23 (1 N.D.)	8/27 (3 N.D.)	9/7 (1 N.D., 0.08)
H	July 27	16	no sample	8/25 (0.139)	no sample
		8	no sample	8/25 (1 N.D., 0.07)	no sample
I	August 7	16	no sample	8/26 (1.807)	9/2 (1.123)
		8	no sample	8/26 (0.703)	9/2 (0.29)
		4	no sample	8/26 (0.303)	9/2 (0.223)

1. N.D: no residues were detected on a specified number of pooled samples collected on that date.
2. Harvest date.

appropriately until later analysis.

After the initial collection period (end of June) had been completed, the EPA published two relevant draft guidelines which resulted in a modification of the above protocol to comply more closely with EPA guidance. Specifically, we henceforth collected three composite samples from each treatment block on each sample date, with the last sample date corresponding to the pre-harvest interval (PHI) for the material. By the time the draft EPA guidance was published (7/29/99), it was impossible to comply with certain suggested aspects of the EPA protocol, including collection of a control sample prior to any application of pesticide or collec-

Table 3. Sample dates and azinphosmethyl residues found on pooled samples of McIntosh apple. Also included are the dates of the last azinphosmethyl application. 1999 Azinphosmethyl Bridging Study.

Orchard	Date of last azinphos-methyl application	Rates	Sample collection dates (residues of azinphosmethyl in µg/g)		
J	---	8 oz./100	8/24 (0.23)	8/31 (0.1133)[1]	no sample
		4 oz./100	8/24 (0.085)	8/31 (0.086)[1]	no sample
K	August 18	10 oz./100	8/24 (1.18)	8/26 (1.753)[1]	9/9 (0.483)
		5 oz./100	8/24 (1.09)	8/26 (0.527)[1]	9/9 (0.247)
		2.5 oz./100	no sample	8/26 (0.07)[1]	9/9 (0.063)

1. Samples taken at the 14-day pre-harvest interval prior to estimated harvest date.

tion of samples immediately after application.

Sample extraction and analysis. Azinphosmethyl and phosmet residues were analyzed as reported previously (S. Wright, et al., 1998, *Fruit Notes* 63(2):1-3). Residues were analyzed from extracted whole apples using gas chromatography with nitrogen-phosphorus and Mass-selective detection. Pesticide recoveries from organic apples fortified with azinphosmethyl and phosmet (0.05 Fg/g - 2.0 Fg/g, N=38) were 98.5 % ± 15 and 105 ± 16, respectively. Residues of azinphosmethyl and phosmet were never detected on any (N=38) of the laboratory control samples (organic apples).

Residue Decline Study Results and Discussion

Not surprisingly, residues of azinphosmethyl were detected on samples collected approximately one month after the last actual application in all seven treatment blocks (Table 1). However, largely in keeping with our original hypothesis, there were no detectable azinphosmethyl residues (limit of detection = 0.04 Fg/g) on any fruit collected 14 days prior to harvest in six out of seven sampled ARDS blocks. This result was consistent with a study conducted by Wright et al. in 1997 (*Fruit Notes* Vol. 63 (2):1-3, 1998.) where they found no detectable residues at harvest in five third-level IPM blocks which received no azinphosmethyl applications after June 30.

In one orchard, small amounts of azinphosmethyl were detected prior to harvest (0.12 and 0.11 Fg/g respectively), in two out of ten composite samples taken. This was in spite of the fact that no Azinphosmethyl was detected on samples taken on three previous dates in that block. We are unable to explain fully the presence of these residues, since the grower assures us that no azinphosmethyl had been applied to the block or anywhere else in the entire orchard after May 27. We suspect that results reflected the extremely dry summer experienced in Massachusetts in 1999. Presence of small residues in two out of nine pooled samples collected on 9/7 reaffirms the need for multiple samples in order to account for residue variation among individual fruits growing on different trees or at different positions on trees.

Bridging Study Results and Discussion

In the three orchards which participated in the phosmet bridging study, there appeared to be a trend toward correlation between rates applied and resultant residues (Table 2). In one PBS block, azinphosmethyl residues just above the analytical limit of detection (data not shown) were found at the PHI in trees which the grower reports had received no deliberate applications of that material. Based on the grower's spray records, we suspect that this may have been due to drift from adjacent blocks of trees that received a late season application of a low rate of azinphosmethyl against apple maggot fly.

In the two orchards which conducted the azinphosmethyl bridging study, there was a much better relationship between rates used and resultant residues (Table 3). The differences can not be explained conclusively, although variation in mixing/loading procedures, weather during application, or sprayer calibration likely contributed.

Conclusion

Based on these results, it appears that our original hypothesis (that restricting azinphosmethyl applications only to early-season pests) typically will result in no detectable residues at harvest. Such a potential strategy is essentially the same as increasing the PHI to 90 days, far more than the current requirement of 14 to 21 days (depending on rate of last application). Given the extremely low rainfall during the 1999 growing season, this test can be considered to be a "worst-case scenario," given that weathering by rainfall is a significant source of residue removal from fruit under more normal conditions. Results also point out the substantial variability of application outcomes from orchard to orchard. This variability likely results not only from use of different sprayers, travel speeds, rates of concentration (e.g., 3X, 6X, etc.), and frequency of calibration, but also from individual grower's mixing/loading and application style.

Regarding use of lower-than-maximum label rates, our data confirm that residues of azinphosmethyl at harvest, while affected by the date of last insecticide application, are also related to rate of formulated product used. Thus, using the lowest effective rates not only makes good economic sense, but also provides an additional margin of safety regarding potential residues at harvest. Such a low-dose strategy also can be a resistance-management tool given that pest resistance typically develops to the highest rate to which pests have been exposed.

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