ENVIRONMENTAL MONITORING OF THE 1987 APPLE MAGGOT PROJECT

MAY, 1988

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

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Pest Management, Environmental Protection
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EH 88—4

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by

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ABSTRACT

Residues of phosmet were measured on samples of apples and leaves and in soil and water collected during the 1987 apple maggot fruit fly treatment program. The samples were analyzed to examine the dissipation of phosmet over time between successive sprays. The effect of climate on the environmental fate of phosmet was studied by monitoring and comparing results from one coastal and two inland sites. Residue levels in 1987 were lower for soil and higher for fruit than those levels found in 1986. Quality control samples indicated that these differences may have been attributed to a change in the laboratory that conducted the analyses. The 10 ppm tolerance level for apple fruit was exceeded in only one sample collected the day after phosmet was applied. At both inland sites, phosmet levels on fruit samples taken the day following application were higher with successive applications. Possibly, shorter spray intervals accounted for this trend. No phosmet or phosmetoxon was detected (detection limit 1 ppb) in any of the surface or ground water samples that were collected. Due to inadequate sampling replication, degradation patterns were not always discernible.

ACKNOWLEDGEMENTS

Thanks to all the EHAP personnel who helped conduct this study.

Thanks also to the people of the Apple Maggot Project for their assistance and cooperation.

Thank you, Joan Fleck, for your computer graphics contribution.

And thank you to all those too numerous to mention for your comments and help with the writing of this report.

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INTRODUCTION

The apple maggot fruit fly, Rhagoletis pomonella, was first found in California in August 1983. It is known to be a serious pest of apples, crabapples, and hawthorne in eastern North America and has spread to most western states. The California Department of Food and Agriculture (CDFA) was directed by the Governor in 1984 to establish the Apple Maggot Fruit Fly (AMFF) Project in an effort to eradicate the pest (CDFA, 1985).

Efforts by the CDFA to eradicate the AMFF using phosmet (Imidan®) began in the summer of 1985. However, the program was interrupted mid-season due to a court ruling. CDFA resumed its Apple Maggot Project during the 1986 season. At that time, the CDFA's Environmental Hazards Assessment Program (EHAP) undertook a comprehensive monitoring program to estimate and document the concentrations of phosmet and study its behavior in the environment (Gonzalez et al., 1987).

The Apple Maggot Project as well as the EHAP's monitoring efforts resumed during the 1987 season. For 1987, the monitoring plan included two "inland" sites which were treated in 1986 but were not monitored. Data from these two sites were compared with data from coastal sites monitored in 1986 and 1987 to investigate the effect of a warmer and drier climate on the environmental fate of phosmet.

MATERIALS AND METHODS

Treatment Area

Personnel from the apple maggot project applied phosmet to all host trees (apple, crabapple, hawthorne) in which apple maggot flies were trapped from 1985-1987. Treatment of host trees in 1987 occurred in eight northern California counties: Del Norte, Humboldt, Mendocino, Shasta, Trinity, Siskiyou, Lake, and Sonoma (Figure 1). In addition to spraying host trees in which flies were found, all host trees within a 0.25 mile radius of the trapped fly were also sprayed with phosmet.

Treatment Methods

Trees were sprayed to the point of drip with Imidan® 50 WP at a concentration of 1.5 lbs of product per 100 gallons of water using truck mounted spray rigs. This dilution corresponded to a solution having 0.090% active ingredient. All properties with a fly find during the 1985 or 1986 treatment season received their initial phosmet application between June 15 and July 15, 1987. When a fly was found during the 1987 treatment season, that host tree and all others within a 0.25 mile radius were sprayed with phosmet within 72 hours of confirmation. At each site, applications were repeated on a 14-21 day interval throughout the treatment season which ended October 31,1987.

Study Design

As part of the Apple Maggot Project Workplan for 1987, personnel from the EHAP continued a chemical treatment monitoring program begun during the 1986 season. Monitoring consisted of measuring phosmet and phosmetoxon residues in water, soil, foliage, and fruit samples collected from sites in Humboldt,

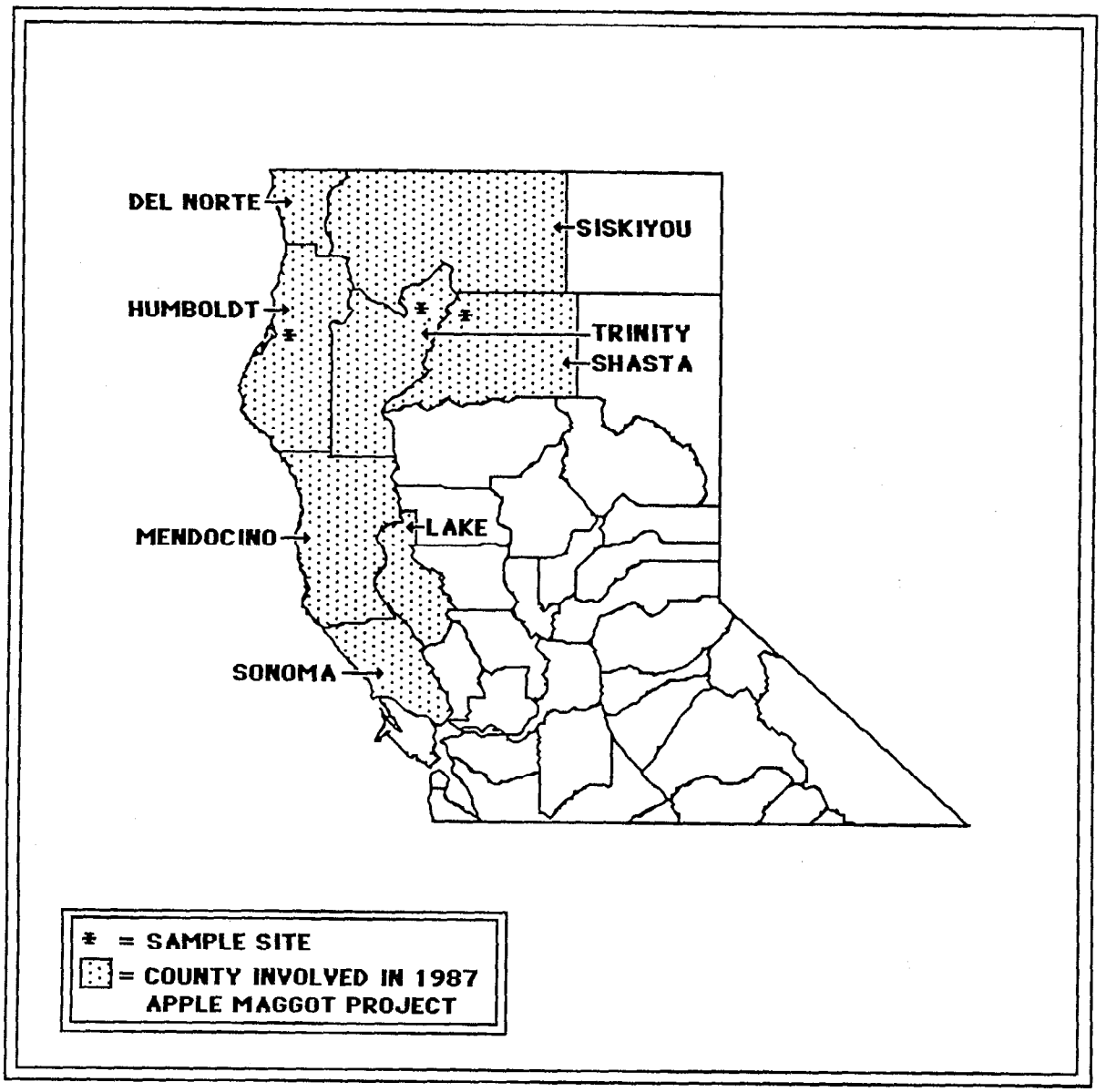


FIG. 1. NORTHERN CALIFORNIA COUNTIES INCLUDED IN THE 1987 APPLE MAGGOT PROJECT.

Shasta, and Trinity Counties. Monitoring conducted in Humboldt County provided a second year of information on the environmental fate of phosmet in this northern coastal county. Monitoring sites in Shasta and Trinity Counties provided data on the fate of phosmet in these warmer and drier locations.

The locations of specific sampling sites in each county were selected according to accessibility of the property, property owner's permission, and the presence of sufficient amounts of fruit and foliage on the host trees.

The site in Humboldt County was on public property administered by the Humboldt Bay Municipal Water District (HBMWD) located on Warren Creek Road, west of Arcata (Figure 2). Leaf, fruit, and soil samples were collected randomly from three of six apple trees on the property. Each fruit sample was a composite sample taken from three trees with each tree contributing an equal number of apples. Limited availability of apples prevented collection of replicate fruit samples. Soil subsamples, taken from beneath the tree canopy, were collected from the three trees and combined into one composite sample. Two composite soil samples were collected at this site. Two composite leaf samples were collected from the three trees using the procedure described for soil.

The site in Trinity County was located on United States Forest Service (USFS) property at the Guard Station north of Trinity Center (Figure 3). Samples from this site were collected from two apple trees in the same manner as those described for the HBMWD site.

A different sample collection method was used at the third site in Shasta County at Castle Crags State Park, located near Dunsmuir (Figure 4). Three apple trees were monitored; instead of combining subsamples from the three

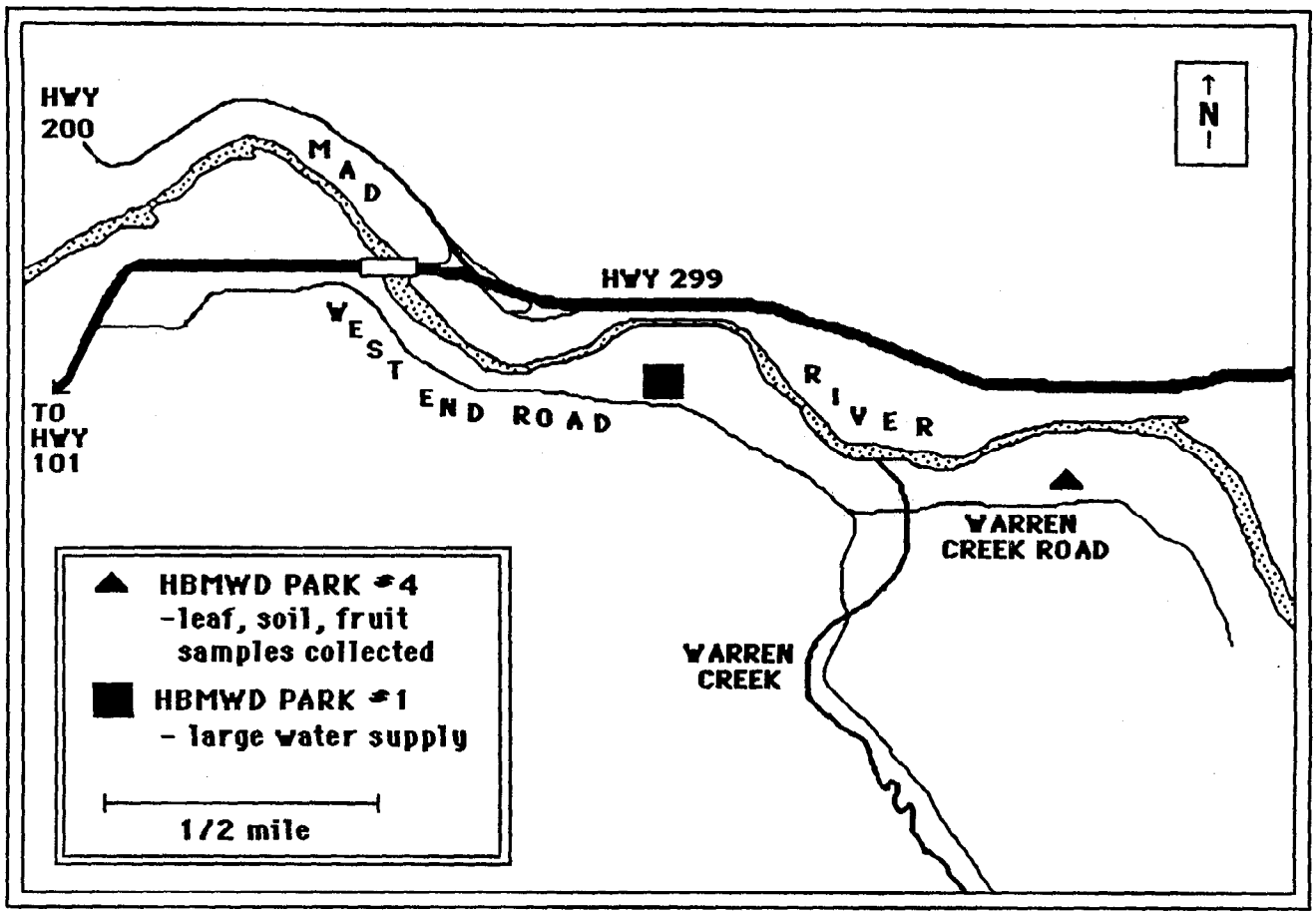


FIG 2. MONITORING SITES IN HUMBOLDT COUNTY FOR THE 1987 APPLE MAGGOT PROJECT.

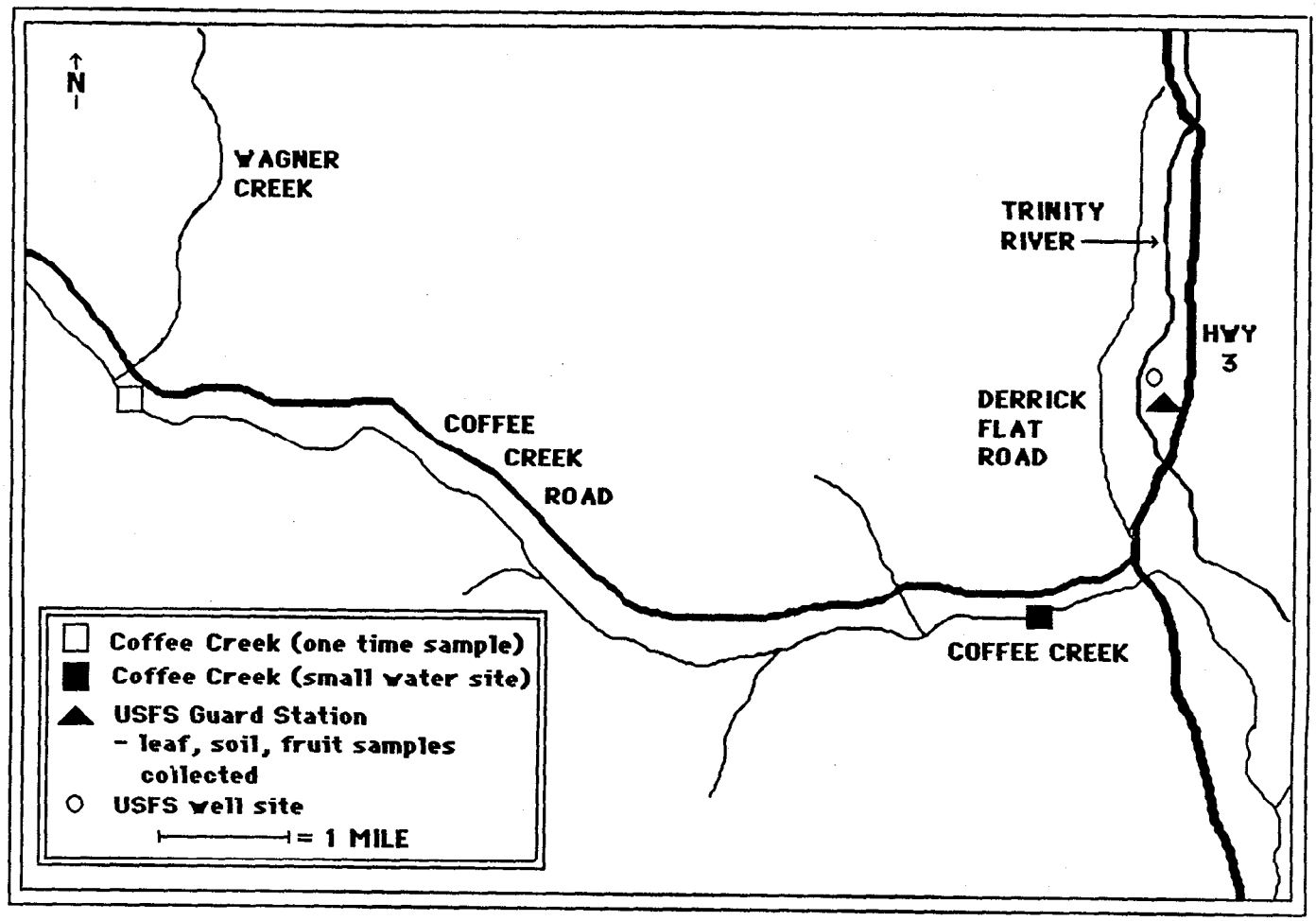


FIG. 3. MONITORING SITES IN TRINITY COUNTY FOR THE 1987 APPLE MAGGOT PROJECT.

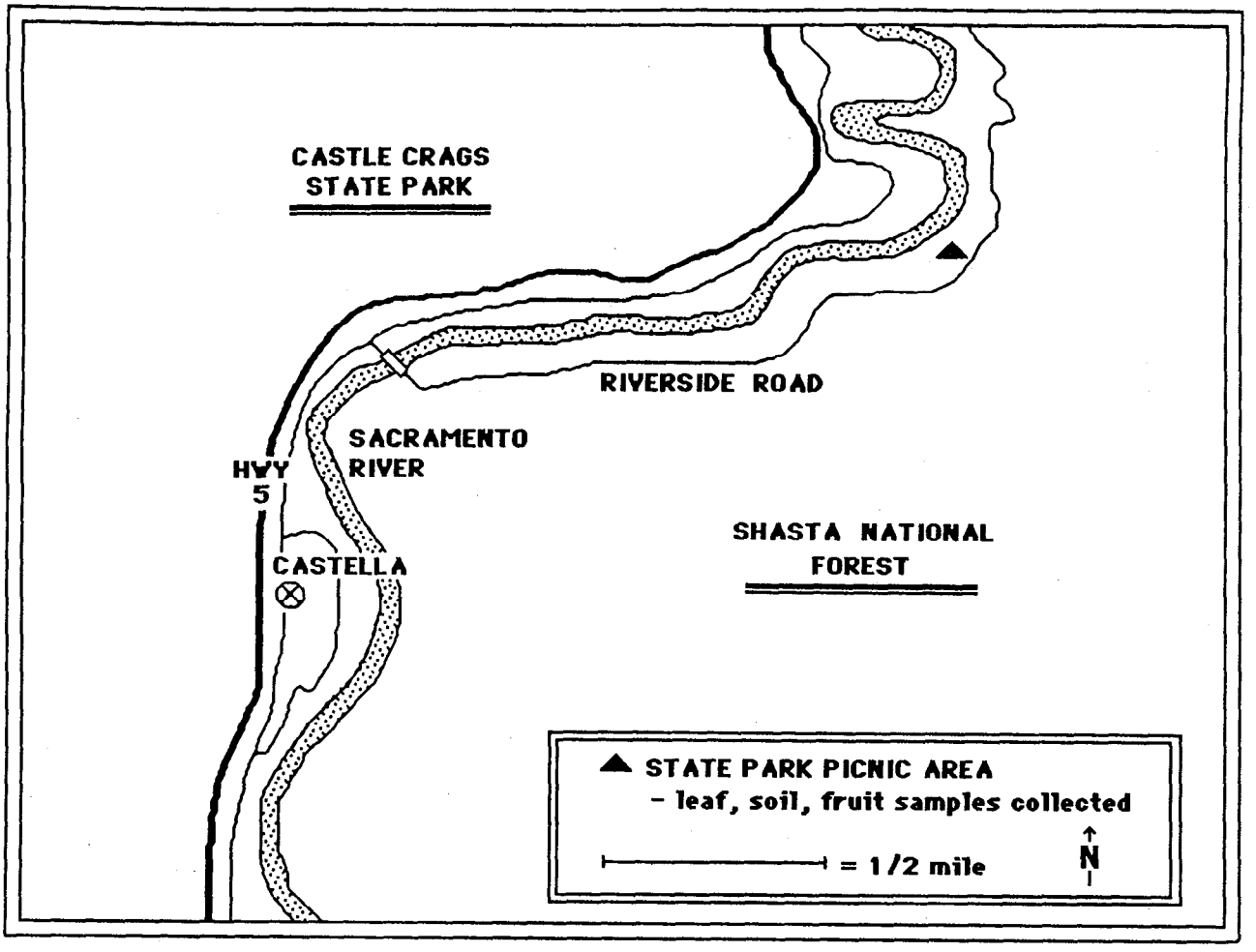


FIG. 4. MONITORING SITE IN SHASTA COUNTY FOR THE 1987 APPLE MAGGOT PROJECT.

trees, each leaf, fruit, and soil sample was collected from only one individual tree. Samples from the second and third trees represented their respective trees only, thus providing three replicates for each sample matrix on each monitoring day at this site.

Background samples were collected from each of the sites during the week prior to the site's initial spray. Leaf, fruit, and soil samples were collected on the day following each application to estimate maximum pesticide residue levels. Additional samples were collected weekly from each site during the time between sprays with the sites monitored for eight weeks from the date spraying began.

Water samples, taken from locations in Humboldt and Trinity counties, were collected within 24 hours after a site was sprayed and then at weekly intervals between sprays. In Humboldt County, water samples were taken at the drinking water intake at HBMWD, Park #1, on the Mad River (Figure 2). Samples were also collected on a similar schedule at the drinking water intake on Coffee Creek in Trinity County (Figure 3). Four well water samples from the USFS Guard Station were taken over the course of the monitoring program. An additional site on Coffee Creek was monitored only once. This site was sampled because a small stream flowed through a heavily treated area and emptied into Coffee Creek. Samples were collected immediately following application of trees surrounding the tributary.

Sampling Methods

Foliage--Leaf samples were collected from the trees by cutting each leaf off at the petiole with scissors and placing it directly into a 1-quart glass jar. Samples consisted of approximately 30 leaves per jar gathered throughout the

tree's canopy. The jar was sealed with a foil-lined lid and cooled immediately on wet ice.

Soil--Approximately 40 surface-soil plugs (2.5 cm long, 2 cm diameter) were collected using a stainless steel Oakfield® tube. These 40 plugs collectively weighing approximately 500 g were taken randomly from beneath the tree's canopy and placed in a 1-quart glass jar. A foil-lined lid sealed the jar which was cooled immediately on dry ice.

Fruit--Approximately 500 g of apples (5-10) were collected throughout the tree canopy using a wire basket fruit picker. Samples were transferred to a polyethylene bag, sealed, and immediately stored on dry ice.

Water--One-liter, narrow-neck, amber glass bottles were filled using a hand powered vacuum pump. Water was pumped up through 1/4 inch diameter Teflon® tubing which was submerged below the surface of the water. The sample was acidified by adding a predetermined amount of 1N sulfuric acid solution, usually 3-5 drops, to reduce the rate of phosmet hydrolysis. The pH and temperature of the sample were recorded. Daily flow rate data were obtained for the Mad River site from the HBMWD and for Coffee Creek, from the United States Geological Survey.

Samples from the well at the USFS Guard Station were collected directly from a valve on the well head after flushing the standing water in the well's casing for a minimum of 10 minutes. Well water samples were preserved in the same manner as the surface water samples.

Laboratory Methods

North Coast Laboratories, located in Arcata, California, was the primary laboratory that conducted the pesticide analyses. Leaf, apple, soil and water samples were analyzed for the presence of phosmet and phosmetoxon using gas

chromatography (GC). The extraction procedures and operating conditions for GC analyses are included in the methods section in Appendix I.

Quality assurance guidelines were followed throughout this study for methods development, continuing quality control, and split samples. Split samples were analyzed by the CDFA Chemistry Lab Services. Appendix II contains the results of these analytical guidelines.

Statistical Methods

The analysis of variance model applied to the foliar, fruit and soil phosmet concentrations included factors for location, replication within location, pesticide spray number, and number of days post application, together with all associated two and three factor interactions. Shown below is the general analysis of variance table. Degrees of freedom varied according to the number of replicate samples obtained for the particular sampling matrix.

Analysis of Variance

Source of Variation	Degrees of Freedom	F-Test
Location	L-1	MS_L/MS_R
Replication(Location)	R	MS_R
Spray	S-1	MS_S/MS_{Error}
Days Post Application	D-1	MS_D/MS_{Error}
Location X Spray	(L-1)*(S-1)	MS_{LXS}/MS_{Error}
Location X Days Post	(L-1)*(D-1)	MS_{LXD}/MS_{Error}
Spray X Days Post	(S-1)*(D-1)	MS_{SXD}/MS_{Error}
Location X Spray X Days Post	(L-1)*(S-1)*(D-1)	MS_{LXSXD}/MS_{Error}
Error	by subtraction	
Corrected total	N-1	

The monitoring schedule called for sampling on days 1, 7 and 14 following the first phosmet spray while samples were collected on days 1 and 7 following the next two sprays. Additional samples were taken on the day immediately following a fourth spray at the Castle Crags and Coffee Creek inland locations. In order to present a more coherent analysis and avoid the statistical ambiguity subsequent to interpreting results from analyses with missing data, the primary analyses focused on sampling days 1 and 7 for all three locations and spray 1 through 3 combinations.

An additional analysis addressed trends over a longer time period for all three locations for samples taken on days 1, 7 and 14 following the first spray only. This analysis included the factors location, replication within location, and days post application.

The main effects of location, spray and days post application were analyzed only if they were not involved in a statistically significant interaction. In the presence of a significant interaction (such as an observed increase in residue levels at one site a week following a particular application when all other levels decreased following applications at the remaining sites), one of the factors responsible for the differential response pattern was examined separately.

Pairwise comparisons were made only if the overall F test for a main effect was significant ($P \leq 0.05$). Pairwise comparisons with unequal replicates necessitated construction of estimated standard errors rather than employing those generated by computing packages which are generally incorrect. Variance

components for these standard errors were estimated using restricted maximum likelihood methods.

Due to the limited number of positive ($\geq$ minimum detectable limit) phosmetoxon concentrations, formal statistical analyses were not performed; results are presented in a descriptive manner only.

Analyses were performed using Type III Sums of Squares in the General Linear Models procedure of the SAS® System Version 6 for Personal Computers. Following standard statistical practice, results are declared statistically significant if the P-value is less than or equal to 0.05. Results are said to be marginally significant if the P-value is greater than 0.05 but less than or equal to 0.10 ($0.05 < P < 0.10$).

Due to the unequal number of replicates, the ratio of the mean squares presented in the preceeding analysis of variance table have only approximate F distributions. The reader is urged to interpret the importance of individual P values with caution due to the imbalanced design (unequal replicates) of this experiment leading to approximate F tests. Conclusions and inferences should be based on trends such as $P \leq 0.05$ or $P \leq 0.10$ rather than on specific P values such as $P = 0.06$.

Foliar concentrations of phosmet and phosmetoxon are reported in both micrograms per square centimeter (dislodgeable residue, surface area basis) and parts per million (total, dry weight basis). Soil residues are reported in parts per million on a dry weight basis while total fruit residues are presented in parts per million, wet weight.

RESULTS

Foliage

Results from the chemical analysis of foliar residues for phosmet are presented in Tables 1A and 1B as well as Figures 5A and 5B. Four of the seven background samples yielded observable dislodgeable phosmet residue levels (Appendix III, Table III-10). Background residues ranged from 0.002 to 0.01 ug/cm^2 with ppm levels of 0.3 to 1.7. Both Coffee Creek samples were above the minimum detectable level while the other two positive phosmet residues were observed at Castle Crags. None of these seven samples yielded measurable amounts of phosmetoxon. No adjustments for background values were made to the statistical analyses or resulting estimates.

Following application, foliage levels of phosmet ranged from 0.26 ug/cm^2 to 5.7 ug/cm^2. When the foliar samples were expressed as residues determined in parts per million, the corresponding minimum and maximum values were 43 and 700 ppm. respectively.

Both formal statistical analyses and graphical analyses revealed that phosmet residues at the inland location, Castle Crags, degraded differently than at the other two locations (Figures 5A and 5B). At Castle Crags, average foliar residues appeared to increase from the first to the seventh day following the first spray. Degradation following the second and third spray appeared to occur at a higher rate at Castle Crags as compared with results for these two sprays at the remaining locations. This apparent increase following the first spray may have been due to sampling variability. Due to this inconsistent pattern, comparisons for sprays and days since application were made within Castle Crags

Table 1A. Concentrations of Phosmet on Foliar Samples Collected for the Apple Maggot Project 1987 in parts per million.

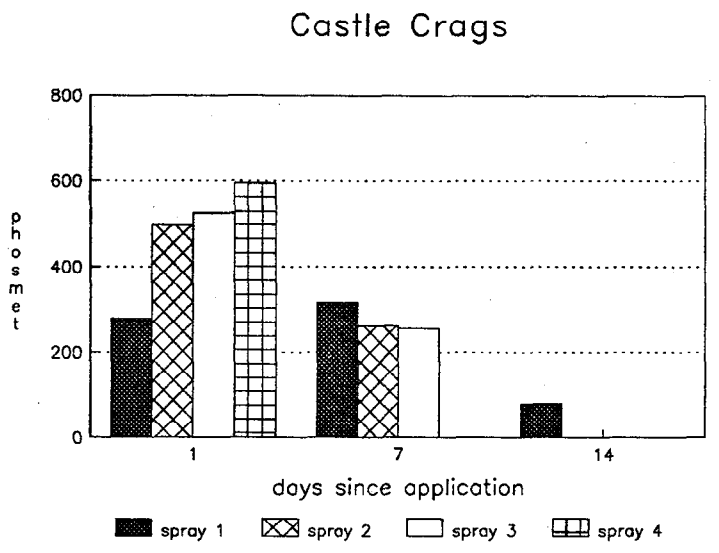
		Days Post Application											
		1				7				14			
Location	Spray	N	Mean	Min	Max	N	Mean	Min	Max	N	Mean	Min	Max
Castle Crags	1	2	279	259	300	3	317	265	400	3	80.6	42.6	146
	2	3	497	389	583	3	261	215	284		NS[a]		
	3	3	526	471	609	3	256	209	289		NS		
	4	3	595	394	700		NS				NS		
Coffee Creek	1	2	411	211	610	2	241	228	254	2	143	109	177
	2	2	386	345	426	2	251	229	273		NS		
	3	2	417	396	439	2	299	239	359		NS		
	4	2	405	310	500		NS				NS		
Humboldt Bay	1	2	500	485	514	2	239	190	289	2	200	155	245
	2	2	299	289	310	2	204	200	209	2	176	136	217
	3	2	379	357	400	2	256	241	271		NS		

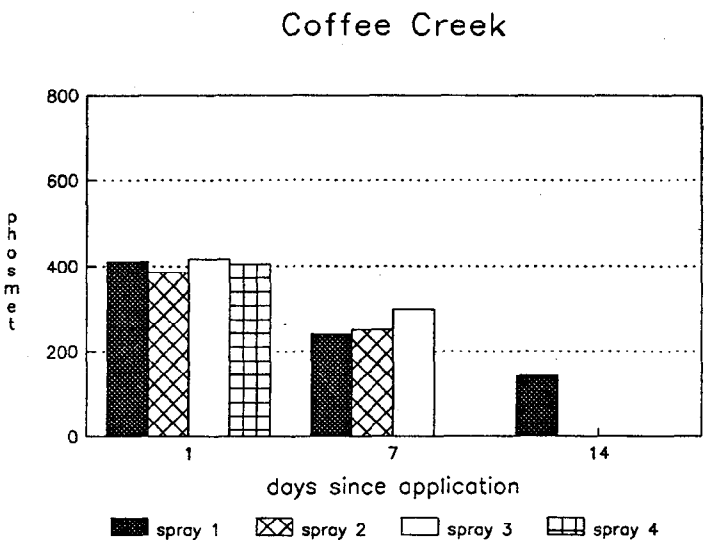
a) NS: Not Sampled

Table 1B. Concentrations of Phosmet on Foliar Samples Collected for the Apple Maggot Project 1987 in micrograms per square centimeters.

		Days Post Application											
		1				7				14			
Location	Spray	N	Mean	Min	Max	N	Mean	Min	Max	N	Mean	Min	Max
Castle Crag	1	2	1.8	1.5	2.0	3	2.1	1.7	2.4	3	0.6	0.3	1.0
	2	3	3.4	3.2	3.5	3	1.8	1.6	2.0		NS[a]		
	3	3	3.7	3.1	4.3	3	1.9	1.3	2.5		NS		
	4	3	4.0	2.1	5.7		NS				NS		
Coffee Creek	1	2	3.0	1.8	4.2	2	1.5	1.5	1.5	2	0.9	0.8	1.1
	2	2	2.8	2.4	3.2	2	1.8	1.7	1.8		NS		
	3	2	2.8	2.7	2.9	2	1.9	1.6	2.2		NS		
	4	2	3.0	2.5	3.6		NS				NS		
Humboldt Bay	1	2	3.4	3.1	3.8	2	1.6	1.2	1.9	2	1.3	1.0	1.6
	2	2	2.1	1.9	2.2	2	1.4	1.4	1.5	2	1.2	0.9	1.5
	3	2	2.7	2.6	2.7	2	1.7	1.7	1.8		NS		

a) NS: Not Sampled





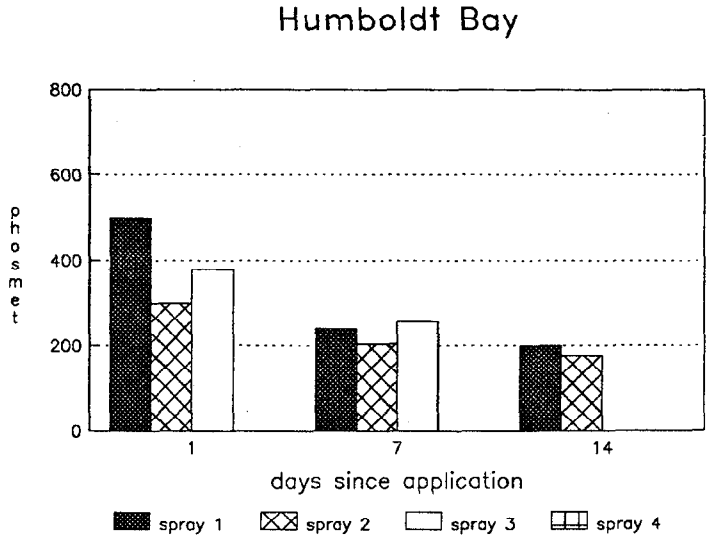
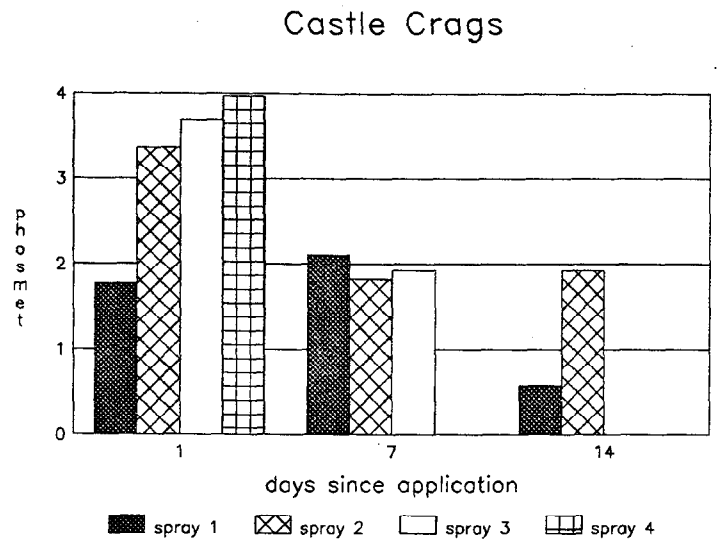
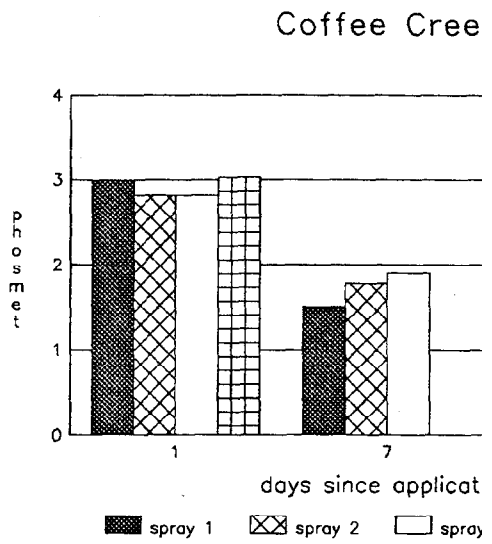


Figure: 5A
Mean Phosmet Concentration in Foliar Samples (ppm)

(no bar denotes no samples taken)





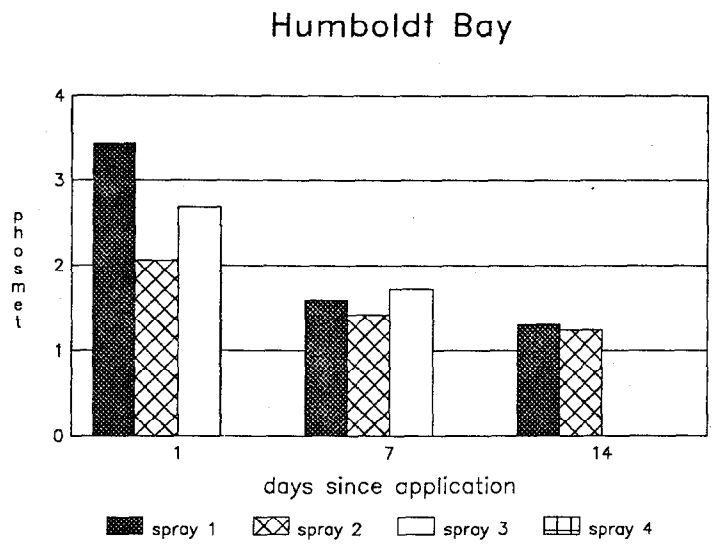


Figure: 5B
Mean Phosmet Conc
in Foliar Sampl
(ug/sq cm)

(no bar denotes no samples

and then between the Coffee Creek and Humboldt Bay locations. The analyses did not reveal any overall difference in foliar residues between the Coffee Creek and Humboldt Bay locations (Appendix III, Table III-1 and Table III-3). Mean foliar residues after adjusting for all other factors were 2.3 ug/cm^2 and 2.2 ug/cm^2 for these inland and coastal locations, respectively. The corresponding total foliar residues were 334 and 313 ppm. No significant difference among the three sequential sprays was revealed by the analysis of the Coffee Creek and Humboldt Bay data. Overall adjusted means were 2.4, 2.0 and 2.3 ug/cm^2 for sprays one, two and three, respectively. Similar results were noted when the data were expressed in parts per million (Appendix III, Table III-1 and Table III-3).

Significant differences in foliar residues between the first and seventh day since application were revealed for the Coffee Creek and Humboldt Bay locations ($P<0.001$). On the average, dislodgeable foliar residues decreased from 2.8 to 1.7 ug/cm^2 and decreased an average of 151 ppm from 399 to 248 ppm for these two locations.

The analysis addressing continued degradation through day 14 excluded data from Castle Crags due to the aforementioned increase in phosmet concentrations from day 1 to day 7 following the first phosmet spray. A steady and parallel decrease in phosmet concentrations for both the remaining locations was observed. On the average, a decrease of approximately 50% is noted for day 1 to day 7, while the rate of decrease from day 7 to day 14 slowed somewhat demonstrating an overall decrease from day 1 to day 14 close to 66% (Appendix III, Table III-3 and Table III-4).

Soil

Results from the chemical analysis of soil residues for phosmet are presented in Table 2 and in Figure 6. Prior to the first spray, phosmet residues in surface soil samples were detected at both the Castle Crags and Coffee Creek inland sites for all five samples (Appendix III, Table III-9). Phosmet residue levels ranged from 0.04 to 0.18 ppm (dry weight basis). No pre-treatment residues were found at the Humboldt Bay coastal site.

Post-treatment, all samples contained measurable amounts of phosmet ranging from 0.05 to 2.25 ppm. No clearcut tendencies or degradation patterns were evidenced for these soil data. Phosmet soil residues appeared to increase, though not at a constant rate, for all three sprays at Castle Crags while no discernible pattern arose for the remaining two locations. This lack of a discernible pattern coupled with high variability precluded any meaningful statistical analyses (Appendix III, Table III-5). As a high degree of variability is typically inherent in soil surface sampling a greater number of replicates would be required to detect underlying trends and to calculate reliable estimates of soil residues.

Phosmetoxon residues were not detected at any time during the course of monitoring.

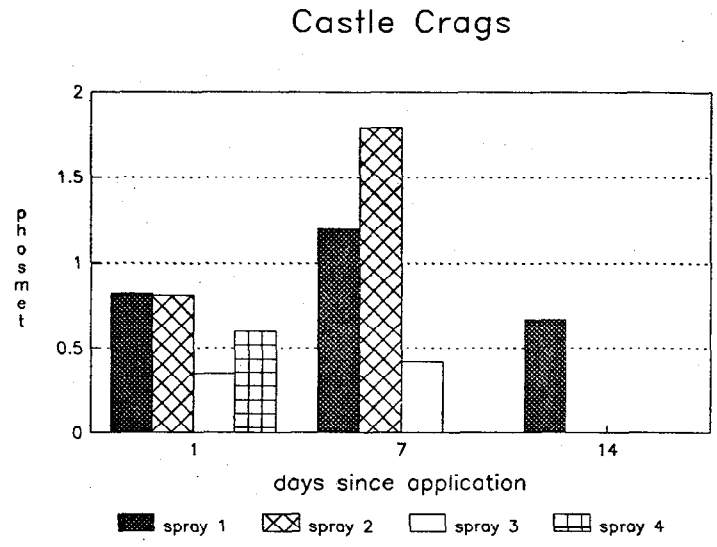
Fruit

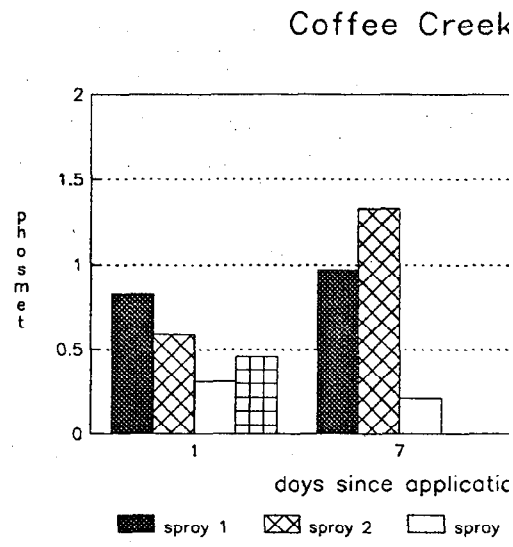
Total fruit phosmet residues (ppm wet basis) are presented in Table 3 and presented graphically in Figure 7. Phosmet fruit residues were not detected prior to pesticide application. Phosmet concentrations post-treatment ranged from 0.10 to 14 ppm. The current established tolerance limit of 10 ppm was

Table 2. Concentrations of Phosmet on Soil Samples Collected for the Apple Maggot Project 1987 in parts per million.

		Days Post Application											
		1				7				14			
Location	Spray	N	Mean	Min	Max	N	Mean	Min	Max	N	Mean	Min	Max
Castle Crags	1	2	0.8	0.6	1.1	3	1.2	0.8	2.0	3	0.7	0.5	0.8
	2	3	0.8	0.6	1.1	3	1.8	1.2	2.2		NS[a]		
	3	3	0.3	0.1	0.6	3	0.4	0.2	0.5		NS		
	4	3	0.6	0.5	0.7		NS				NS		
Coffee Creek	1	2	0.8	0.5	1.2	2	1.0	0.9	1.0	2	1.0	1.0	1.0
	2	2	0.6	0.5	0.7	2	1.3	0.9	1.8		NS		
	3	2	0.3	0.2	0.4	2	0.2	0.2	0.2		NS		
	4	2	0.5	0.4	0.6		NS				NS		
Humboldt Bay	1	2	1.1	1.1	1.1	2	0.2	0.1	0.3	2	0.1	0.1	0.1
	2	2	0.1	0.1	0.1	2	0.1	0.1	0.2	2	0.1	0.1	0.1
	3	2	0.6	0.6	0.7	2	0.1	1.1	1.1		NS		

a) NS: Not Sampled





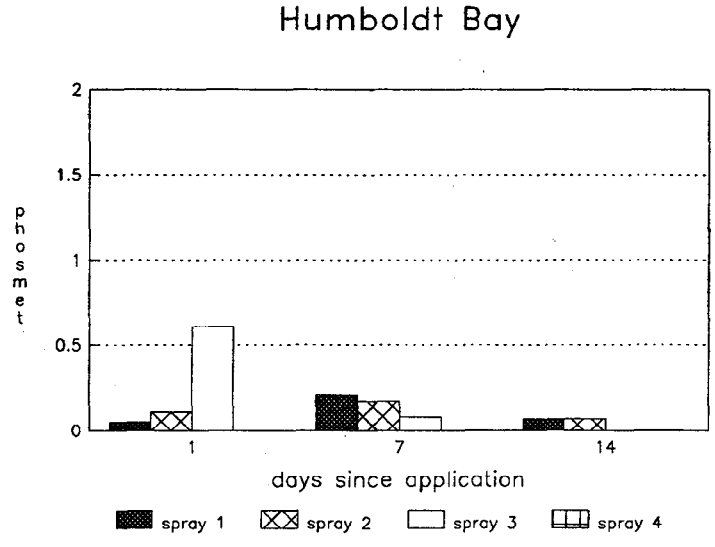


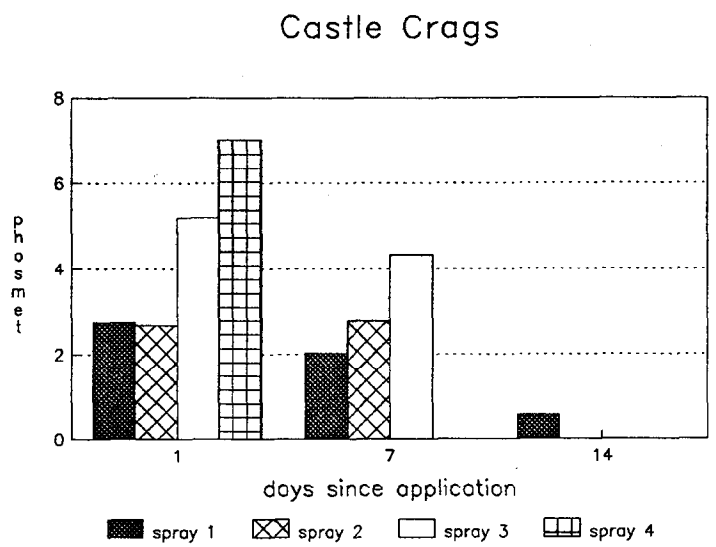
Figure: 6
Mean Phosmet Con
in Soil Sampl
(ppm)

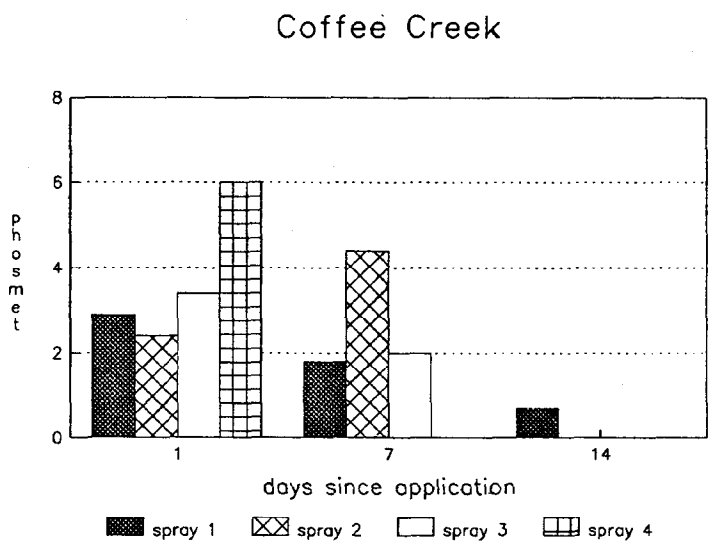
(no bar denotes no samp

Table 3. Concentrations of Phosmet on Fruit Samples Collected for the Apple Maggot Project 1987 in parts per million.

		Days Post Application											
		1				7				14			
Location	Spray	N	Mean	Min	Max	N	Mean	Min	Max	N	Mean	Min	Max
Castle Crags	1	2	2.7	2.6	2.9	3	2.0	1.4	2.5	3	0.6	0.2	1.1
	2	3	2.6	2.0	3.2	3	2.8	1.6	3.8		NS[a]		
	3	3	5.2	4.8	5.6	3	4.7	2.6	7.4		NS		
	4	3	7.5	3.6	13.8		NS				NS		
Coffee Creek	1	1	2.9	2.9	2.9	1	1.8	1.8	1.8	1	0.7	0.7	0.7
	2	1	2.4	2.4	2.4	2	4.4	4.4	4.4		NS		
	3	1	3.4	3.4	3.4	1	2.0	2.0	2.0		NS		
	4	1	6.4	6.4	6.4		NS				NS		
Humboldt Bay	1	1	1.3	1.3	1.3	1	0.9	0.9	0.9	1	1.2	1.2	1.2
	2	1	1.6	1.6	1.6	1	0.1	0.1	0.2	1	0.2	0.2	0.2
	3	1	1.2	1.2	1.2	1	0.7	0.7	0.7		NS		

a) NS: Not Sampled





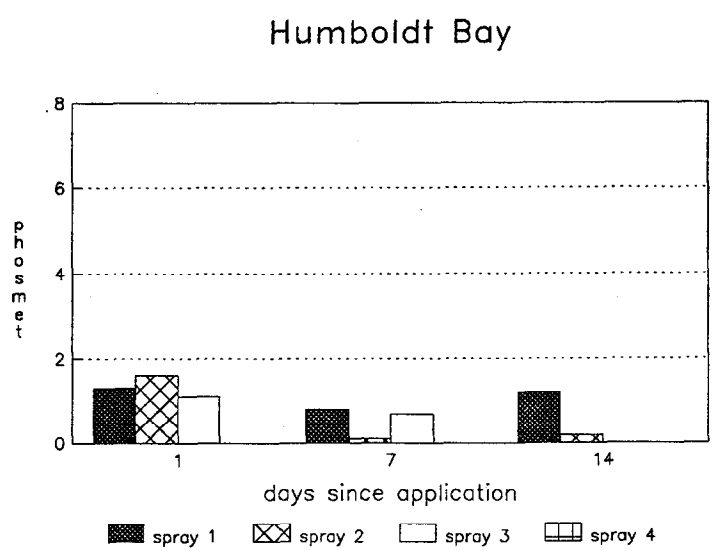


Figure: 7
Mean Phosmet Concentration in Fruit Samples (ppm)

(no bar denotes no samples taken)

exceeded for one sample on the day immediately following the fourth spray. The fruit sample with the next highest residue level was 7 ppm seven days after the third spray. No detectable phosmetoxon residues were found in fruit at any time of the study.

Inspection of the total fruit phosmet concentrations presented in Figure 7 indicated an increase in phosmet residues from day 1 to day 7 post-application for the second spray at Coffee Creek. This increasing trend was not observed for the other sprays at any location.

To increase the chance of detecting statistically significant trends when no significant statistical interactions were detected (Appendix III, Table III-6), an additional analysis was performed using only the main effects of location, spray number and days since application (Appendix III, Table III-7). This modified analysis procedure had no effect on the nearly significant test for differences among the three locations ($0.05 < P \leq 0.10$). Overall adjusted means for Castle Crags, Coffee Creek and Humboldt Bay were 3.3, 2.8 and 0.9 ppm, respectively.

The analyses of the modified model demonstrated a significant difference in fruit residues among the sprays ($P<0.05$) but no significant degradation in fruit residues from the first to seventh day since application. On the average, fruit residues were 2.6 ppm on the first day after application compared with 2.1 ppm seven days after application. Examination of these data for the three sprays demonstrated significant increasing fruit residues over the three sprays with adjusted means of 1.9, 2.3, and 2.8 ppm, respectively. Further increases from the third to fourth spray were seen for both inland locations.

Examination of degradation data through day 14 following the first phosmet spray indicated that, on the average, significantly lower residues were seen for Humboldt Bay as compared with both inland sites ($P < 0.05$) (Appendix III, Table III-8). Phosmet fruit residues, adjusted for days since application, were 1.1 ppm for Humboldt Bay while an average total fruit residue level of 1.8 ppm was noted at both the inland sites. Although the overall analyses for all three sprays did not reveal statistically significant degradation from day 1 to day 7, analyses only focusing on the first spray yielded significant degradation of about thirty percent ($P \leq 0.01$) between day 1 and day 7 following application. The overall decrease from day 1 to day 14 following the first spray was seventy-three percent.

It is difficult to discern here if some of the patterns discussed above reflect true underlying trends or are the result of sampling without replication at Coffee Creek and Humboldt Bay.

Surface Water

Neither phosmet nor phosmetoxon were detected in background surface water samples nor in the 25 samples taken subsequent to phosmet applications. During the sampling period, stream flows for the Mad River and Coffee Creek ranged from 102-127 and 43-81 cubic feet per second, respectively. The pH range values corresponding to the Mad River and Coffee Creek sites were 7.2 to 8.3, and 7.1 to 8.1, respectively.

Quality Control

Five apple, seven soil and two water samples were selected for ongoing quality control analyses. One-half of each sample was analyzed by the primary laboratory, NCL, while the other half was analyzed by CDFA Chemistry Lab Services.

Results for four of the seven split soil samples differed markedly between the two laboratories. Good agreement was observed for two pairs at the low end of the residue range (0.66,0.77 and 0.72,0.95 ppm for NCL and CDFA, respectively), and for one other split sample with higher residues (1.1,1.1 for NCL and CDFA, respectively. However, mid-range phosmet residue levels analyzed by NCL yielded consistently lower phosmet residues than those samples analyzed by CDFA. For example, one split soil sample was reported by NCL as containing 0.68 ppm of phosmet while the other half of the sample analyzed by CDFA was analyzed as containing 1.7 ppm of phosmet (Appendix II, Table II-16).

The amount of phosmet detected for split fruit samples analyzed by NCL was significantly higher than CDFA as determined by a paired t-test (Appendix II, Table II-15). On the average, total phosmet residue levels reported by NCL were 1.4 ppm higher than those reported by the CDFA laboratory. The primary laboratory, NCL, reported the levels of phosmet in the split samples to be approximately 2-4 times higher than those sent to CDFA.

No detectable residues were found in any of the surface water samples.

DISCUSSION

Background Samples

Background water and apple samples showed no detectable levels of phosmet or phosmetoxon at any of the monitoring sites. However, at both of the two inland sites background leaf and soil samples contained low levels of phosmet. The possibility exists that these samples were contaminated during collection, but this is unlikely since spraying by CDFA had not yet begun in the vicinity of these areas. Private or commercial use of phosmet near the monitoring sites could be a possible reason it was detected in the samples, but this is only speculation. Various studies do not support the idea that phosmet would persist in the soil for the nine months after the 1986 treatment was completed (Lamoreaux and Newland, 1977 and Menn et al., 1965). However, further soil sampling over time would be needed to investigate this possibility.

Foliage

Phosmet residue levels on foliage samples demonstrated a similar pattern of dissipation for 1986 and 1987 except for an apparent accumulation of foliar residues at the Castle Crags site in 1987. Though the degradation patterns were similar, foliar residues were slightly higher for 1987. Residue levels ranged from 0.26 to 5.7 ug/cm^2 for 1987 versus 0.27 to 3.6 ug/cm^2 for 1986. Only 11 of 62 leaf samples (17%) collected were positive for phosmetoxon. The highest level observed was 0.03 ug/cm^2.

Dissipation trends were apparent at all three monitoring sites. However, at the Castle Crags site, the trend was not consistent with the two other sites. A low residue level was measured one day following the first spray. This low

level is questionable considering that the phosmet level in the sample collected six days later was higher rather than lower as would be expected. This anomaly probably resulted from sampling variation. Additionally, at Castle Crags, dissipation following the second and third sprays appeared to occur at a higher rate as compared with results for these two sprays at Coffee Creek and Humboldt Bay. Though at differing rates between Castle Crags and the other two sites, generally speaking, the concentration of phosmet decreased between sprays.

As there was no overall difference in mean foliar residue levels between the coastal site (HBMWD) and the inland site at Coffee Creek, climate did not appear to affect the rate of phosmet decay. There was an apparent trend towards more rapid dissipation at the Castle Crags site but it wasn't clear whether this was an actual process taking place or an effect caused by sampling variation.

Soil

The concentrations of phosmet in soil samples were much lower during the 1987 treatment season than they were for the 1986 season. Soil concentrations in 1987 ranged from 0.05 to 2.25 ppm and in 1986 the range was from 0.16 to 5.6 ppm. Since there was no known change in phosmet application procedures between the two successive years, differences may have been attributable to sampling variation and to the change of the primary laboratory assignment from CDFA to North Coast Laboratory (NCL). As shown by the quality control analyses, when soil samples were split into two equal portions, the half analyzed by CDFA was, with one exception, always reported to contain higher concentrations of phosmet than NCL's half of the sample. This suggests that the lower concentrations found in soil in 1987 were probably a result of laboratory variability.

Due to the variation observed in the samples, no dissipation patterns nor site differences attributable to climate were seen.

Phosmetoxon was not found in any of the 61 soil samples collected. The minimum detection level was 0.05 ppm.

Fruit

Variability in fruit residue levels caused by inadequate replication masked any clear dissipation trends. However, to some degree, dissipation between sprays was observed at each of the three sites. Though the overall mean phosmet levels at the Humboldt Bay site were lower than the levels at the two inland sites, the dissipation pattern was similar at all three locations.

Except for the second spray, results for both inland sites showed increasing residue levels immediately following each successive application. Several factors could account for this apparent residue accumulation. First, the inland sites had a shorter time interval between sprays than the coastal site (14 days versus 21 days); consequently the expected amount of residue dissipation would be less. Secondly, it is possible that more phosmet was used during applications later in the season. Finally, the apparent accumulation could be a result of variation within the samples and not an actual trend. Future monitoring programs should include more frequent sampling with increased replication at each site.

For 1987, the phosmet concentrations in fruit were higher than in 1986. The highest level for 1987, 14 ppm, was detected in a single sample (all other samples were less than 10 ppm) and for 1986 it was 2.5 ppm. The difference in the two treatment years may be explained by the change in analytical

laboratories. Samples collected for quality control purposes had higher concentrations when analyzed by NCL and lower concentrations when analyzed by CDFA. The effect of climatic differences on the breakdown rate of phosmet at the coastal and inland sites was not apparent.

Surface Water

Hydrolysis is a major pathway for the degradation of phosmet (Freed et al., 1979). Considering the pH range found in the water samples collected, it is unlikely that phosmet would have persisted for more than a few hours. Additionally, proper application methods used by the AMEP spray crews were an important factor in keeping phosmet from moving off site.

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APPENDIX 1

LABORATORY ANALYTICAL METHODS

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North Coast Laboratories, LTD.
5680 West End Road
Arcata, California 95521
(707)822-4649

Original Date:
Supercedes:
Current Date: 3/15/88

Imidan in Leaf Samples

SCOPE:

This method is for the determination of residues of Imidan in leaf samples.

REAGENTS AND EQUIPMENT:

1. Suf-ten.
2. Pesticide grade toluene.
3. Sodium sulfate.
4. 125 ml separatory funnel.
5. 1000 ml beaker.
6. 40 ml VOA vial.

ANALYSIS:

1. Add 200 ml of DI to a sample jar containing the leaves to be tested.
2. Add 4 drops of suf-ten.
3. Shake jar 5 minutes.
4. Decant aqueous portion into a 1000 ml beaker.
5. Repeat steps 2 and 3 two more times.
6. Decant 60 ml of aqueous extract into 125 ml sepratory funnel (this is a 1:10 dilution).
7. Add 10 ml of Toluene and shake for two minutes.
8. Allow mixture to stand for approx. ten minutes.
9. Drain lower aqueous phase.
10. Drain toluene into 40 ml vial and add sodium sulfate.
11. Decant toluene into a 1.5 ml storage vial.

EQUIPMENT CONDITIONS:

Gas Chromatograph - Varian 600 with 402 data system.

Detector: TSD m.v. between 8-15
Column: J & W DB1301 megabore.

Column Temp.: 230°

Inj. Temp.: 205°

Ion oven: 210°
Flow: 300 on flow control valve (30 ml/min.).

CALCULATIONS:

Spike with 100 ul of 1000 ppm Imidan.

$$(100\ ul)\ \frac{(1000\ ng)}{ul} = \frac{100000\ ng}{sample} = \frac{100\ ug}{sample} = \frac{0.1\ mg}{sample}$$

Unextracted STD - 100 ul of 1000 ng/ul Imidan and Imidoxone into 10.0 ml toluene = 100 ug/sample (all samples are a 1:10 dilution) or 10 ul of 1000 ng/ul Imidan and Imidoxone into 10.0 ml toluene = 100 ug/sample (all samples are <u>not</u> diluted).

Detection limit = 0.5 ug/sample.

North Coast Laboratories, LTD.
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Original Date:
Supercedes:
Current Date: 3/15/88

Imidan in Soil

SCOPE:

This method is for the determination of residues of Imidan in soil.

REAGENTS AND EQUIPMENT:

1. Pesticide grade ethyl acetate.
2. 1 gram sodium sulfate.
3. 40 ml VOA vial.
4. 300 ml BDD bottle.
5. Wrist arm shaker.

ANALYSIS:

1. Add 50 grams of soil sample to a 300 ml BDD bottle. Add Spk.
2. Add 10 ml of DDI.
3. Add 100 ml of ethyl acetate and shake on a wrist arm shaker for 30 min.
4. Add 5 ml of the extract to a 40 ml VOA vial with 1 gram sodium sulfate and shake for 30 seconds.
5. Decant to a 1.5 ml storage vial.

EQUIPMENT CONDITIONS:

Gas Chromatograph - Varian 600 with 402 data system.

Detector: TSD m.v. between 8-15
Column: J & W DB1301 megabore.
Column Temp.: 230°
Inj. Temp.: 205°
Ion oven: 210°
Flow: 300 on flow control valve (30 ml/min.).

CALCULATIONS:

Spike with 250 ul of 1000 ppm Imidan.

$$(250\ ul)\ \frac{(1000\ ng)}{ul} = \frac{250000\ ng}{50\ grams} = \frac{5000\ ng}{gram} = \frac{5\ ug}{gram}\ (PPM)$$

Unextracted STD - 250 ul of 1000 ng/ul Imidan and Imidoxone into 100 ml ethyl acetate = 5 ppm STD or 25 ul of 1000 ng/ul Imidan and Imidoxone into 10 ml ethyl acetate = 5 ppm.

Detection limit = 0.01 ppm

North Coast Laboratories, LTD.
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(707)822-4649

Original Date:
Supercedes:
Current Date: 3/15/88

Imidan in Apple Samples

SCOPE:

This method is for the determination of residues of Imidan in apple samples.

REAGENTS AND EQUIPMENT:

1. Pesticide grade Acetonitrile.
2. Sodium sulfate.
3. Pesticide grade Acetone.
4. 10 ml KD vial.
5. 250 ml Erlenmeyer flask.

ANALYSIS:

1. Chop entire sample bag of apples.
2. Place 50 grams of sample into a blender and add 100 ml of Acetonitrile. Add spk.
3. Blend on high for 2 minutes.
4. Decant acetonitrile through sodium sulfate into a 250 ml wide-mouth erlenmeyer flask.
5. Add 10 grams of NaCl and shake for 1 minute, venting frequently.
6. Allow layers to seperate for 5 min.
7. Pipet 5 ml of upper phase into a KD vial; add 10 ml acetone (1:20 dilution).
8. Blow to near dryness.
9. Repeat step 7 & 8 if water is present.
10. Take up in 1 ml of acetone.
11. Transfer to a 1.5 ml storage vial.

EQUIPMENT CONDITIONS:

Gas Chromatograph - Varian 600 with 402 data system.

Detector: TSD m.v. between 8-15
Column: J & W DB1301 megabore.
Column Temp.: 230°
Inj. Temp.: 205°
Ion oven: 210°
Flow: 300 on flow control valve (30 ml/min.).

CALCULATIONS:

Spike with 250 ul of 1000 ppm Imidan.

$$(250\ ul)\ \frac{(1000\ ng)}{ul} = \frac{250000\ ng}{50\ grams} = \frac{5000\ ng}{gram} = \frac{5\ ug}{gram}\ (PPM)$$

Unextracted STD - 250 ul of 1000 ng/ul Imidan and Imidoxone into 1.0 ml acetone = 5 ppm STD (all samples are a 1:20 dilution) or 12.5 ul of 1000 ng/ul Imidan and Imidoxone into 1.0 ml acetone = 5 ppm (all samples are <u>not</u> diluted).

Detection limit = 0.005 ppm.

North Coast Laboratories, LTD.
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(707)822-4649

Original Date:
Supercedes:
Current Date: 3/15/88

Imidan in Water

SCOPE:

This method is for the determination of residues of Imidan in water.

REAGENTS AND EQUIPMENT:

1. Pesticide grade toluene.
2. 125 separatory funnel.

ANALYSIS:

1. Place 100 ml of sample into a 125 ml spearatory funnel.
2. Add 5 ml of toluene.
3. Shake funnel for 2 minutes.
4. Allow phases to separate for 5 minutes.
5. Drain lower aqueous phase and decant toluene into a 1.5 ml storage vial.
6. Inject 3 ul.

EQUIPMENT CONDITIONS:

Gas Chromatograph - Varian 600 with 402 data system.

Detector: TSD m.v. between 8-15
Column: J & W DB1301 megabore.

Column Temp.: 230°

Inj. Temp.: 205°

Ion oven: 210°
Flow: 300 on flow control valve (30 ml/min.).

CALCULATIONS:

Spike with 5 ul of 100 ppm Imidan and Imidoxone.

$$(5\ ul)\ \frac{(100\ ng)}{ul} = \frac{500\ ng}{100\ ml} = \frac{5\ ng}{ml}\ (ppb)$$

Unextracted STD - 5 ul of 100 ng/ul Imidan and Imidoxone into 5 ml toluene = 5 ppb STD.

Detection limit = 1.0 ppb

APPENDIX II

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QUALITY ASSURANCE RESULTS

Methods Development

For methods development, blank matrix spikes were generated by spiking a known amount of phosmet and phosmetoxon into each matrix. These samples were then extracted and analyzed according to their respective methods, and recoveries were used to set warning and control limits for accuracy within each matrix.

Tables II-1 through II-4 show blank leaf, apple, soil and water samples were spiked with phosmet at 100 and 5000 ug, 0.1 and 5 ppm, 0.1 and 5 ppm, and 5 ppb, respectively; and with phosmetoxon at 100 ug, 0.1 ppm, 0.1 ppm, and 5 ppb, respectively. Tables II-1 through II-4 also show detection limits in leaf, apple, soil and water samples for phosmet as 0.5 ppm, 0.005 ppm, 0.01 ppm, and 1ppb, respectively; and for phosmetoxon as 2.5 ppm, 0.025 ppm, 0.01 ppm, and 1 ppb, respectively.

Table II-5 shows the mean percent recovery and standard deviation (SD) for phosmet in leaf, apple, soil and water samples as 88 +/- 7.6%, 116 +/- 15.1%, 88 +/- 14.9%, and 90 +/- 11.7%, respectively; and for phosmetoxon as 99 +/- 10.9%, 98 +/- 19.3%, 55 +/- 30.3%, and 25 +/- 49.6%, respectively. Table II-5 also shows the warning and control limits set for accuracy within each matrix.

Continuing Quality Control

For continuous quality control during analysis a blank matrix, 2 replicate blank matrix spikes, and 3 multiple measurements of a single extract (replicate extract injections) for each matrix were analyzed for phosmet with each extraction set. Replicate blank matrix spikes were generated and analyzed to show precision of the method. Tables II-7 through II-10 show the mean percent recovery and relative percent difference (RPD) for each matrix. Note that five samples fell outside the lower control limit set for leaf samples at 73%, one fell outside the lower control limit set in apples at 86%, two samples fell outside the upper and lower control limits set in soil at 118% and 58%, respectively, and two fell outside the upper control limit set in water at 113%. Since the method development and sample analysis were completed simultaneously, no corrective action was initiated.

Replicate extract injections were performed on one sample within each extraction set for each matrix to show precision of the GC. Tables II-11 through II-14 show the mean recovery, standard deviation (SD) and coefficient of variation (CV) for replicate extract injections in each matrix. The mean CV for phosmet in leaf, apple, soil and water samples are 5.5, 3.9, 4.7 and 6.9, respectively.

Four water blind spike samples were submitted for analysis, three of these samples were sent to North Coast Lab and one sample was sent to CDFA. Two of the samples were spiked with both phosmet and phosmetoxon at 5 and 2 ppb and 5 and 4 ppb, respectively. One sample was spiked with only phosmet at 3 ppb and one other spiked with only phosmetoxon at 4 ppb.

Samples spiked with both phosmet and phosmetoxon showed 100% and 120% recoveries for North Coast Lab, while CDFA reported 0% and 93% recoveries. The samples spiked only with phosmet or phosmetoxon showed 100% and 0% recoveries for North Coast, respectively (Table II-6). Both laboratories investigated the analysis of their respective samples (EHAP no. 157 and 180) that showed 0% recovery but no conclusions could be drawn.

Split Samples

Five apple, 7 soil and 2 water samples were selected and prepared as interlaboratory control samples. One-half of each sample was analyzed by North Coast Laboratory and the other half by California Department of Food and Agriculture's CDFA Chemistry Lab Services located in Sacramento, California.

All apple and soil split samples showed positive levels for phosmet and non-detected levels for phosmetoxon by both laboratories. The standard deviation in split samples ranged from 65 to 1100 and 8.5 to 511 for apple and soil samples, respectively. Detection limits set by North Coast and CDFA in split apple and soil samples were 25 ppb and 50 ppb, respectively. All split water samples showed non-detected levels for phosmet and phosmetoxon with detection limits set by North Coast and CDFA at 1 ppb and 5 ppb, respectively (Tables II-15 through II-17).

Table II-1. Blank matrix spikes for the Apple Maggot 1987 method validation study: Leaf samples.

Analyte: Phosmet
Matrix: Leaf
Detection Limit: 0.5 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ug)	Spike Level (ug)	Recovery %
1		4580	5000	91
2		3770	5000	75
3		3970	5000	79
4		4300	5000	86
5		4420	5000	88
6	87-110521	93	100	93
7	87-110522	99	100	99
8	87-110523	100	100	100
9	87-110524	83	100	83
10	87-110525	87	100	87

Analyte: Phosmetoxon
Matrix: Leaf
Detection Limit: 2.5 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ug)	Spike Level (ug)	Recovery %
1	87-110521	82	100	82
2	87-110522	91	100	91
3	87-110523	100	100	100
4	87-110524	110	100	110
5	87-110525	110	100	110

Table II-2. Blank matrix spikes for the Apple Maggot 1987 method validation study: Apple samples.

Analyte: Phosmet
Matrix: Apple
Detection Limit: 0.005 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppm)	Spike Level (ppm)	Recovery %
1	87-110526	0.102	0.1	102
2	87-110527	0.106	0.1	106
3	87-110528	0.099	0.1	99
4	87-110529	0.117	0.1	117
5	87-1105210	0.091	0.1	91
6	87-1105211	6.9	5	138
7	87-1105212	6.4	5	128
8	87-1105213	6.1	5	122
9	87-1105214	5.9	5	118
10	87-1105215	6.8	5	136

Analyte: Phosmetoxon
Matrix: Apple
Detection Limit: 0.025 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppm)	Spike Level (ppm)	Recovery %
1	87-110526	0.085	0.1	85
2	87-110527	0.11	0.1	110
3	87-110528	0.076	0.1	76
4	87-110529	0.13	0.1	130
5	87-1105210	0.091	0.1	91

Table II-3. Blank matrix spikes for the Apple Maggot 1987 method validation study: Soil samples.

Analyte: Phosmet
Matrix: Soil
Detection Limit: 0.01 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppm)	Spike Level (ppm)	Recovery %
1		4.71	5	94
2		4.68	5	94
3		4.9	5	98
4		4.15	5	83
5		5.53	5	111
6		0.107	0.1	107
7		0.075	0.1	75
8		0.06	0.1	60
9		0.075	0.1	75
10		0.086	0.1	86

Analyte: Phosmetoxon
Matrix: Soil
Detection Limit: 0.01 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppm)	Spike Level (ppm)	Recovery %
1		0.082	0.1	82
2		0.075	0.1	75
3			0.1	0
4		0.046	0.1	46
5		0.074	0.1	74

Table II-4. Blank matrix spikes for the Apple Maggot 1987 method validation study: Water samples.

Analyte: Phosmet
Matrix: Water
Detection Limit: 1 ppb

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %
1		3.9	5	78
2		4.72	5	95
3		4.25	5	85
4		5.57	5	111
5		4.14	5	83

Analyte: Phosmetoxon
Matrix: Water
Detection Limit: 1 ppb

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %
1		6.21	5	124
2			5	0
3			5	0
4			5	0
5			5	0

Table II-5. Quality Control Limits (% Recovery) for the Apple Maggot 1987 method validation study.

Matrix	X	SD	LWL *	UWL*	LCL**	UCL**
Phosmet:						
Leaf	88	7.6	81	96	73	103
Apple	116	15.1	101	131	86	146
Soil	88	14.9	73	103	58	118
Water	90	11.7	78	102	67	113
Phosmetoxon:						
Leaf	99	10.9	88	110	77	121
Apple	98	19.3	79	117	59	137
Soil	55	30.3	25	85	-5.6	116
Water	25	49.6	-25	75	-74	124

UCL = upper control limit
LCL = lower control limit
UWL = upper warning limit
LWL = lower warning limit

* UWL and LWL = X +/- 1 SD
** UCL and LCL = X +/- 2 SD

Table II-6. Apple Maggot 1987 Continuing Quality Control Data: Blind water spikes.

Analyte: Phosmet and phosmetoxon
Matrix: Water
Detection Limit: 1 ppb

Lab: North Coast Labs
Chemist: BL
Date: 9/9/87

EHAP Sample #	Lab Sample #	Results (ug)	Spike Level (ug)	Recovery %
Phosmet:				
140	36815	5	5	100
151	35955	3	3	100
157	87-0807813	<1	0	
Phosmetoxon:				
140	36815	6	5	120
151	35955	<1	0	
157	87-0807813	<1	4	0

Analyte: Phosmet and Phosemetoxon
Matrix: Water
Detection Limit: 1 ppb

Lab: CDFA
Chemist: J.E.
Date: 9/9/87

EHAP Sample #	Lab Sample #	Results (ug)	Spike Level (ug)	Recovery %
Phosmet:				
180	177	<1	2	0
Phosmetoxon:				
180	177	3.7	4	93

Table II-7. Apple Maggot 1987 Continuing Quality Contol Data: Blank matrix spikes (Leaf samples).

Analyte: Phosmet
Matrix: Leaf
Detection Limit: 0.5 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ug)	Spike Level (ug)	Recovery %	X Recovery	RPD
111		65	100	65		
111		63	100	63	64*	3.1
118		29000	5000	58		
118		3550	5000	71	64*	20.3
888		64	100	64		
888		73	100	73	66*	13.6
116		59	100	59		
116		63	100	63	69*	5.8
86		78	100	78		
86		86	100	86	82	9.8
77		93	100	93		
77		90	100	90	91	3.2
26		66	100	66		
26		64	100	64	65*	3
10		93	100	93		
10		111	100	111	102	17.6
64		77	100	77		
64		71	100	71	74	8.1

* These samples fell outside the lower control limit set for Phosmet in leaf samples at 73 %.

Table II-8. Apple Maggot 1987 Continuing Quality Contol Data: Blank matrix spikes (Apple samples).

Analyte: Phosmet
Matrix: Apple
Detection Limit: 0.005 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppm)	Spike Level (ppm)	Recovery %	X Recovery	RPD
221		4.3	5	86		
221		4.7	5	94	90	8.9
193		6.05	5	121		
193		7.3	5	146	133	18.8
198		4.95	5	99		
198		4.05	5	81	90	20
207		6.3	5	126		
207		3.5	5	70	98	57.1
214		4.8	5	96		
214		4.4	5	88	92	8.7
204		0.23	0.25	92		
204		0.17	0.25	68	80	30
197		0.22	0.25	89		
197		0.29	0.25	117	103	27.1
200		0.23	0.25	95		
200		0.18	0.25	71	83*	29

* Sample no. 200 fell outside the lower control limit set for Phosmet in apples at 86%.

Table II-9. Apple Maggot 1987 Continuing Quality Contol Data: Blank matrix spikes (Soil samples).

Analyte: Phosmet
Matrix: Soil
Detection Limit: 0.01 ppm

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppm)	Spike Level (ppm)	Recovery %	X Recovery	RPD
75		7.8	5	156		
75		8.8	5	176	166*	12
63		5.2	5	104		
63		5.85	5	117	110	11.8
23		5.35	5	107		
23		5.4	5	108	108	0.9
113		2.15	5	43		
113		2.9	5	58	50**	30
19		5.35	5	107		
19		5.4	5	108	108	0.9
89		5.25	5	105		
89		3.55	5	71	88	39
84		3.5	5	70		
84		3.25	5	65	68	7.3
1		3.2	5	64		
1		3	5	60	62	6.4
9		1.55	2.5	62		
9		1.52	2.5	61	62	1.6
66		2.42	2.5	97		
66		1.45	2.5	58	78	50

* Sample no. 74 fell outside the upper control limit set for Phosmet in soil at 118%.

** Sample no. 113 fell outside the lower control limit set for Phosmet in soil at 58%.

Table II-10. Apple Maggot 1987 Continuing Quality Contol Data: Blank matrix spikes (Water samples).

Analyte: Phosmet
Matrix: Water
Detection Limit: 1 ppb

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	X Recovery	RPD
154		6.85	5	137		
154		8	5	160	149*	15
132		5	5	100		
132		4.3	5	86	93	15
124		5.15	5	103		
124		5.25	5	105	104	1.9
		5.95	5	119		
		7	5	140	130*	16
134		4.75	5	95		
134		4.35	5	87	91	8.8
144		3.95	5	79		
144		3.4	5	68	74	15
175		4.35	5	87		
175		4.2	5	84	86	3.5
187		5.15	5	103		
187		4.8	5	96	100	7
291		4.75	5	95		
291		4.3	5	86	91	9.9

* These samples fell outside the upper control limit set for Phosmet in water at 113%.

Table II-11. Apple Maggot 1987 Continuing Quality Contol Data
Replicate Extract Injections (Leaf samples)

Analyte: Phosmet
Matrix: Leaf

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ug)	X Recovery	SD	CV (%)
118	35422	3			
		2.1			
		2.5	2.5	0.4	16
111	35635	1580			
		1330			
		1437	1449	102	7
106	35927	1949			
		1914			
		1762	1875	81	4.3
62	36127	1962			
		2071			
		1728	1920	143	7.4
14	36457	1045			
		984			
		933	987	46	4.7
95	3689	199			
		237			
		208	214	16	7.5
45	36827	1383			
		1369			
		1419	1390	21	1.5
78	37319	1951			
		1999			
		1863	1938	56	2.9
25	87-0807101	1774			
		1793			
		1761	1776	13	0.7
12	87-0812171	3782			
		3236			
		3614	3544	228	6.4
271	87-081914	1320			
		1429			
		1227	1325	82	6.2
233	87-082685	2710			
		2591			
		2663	2654	48	1.8
225	87-082692	3974			
		3682			
		3551	3736	177	4.7

Table II-12. Apple Maggot 1987 Continuing Quality Contol Data
Replicate Extract Injections (Apple samples)

Analyte: Phosmet
Matrix: Apple

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppm)	X Recovery	SD	CV (%)
198	35683	0.052			
		0.048			
		0.046	0.049	0.002	4.1
9003	35945	0.038			
		0.037			
		0.038	0.038	0.0004	1.1
220	36117	0.079			
		0.078			
		0.078	0.078	0.0004	0.5
216	36121	0.096			
		0.092			
		0.088	0.92	0.003	0.3
218	36445	0.062			
		0.061			
		0.066	0.063	0.002	3.2
210	36835	0.066			
		0.053			
		0.063	0.06	0.005	8.3
194	37311	0.082			
		0.08			
		0.078	0.08	0.001	1.3
211	87-080789	0.099			
		0.091			
		0.095	0.095	0.003	3.2
239	87-0812173	0.142			
		0.14			
		0.178	0.153	0.017	11
248	87-0819117	0.179			
		0.195			
		0.159	0.178	0.014	7.9
304	87-082682	0.285			
		0.27			
		0.279	0.278	0.006	2.2

Table II-13. Apple Maggot 1987 Continuing Quality Contol Data
Replicate Extract Injections (Soil)

Analyte: Phosmet
Matrix: Soil

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppm)	X Recovery	SD	CV (%)
99	35939	<0.01			
		<0.01			
		<0.01			
70	36145	0.07			
		0.09			
		0.07	0.08	0.009	11
23	36461	0.1			
		0.1			
		0.09	0.1	0.004	4
16	36471	0.14			
		0.15			
		0.14	0.14	0.004	2.9
46	36849	0.16			
		0.16			
		0.14	0.15	0.009	6
84	37331	0.17			
		0.17			
		0.17	0.17	0	0
5	87-080733	0.36			
		0.37			
		0.33	0.35	0.01	2.9
239	87-0812171	0.23			
		0.29			
		0.3	0.27	0.03	11
272	87-0819115	0.39			
		0.37			
		0.39	0.38	0.009	2.4
227	87-082695	0.47			
		0.48			
		0.44	0.46	0.01	2.2

Table II-14. Apple Maggot 1987 Continuing Quality Contol Data
Replicate Extract Injections (Water)

Analyte: Phosmet and phosmetoxon
Matrix: Water

Lab: North Coast Labs
Chemist: BL
Date: 12/6/87

EHAP Sample #	Lab Sample #	Results (ppb)	X Recovery	SD	CV (%)
Phosmet:					
140	36315	7.4			
		7.6			
		7.1	7.3	0.2	2.7
151	35955	2.1			
		1.6			
		2.1	1.9	0.2	11
Phosmetoxon:					
140	36315	4.7			
		5.1			
		5.1	5	0.2	4
151	35955	2.5			
		1.6			
		2.2	2.1	0.4	19

Table II-15. Apple Maggot 1987 Split/Confirmation Analyses.

Analyte: Phosmet
Matrix: Apple
Detection Limit (CDFA): 5 ppb
Detection Limit (North Coast): 5 ppb

Chemist (CDFA): J.E.
Chemist (N.C.): B.L.
Date: 9/9/87

EHAP Sample #	Lab Sample #	CDFA (ppb)	North Coast (ppb)	X	SD	CV (%)
40	304	1200				
203	37313		2300	1750	550	31
37	301	900				
194	37311		3100	2000	1100	55
38	302	600				
200	37307		2000	1300	700	54
39	303	700				
202	37309		2800	1750	1050	60
41	305	50				
206	37315		180	115	65	57

Analyte: Phosmetoxon
Matrix: Apple
Detection Limit (CDFA): 25 ppb
Detection Limit (North Coast): 25 ppb

Chemist (CDFA): J.E.
Chemist (N.C.): B.L.
Date: 9/9/87

EHAP Sample #	Lab Sample #	CDFA (ppb)	North Coast (ppb)	X	SD	CV (%)
40	304	<25				
203	37313		<25			
37	301	<25				
194	37311		<25			
38	302	<25				
200	37307		<25			
39	303	<25				
202	37309		<25			
41	305	<25				
206	37315		<25			

Table II-16. Apple Maggot 1987 Split/Confirmation Analyses.

Analyte: Phosmet
Matrix: Soil
Detection Limit (CDFA): 50 ppb (dry weight basis)
Detection Limit (North Coast): 10 ppb (dry weight basis)

Chemist (CDFA): J.E.
Chemist (N.C.): B.L.
Date: 9/9/87

EHAP Sample #	Lab Sample #	CDFA (ppb)	North Coast (ppb)	X	SD	CV (%)
50	289	1700				
76	37343		678	1189	511	43
51	290	930				
75	37341		506	718	212	30
52	291	95				
53	37337		72	84	11.5	14
54	292	77				
55	37339		60	69	8.5	12
79	293	800				
80	37335		584	692	108	16
81	294	980				
82	37333		699	840	141	17
83	295	1070				
84	37331		1141	1106	36	3.3

Analyte: Phosmetoxon
Matrix: Soil
Detection Limit (CDFA): 50 ppb (dry weight basis)
Detection Limit (North Coast): 50 ppb (dry weight basis)

Chemist (CDFA): J.E.
Chemist (N.C.): B.L.
Date: 9/9/87

EHAP Sample #	Lab Sample #	CDFA (ppb)	North Coast (ppb)	X	SD	CV (%)
50	289	<50				
76	37343		<50			
51	290	<50				
75	37341		<50			
52	291	<50				
53	37337		<50			
54	292	<50				
55	37339		<50			
79	293	<50				
80	37335		<50			
81	294	<50				
82	37333		<50			
83	295	<50				
84	37331		<50			

Table II-17. Apple Maggot 1987 Split/Confirmation Analyses.

Analyte: Phosmet
Matrix: Water
Detection Limit (CDFA): 1 ppb
Detection Limit (North Coast): 1 ppb

Chemist (CDFA): J.E.
Chemist (N.C.): B.L.
Date: 9/9/87

EHAP Sample #	Lab Sample #	CDFA (ppb)	North Coast (ppb)	X	SD	CV (%)
173	175	<1				
175	37345		<1			
177	176	<1				
179	37347		<1			

Analyte: Phosmetoxon
Matrix: Water
Detection Limit (CDFA): 5 ppb
Detection Limit (North Coast): 1 ppb

Chemist (CDFA): J.E.
Chemist (N.C.): B.L.
Date: 9/9/87

EHAP Sample #	Lab Sample #	CDFA (ppb)	North Coast (ppb)	X	SD	CV (%)
173	175	<5				
175	37345		<1			
177	176	<5				
179	37347		<1			

APPENDIX III

STATISTICAL ANALYSIS RESULTS

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Table III-1 Analysis of Variance Results for Concentrations of Phosmet in Foliar Samples (ppm)

Source of Variation	Degree of Freedom	Mean Square[1]	F-Test P-Values[2]
Location	2	64.109	
Replication (Location)	4	43.489	
Spray	2	53.416	
Days Post Application	1	2278.59	
Location X Spray	4	119.768	
Location X Days Post	2	2.823	
Spray X Days Post	2	13.555	
Location X Spray X Days Post	4	207.774	<0.05
Residual	19	68.404	

1. Overall F-Tests were constructed using the residual mean square in the denominator except for the test for location which used the random component replication (location) as the error term.

2. P-Values are not presented for main effects in the presence of significant interaction.

Least Squares Means[3]

Location	Mean
Coffee Creek	334.1
Humboldt Bay	312.8

Spray	Mean
1	347.7
2	285.0
3	337.7

Days Post Application	Mean
1	398.5
7	248.4

3. Least squares means were estimated excluding data from Castle Crags.

Table III-2 Analysis of Variance Results for Concentrations of Phosmet in Foliar Samples - First Spray (ppm)

Source of Variation	Degree of Freedom	Mean Square[1]	F-Test P-Values
Location	1	69.221	.53
Replication (Location)	2	162.700	
Days Post Application	2	875.192	.06
Location X Days Post	2	20.948	.87
Residual	4	147.811	--

Least Squares Means

Location		Days Post Application	
Coffee Creek	265.0	1	455.1
Humboldt Bay	313.0	7	240.2
		14	171.7

1. Overall F-Tests were constructed using the residual mean square in the denominator except for the test for location which used the random component replication (location) as the error term.

Table III-3 Analysis of Variance Results for Concentrations of Phosmet in Foliar Samples (ug/cm^2)

Source of Variation	Degree of Freedom	Mean Square[1]	F-Test P-Values[2]
Location	2	0.282	
Replication (Location)	4	0.338	
Spray	2	0.245	
Days Post Application	1	11.809	
Location X Spray	4	0.697	
Location X Days Post	2	0.345	
Spray X Days Post	2	0.042	
Location X Spray X Days Post	4	1.043	<.0117
Residual	19	0.241	

1. Overall F-Tests were constructed using the residual mean square in the denominator except for the test for location which used the random component replication (location) as the error term.

2. P-Values are not presented for main effects in the presence of significant interaction.

Least Squares Means[3]

Location	Mean
Coffee Creek	2.30
Humboldt Bay	2.15

Spray	Mean
1	2.39
2	2.02
3	2.28

Days Post Application	Mean
1	2.80
7	1.65

3. Least squares means were estimated excluding data from Castle Crags.

Table III-4 Analysis of Variance Results for Concentrations of Phosmet in Foliar Samples (ug/cm^2)

Source of Variation	Degree of Freedom	Mean Square[1]	F-Test P-Values
Location	1	0.260	.60
Replication (Location)	2	0.704	
Days Post Application	2	4.896	.04
Location X Days Post	2	0.036	.94
Residual	4	0.576	--

Least Squares Means

Location		Days Post Application	
Coffee Creek	1.8	1	3.2
Humboldt Bay	2.1	7	1.6
		14	1.1

1. Overall F-Tests were constructed using the residual mean square in the denominator except for the test for location which used the random component replication (location) as the error term.

Table III-5 Analysis of Variance Results for Concentrations of Phosmet in Soil Samples (ppm)

Source of Variation	Degree of Freedom	Mean Square[1]	F-Test P-Values[2]
Location	2	1.542	
Replication (Location)	2	0.805	
Spray	1	0.410	
Days Post Application	2	0.248	
Location X Spray	2	0.516	.01
Location X Days Post	4	0.445	.02
Spray X Days Post	2	0.040	.13
Location X Spray X Days Post	4	0.207	.83
Residual	18	0.107	

1. Overall F-Tests were constructed using the residual mean square in the denominator except for the test for location which used the random component replication (location) as the error term.

2. P-Values are not presented for main effects in the presence of significant interaction.

Least Squares Means

Location	Mean
Castle Crags	0.90
Coffee Creek	0.71
Humboldt Bay	0.20

Spray	Mean
1	0.68
2	0.80
3	0.33

Days Post Application	Mean
1	0.50
7	0.71

Table III-6 Analysis of Variance Results for Concentrations of Phosmet in Fruit Samples (ppm)

Source of Variation	Degree of Freedom	Mean Square[1]	F-Test P-Values[2]
Location	2	12.701	.09
Replication (Location)	2	1.264	
Spray	2	1.265	.48
Days Post Application	1	1.518	.36
Location X Spray	4	2.245	.31
Location X Days Post	2	0.160	.91
Spray X Days Post	2	0.738	.65
Location X Spray X Days Post	4	0.775	.75
Residual	9	1.625	

1. Overall F-Tests were constructed using the residual mean square in the denominator except for the test for location which used the random component replication (location) as the error term.

2. P-Values are not presented for main effects in the presence of significant interaction.

Least Squares Means

Location	Mean
Castle Crags	3.29
Coffee Creek	2.81
Humboldt Bay	0.93

Spray	Mean
1	1.93
2	2.32
3	2.79

Days Post Application	Mean
1	2.59
7	2.10

Table III-7 Revised Analysis of Variance Results for Concentrations of Phosmet in Fruit Samples (ppm)

Source of Variation	Degree of Freedom	Mean Square[1]	F-Test P-Values[2]
Location	2	12.809	0.09
Replication (Location)	2	1.329	
Spray	2	5.145	0.04
Days Post Application	1	2.122	0.23
Location X Spray	--	--	--
Location X Days Post	--	--	--
Spray X Days Post	--	--	--
Location X Spray X Days Post	--	--	--
Residual	21	1.379	--

1. Overall F-Tests were constructed using the residual mean square in the denominator except for the test for location which used the random component replication (location) as the error term.

2. P-Values are not presented for main effects in the presence of significant interaction.

Table III-8 Analysis of Variance Results for Concentrations of Phosmet in Fruit Samples - First Spray (ppm)

Source of Variation	Degree of Freedom	Mean Square[1]	F-Test P-Values
Location	2	0.488	.03
Replication (Location)		0.164	
Days Post Application	2	3.27	.02
Residual			

Least Squares Means

Location		Days Post Application	
Castle Crags	1.77	1	2.37
Coffee Creek	1.80	7	1.68
Humboldt Bay	1.13	14	0.65

1. Overall F-Tests were constructed using the residual mean square in the denominator except for the test for location which used the random component replication (location) as the error term.

Table III-9 Listing of Positive Phosment Background Data.

Location	Sample Matrix	Phosmet (ppm)
Castle Crags	Foliar	0.3
Castle Crags	Foliar	0.7
Castle Crags	Soil	0.07
Castle Crags	Soil	0.04
Castle Crags	Soil	0.08
Coffee Creek	Foliar	1.7
Coffee Creek	Foliar	0.7
Coffee Creek	Soil	0.18
Coffee Creek	Soil	0.07

Table III-10 Listing of Positive Phosmetoxon Foliar Data.

Location	Spray	Days Post Application	Phosmet Concentrations ppm	ug/cm^2
Castle Crags	3	1	.06	.006
Castle Crags	3	1	.09	.005
Castle Crags	3	7	.13	.012
Castle Crags	4	1	.08	.006
Castle Crags	4	1	.16	.009
Coffee Creek	1	1	.05	<.001
Coffee Creek	2	7	.06	.004
Coffee Creek	2	7	.12	.008
Coffee Creek	3	1	.12	.008
Coffee Creek	3	1	.002	<.001
Coffee Creek	3	7	.003	<.001
Humboldt Bay	1	14	.13	.007