ENVIRONMENTAL MONITORING OF THE 1986 APPLE MAGGOT ERADICATION PROJECT IN HUMBOLDT AND DEL NORTE COUNTIES

NOVEMBER, 1987

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

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EH 87—07

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by

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November, 1987

EXECUTIVE SUMMARY

The 1986 Apple Maggot Eradication Project required use of the insecticide phosmet (Imidan®) over large areas in six counties of northern California. This chemical had no previous use on eradication projects in California, was not registered for use on crabapples and had incomplete information on its environmental fate. Therefore, the Environmental Hazards Assessment Program of the California Department of Food and Agriculture was directed to develop a comprehensive monitoring program to evaluate the environmental levels of phosmet and phosmetoxon, a toxic degradation product. A combined total of 625 air, fruit, leaf, water, soil and tank mixture samples were collected at 11 sites for six applications over a three month period. In addition, dissipation studies of phosmet and phosmetoxon over time were conducted with water, fruit and tank samples.

No phosmet or phosmetoxon was detected (detection limit 1 ppb) in any of the surface or ground water samples. Phosmet residue concentration levels in surface soil samples ranged from 0.16 to 5.6 ppm in a total of 120 samples. Phosmetoxon was detected in only one set of soil samples. A total of 96 air samples were collected before, during, and after each application. Phosmet residues were detected in concentrations up to 285 nanograms per cubic meter. No phosmetoxon was detected in any of the air samples. A total of 120 leaf samples were collected. The phosmet and phosmetoxon residue concentrations based on leaf weight ranged from 67.3 ppm to 695 ppm and 0.32 ppm to 5.2 ppm, respectively. This equates to a surface area concentration range of 0.27 ug/cm^2 to 3.56 ug/cm^2 and 0.0016 ug/cm^2 to 0.029 ug/cm^2 for phosmet and phosmetoxon, respectively. A total of 100 fruit samples were collected with the range of phosmet residue concentration being 0.11 to 2.5 ppm, well below the established tolerance level of 10 ppm. No phosmetoxon was detected in any of the fruit samples. The half-life estimates for phosmet and phosmetoxon on foliage were 15.1 days and 19.4 days, respectively. The half-life estimates for phosmet in soil and apple fruit were 19.5 days and 17.2 days, respectively.

Water dissipation studies showed toluene to be effective in extracting and maintaining concentrations of phosmet over time at different water pH values. Also, phosmet concentrations in water were efficiently maintained over time under acidic conditions. In both studies, phosmetoxon appeared to be very unstable during the first five hours but developed degradation patterns similar to the parent as time progressed. An apple fruit dissipation study was conducted to determine the maximum concentrations present, and how much pesticide could be washed off. The concentration of phosmet remaining in apple samples after two surface washes was higher than expected, but the overall concentration was acceptable.

The results of this study indicated a general decrease in phosmet and phosmetoxon concentrations over time in the environmental samples collected, and the degradation rate of phosmet in all the types of sampled media was within an acceptable range.

ACKNOWLEDGMENTS

A very grateful thanks is extended to all the Environmental Hazards Assessment Program (EHAP) field, laboratory and office personnel too numerous to list for all their valuable contributions to this project.

Thanks to the people of the Apple Maggot Eradication Project for their assistance and cooperation in the coordination of this study. Additional thanks to Humboldt and Del Norte County Agricultural Commissioners and their staff along with the Humboldt Bay Municipal Water District for their help and information. Thanks also to the North Coast Laboratories for their assistance, service and hospitality.

A special thanks to Sally Powell for her statistical assistance and computer graphics.

Disclaimer

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such product.

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I. INTRODUCTION

History

In August of 1983, the first apple maggot fruit fly, Rhagoletis pomonella, was found in California. The original find was located in Del Norte County with subsequent finds occurring in Humboldt, Shasta, Mendocino, Trinity, and Siskiyou Counties. A native of eastern North America, the apple maggot is considered a serious pest of apples, crabapples and hawthorne in that region. Established populations of apple maggot were discovered in areas of Oregon and Washington in 1979 and 1980, respectively. The detection of apple maggot in California produced concern in the agriculture industry that significant economic loss could result from an established population of this pest. Additional impact could also result from it becoming a pest in pear, plum and cherry crops.

As a result of legislation signed by the Governor in 1984, the California Department of Food and Agriculture (CDFA) was directed to establish the Apple Maggot Fruit Fly (AMFF) Project. The purpose of this project was to demarcate the area of infestation, to control movement of apples out of the infested areas, and to eradicate all initial infestations in a buffer area around the core of the AMFF population (1). The chemical phosmet (Imidan®) was selected by the Apple Maggot Science Advisory Panel for use in eradication treatments. In 1985, the program was stopped in mid-season by a court ruling requiring the CDFA to conduct an Environmental Impact Report (EIR) on the project. Subsequent legislation (AB 1525) was passed establishing new guidelines for judicial challenges to eradication programs and exempting the CDFA from EIR

requirements when programs of the Department have protection of the environment as one of their principal purposes. This legislation prompted reactivation of the Apple Maggot Eradication Project (AMEP) for the 1986 season.

To enhance the integrity of the AMEP, the Environmental Hazards Assessment Program (EHAP) of the CDFA developed a comprehensive monitoring plan with the specific objectives of documenting the behavior and concentrations of phosmet in the environment.

Phosmet (Imidan®) - Properties and Use

Phosmet is a broad spectrum organophosphate insecticide developed by Stauffer Chemical Company and first registered for use in the United States in 1966. It is marketed under the trade names Imidan®, PMP®, Phtalofos®, Kemolate®, Prolate®, R-1504®, and Appa®. Phosmet is formulated into dusts, wettable powders, impregnated resins and emulsifiable concentrate for end-use application. It is an off-white crystalline solid having a solubility in water of 25 ppm at 20°C with an empirical formula of $C_{11}H_{12}NO_4PS_2$. The major degradation product of environmental concern is phosmetoxon, the oxygen analog. It has the toxicity of the parent compound but is less persistent in the environment.

Approximately 80% of the product used annually in the U.S. is applied to apples, 6% is applied to pears, with 9% being distributed among other tree and vine fruits. The remaining product is applied to alfalfa, corn, cotton, ornamental plants and shrubs, fire ant mounds, pets and livestock (2).

II. MATERIALS AND METHODS

Treatment Area

Chemical treatment with phosmet involved any host tree (apple, crabapple and hawthorne) on properties within Del Norte, Humboldt, Mendocino, Shasta, Trinity and Siskiyou counties where a positive find was recorded from 1983 to 1986 as well as those host trees within a 0.25 mile radius of a confirmed find.

Study Design

Trees were sprayed to the point of drip with Imidan® 50 WP at a rate of 1.5 lbs of product per 100 gallons of water using truck mounted spray rigs. This formulation corresponds to a solution having 0.0904% active ingredient. All areas with 1983-85 finds were treated between June 15 and July 1, and 1986 fly finds were treated within 72 hours of confirmation. Applications were repeated at 2 week intervals until the project's completion in September, 1986.

As part of the Apple Maggot Eradication Workplan for 1986, personnel from the EHAP established and conducted a chemical treatment monitoring program. This program provided monitoring to determine phosmet and phosmetoxon residue data for air, water, soil, foliage, fruit, and pesticide formulation, ascertain the efficacy of the treatments, and furnish environmental degradation information.

Of the six northern California counties within the eradication treatment area, Del Norte and Humboldt were selected for monitoring because the greatest

amount of pesticides was expected to be applied there. Monitoring was initiated at the onset of the treatment program (June 19, 1986) and continued through the completion of six applications (September 23, 1986).

Three residential properties were selected for the collection of soil, fruit, air, foliage and tank samples based on accessibility, permission of owner, presence of sufficient suitable host foliage and fruit for monitoring to extend through six applications, and availability of an external energy source for air sampler operation. Residences were chosen in the Fieldbrook area of Humboldt County (Figure 1), and Smith River and Gasquet areas of Del Norte County (Figure 2). Air monitoring took place at the Smith River and Fieldbrook locations only.

Two large (>200 connections) and two small (<200 connections) drinking water system intakes were selected as surface water monitoring sites based on amount of pesticide applied within the water course drainage area, the amount of water flow, and accessibility. The large systems selected were the Humboldt Bay Municipal Water District, Mad River Ranney well plant #1 in Humboldt County (Figure 1), and the Crescent City Municipal Water District, Smith River Ranney well on South Bank Rd. (Figure 2). As no small system intakes were accessible, Lindsay Creek, a tributary of the Mad River, was selected to represent one of the small systems (Figure 1). The sampling site on Lindsay Creek was located at the over-crossing of Highway 299 and Fieldbrook Road. Jordan Creek at Lake Earl Drive (Figure 2) was selected to represent the second small system. However, Jordan Creek was replaced on July 14 by the

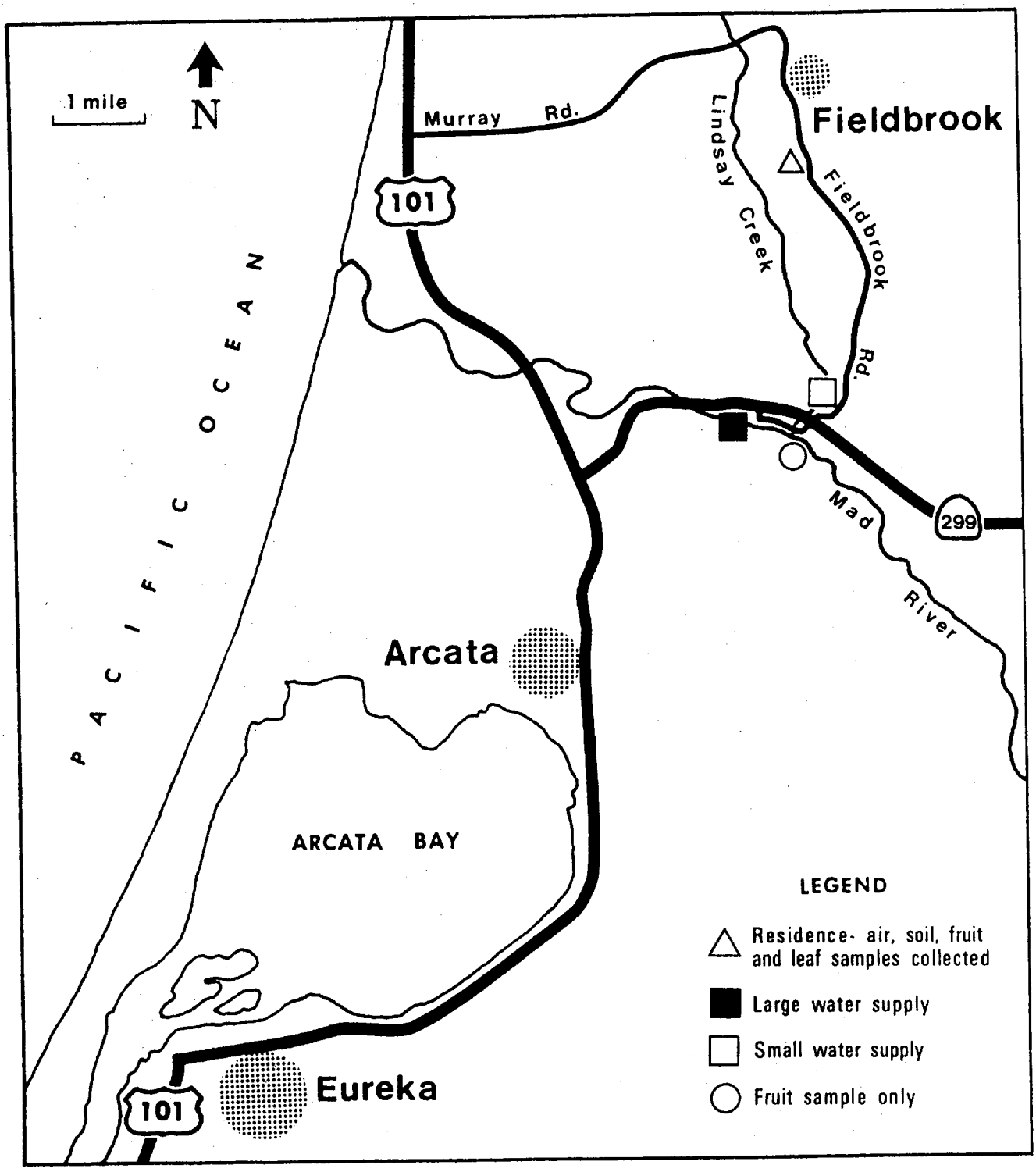

Figure 1. Monitoring sites in Humboldt County for the 1986 Apple Maggot Project.

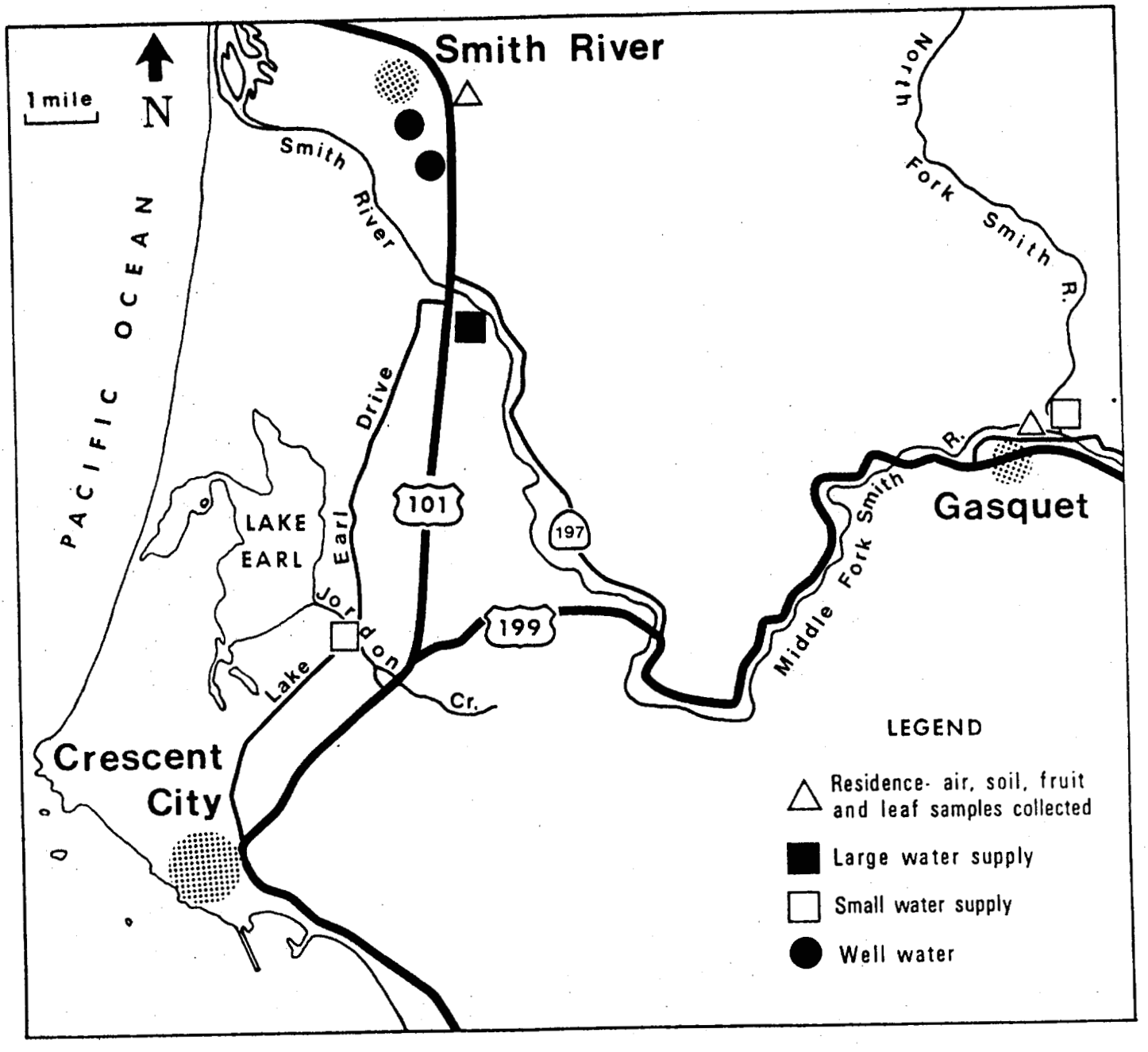

Figure 2. Monitoring sites in Del Norte County for the 1986 Apple Maggot Project.

Smith River North and Middle Fork Confluence in Gasquet (Figure 2) because this location did have a small system intake.

Municipal water for many towns in Humdoldt and Del Norte Counties is supplied from intakes beneath river beds known as Ranney Wells. Both ground and river water is drawn by the buried horizontal shafts including flow deposited from adjoining tributaries that pass through phosmet treated areas.

Two private wells were monitored in Smith River (Figure 2). Selections were based on the area's high water table, the density of application in the vicinity, and owner's permission.

Sample Schedule

Background samples for all environmental media, except air, were collected prior to the onset of the spraying program. The air sampling schedule and subsequent sampling for the other media took place according to the following timetable:

foliage - 1, 5, 9, 13 day post

soil - 1, 5, 9, 13 day post

fruit - 1, 7 day post, day before next application

tank - day of application

air - 1. background at 5-8 a.m. day of application
2. start of application to 10 minutes post
3. immediately after application (3 hours in duration)
4. 24 hour post (3 hours in duration)

water

- 1. large systems - every other day and every 3-4 hours during the first major rainstorm (defined as having the potential to cause pesticide runoff from treated properties using the criteria of amount of water flowing in gutters and storm drains).
- 2. small systems - every day while spraying is taking place in that drainage area, every 3-4 hours during the first major rainstorm.

wells

- once a month for 3 months.

All samples were collected in replicate excluding the sample from the sprayer tank. Only one sample was taken from the tank.

Sampling Methods

Foliage - Samples, which consisted of approximately 30 apple leaves, were collected using a Corona 5000® avocado picker. Leaves, selected at random from each quadrant of several trees, were put into a 12 in. x 18 in. polyethylene bag that lined the nylon sack of the picker. Leaves were transferred to a wide mouth one quart glass jar, sealed with a foil lined lid and cooled immediately on wet ice.

Soil - Samples were collected using a stainless steel Oakfield tube. Each sample consisted of approximately 40 plugs of surface (2.5 centimeter depth) soil each being 2 centimeters in diameter, with an approximate total sample

weight of 500 grams. The plugs were removed at random from each quadrant beneath several trees extending out from the trunk to the tree's dripline. The soil was placed directly into wide mouth one quart glass jars, sealed with foil-lined lids, and stored on dry ice.

Fruit - Samples, which consisted of 8 apples or enough to fill a one quart jar half full, were collected using scissors or a wire fruit harvester, depending on the size of the fruit. Apples were selected at random from each quadrant of several trees and deposited in pre-numbered polyethylene bags. Sample bags were sealed with rubber bands and placed immediately on dry ice.

Air - Samples were initially collected using Anderson® low volume samplers, Model 114. Laboratory results indicated that the low volume flow rate of 28 l/min. may have been insufficient to trap airborne phosmet. Therefore, after July 23, 1986, high volume samplers (General Motor Works®, with Kurz® 3100 flow controller) calibrated at 1 m^3/min. were used. One-hundred and twenty-five ml of XAD-2® resin was used as the trapping media for each sample.

Two samplers were positioned one meter apart in an area of the monitored property where a resident might be allowed to stand if observing the application. Placement under vegetation was avoided to prevent phosmet from invading the sample jar in liquid form. After sampling was completed, the jars were sealed in 9 in. x 15 in. polyethylene bags with rubber bands and stored on dry ice. The ambient temperature and relative humidity at the sampling sites were measured with a sling psychrometer at the onset of each sampling interval and recorded in the remarks section of the chains of custody.

Surface Water - Samples were collected in one quart amber glass bottles using a Nalgene® hand operated pump attached to a 3 ft. length of 1/4 in. O.D. Teflon® tubing. Prior to sampling, bottles were rinsed with sample site water and 50 ml of toluene was added as a preservative. The bottles were then filled only halfway as the Teflon® tube intake was moved back and forth horizontally in the water near the center of the stream flow. Collection took place while walking upstream to avoid the intake of stirred river bottom debris. Bottles were capped with foil-lined lids, shaken for two minutes to trap phosmet in the toluene, and immediately placed on wet ice. The flow rates for the Mad River and Smith River were obtained from the Humboldt Bay Municipal Water District and from the Crescent City Municipal Water District, respectively. Gasquet flow data could not be calculated due to the size and inaccessibility of the site. Lindsay Creek flow rate was calculated at the time of sampling by the formula: width of stream (feet) x depth (feet) x speed of flow (feet per second)= flow rate in ft^3 per second.

Ground Water - Samples were collected in one quart amber glass bottles. The well pumps were run for 15 minutes to flush the casing of standing water. Each bottle was then rinsed with well water, 50 ml of toluene was added and the bottles were filled halfway with water from a sampling port located before the storage tank and any in-line filter systems. The sample bottles were capped with foil-lined lids, shaken for two minutes, and cooled on wet ice. Well water pH and temperature were measured and recorded in the remarks section of the chains of custody.

Tank - A tank sample was collected from the spray rig prior to each application of every monitored application. While the spray rig was agitating, a wide mouth one quart jar was filled half full directly from the spray nozzle. The jar was sealed tight to prevent leakage, placed in two plastic bags, and stored on wet ice.

Laboratory Methods

Two laboratories were utilized for the analysis of the different sample types. The primary lab for all soil, leaf, air, tank and fruit sample analyses was the CDFA Chemistry Laboratory Services Branch in Sacramento. Due to the critical degradation factor of phosmet in water between time of collection and time of analysis, North Coast Laboratories (NCL) in Arcata was selected as the primary laboratory for water analysis. All samples were analyzed for phosmet and its oxygen analog, phosmetoxon, using gas chromatography except tank samples which were analyzed using high pressure liquid chromatography. Detailed descriptions of the laboratory methods are contained in Appendix I.

Quality Control Methods

For quality control purposes, additional soil, fruit and water samples were collected for the production of split matrix samples. Soil splits represented approximately 80 soil plugs collected using the same method described for the field samples. The plugs were mixed in a wide mouth one quart glass jar. After mixing, one-half of the contents was transferred to another similar glass jar. The samples were sealed and stored following the method previously described. This procedure was repeated for a total of four split samples, two

for the CDFA lab and two for NCL. Split fruit samples were produced by collecting double the amount of apples represented in the field samples. The sample was processed following the method described for fruit samples and shipped to the CDFA lab where the sample was placed in a blender and ground to the consistency of apple sauce. One-half of the mixture was placed in a plastic bag, refrozen and delivered to NCL for analysis. It was anticipated that the field water samples would not have detectable amounts of phosmet, so spiked water samples were produced for use in quality control analyses. A one gallon amber glass container, filled with distilled-deionized water, was spiked with a pre-determined amount of phosmet and phosmetoxon by personnel from the CDFA lab. The spiked sample was immediately flown to Humboldt County where EHAP personnel filled three one-liter amber glass bottles half-way with the contents of the spiked solution. The one-liter bottles were then treated in the same manner as the field water samples. Two bottles were delivered to the NCL and one bottle was transported back to the CDFA lab for analysis.

Numerous quality control measures were incorporated into the laboratory analysis that included split matrix samples, replicate sample analysis, and solvent spikes. The primary lab and the quality control lab conducted blank-matrix and blank-matrix spike analyses at the rate of one per extraction set in addition to replicate extract injections of five replicate injections for 2 or 2% of positive samples, whichever was more. Trapping efficiency tests of the air sampling media consisted of replicate analyses of spiked samples. For the purpose of this report, blank-matrix refers to the analyzed matrix (e.g. soil, water, leaves, etc.) having zero amount of pesticide; blank-matrix spike refers to a known amount of pesticide added to the blank-matrix; split matrix

sample refers to one homogeneous sample that was divided into separate aliquots which were analyzed by the CDFA lab and NCL; replicate samples refer to multiple samples collected at the same site at the same time; extract injections refer to multiple measurements of a single extract.

Statistical Methods

Analyses of variance were performed using the General Linear Models procedure of the Statistical Analysis System. Analysis of variance models contained both classification and continuous variables. Paired t tests were performed to compare quality control samples. Tukey's method for all pairwise means comparison was used to evaluate treatment means for dissipation of phosmet and phosmetoxon in toluene and water (Appendix III). Stepwise regression was used to determine the best fitting polynomial regression models for dissipation of phosmet and phosmetoxon in water (Appendix III).

III. RESULTS

Foliage

No phosmet was detected on foliage at any of the sampling sites prior to the first date of pesticide application. Results from chemical analysis of dislodgeable foliar residues for phosmet and phosmetoxon are presented in Appendix II, Tables II-1 thru II-4. The means and standard errors of the means for the micrograms of phosmet and phosmetoxon per square centimeter leaf area are presented in Figures 3 and 4. Following application, levels of phosmet and phosmetoxon in foliage samples above the detection limit ranged from 0.27 per sq. cm (67.3 ppm) to 3.56 ug per sq. cm (695 ppm) and 0.0016 ug per sq. cm (0.32 ppm) to 0.029 ug per sq. cm (5.2 ppm), respectively. In general, the

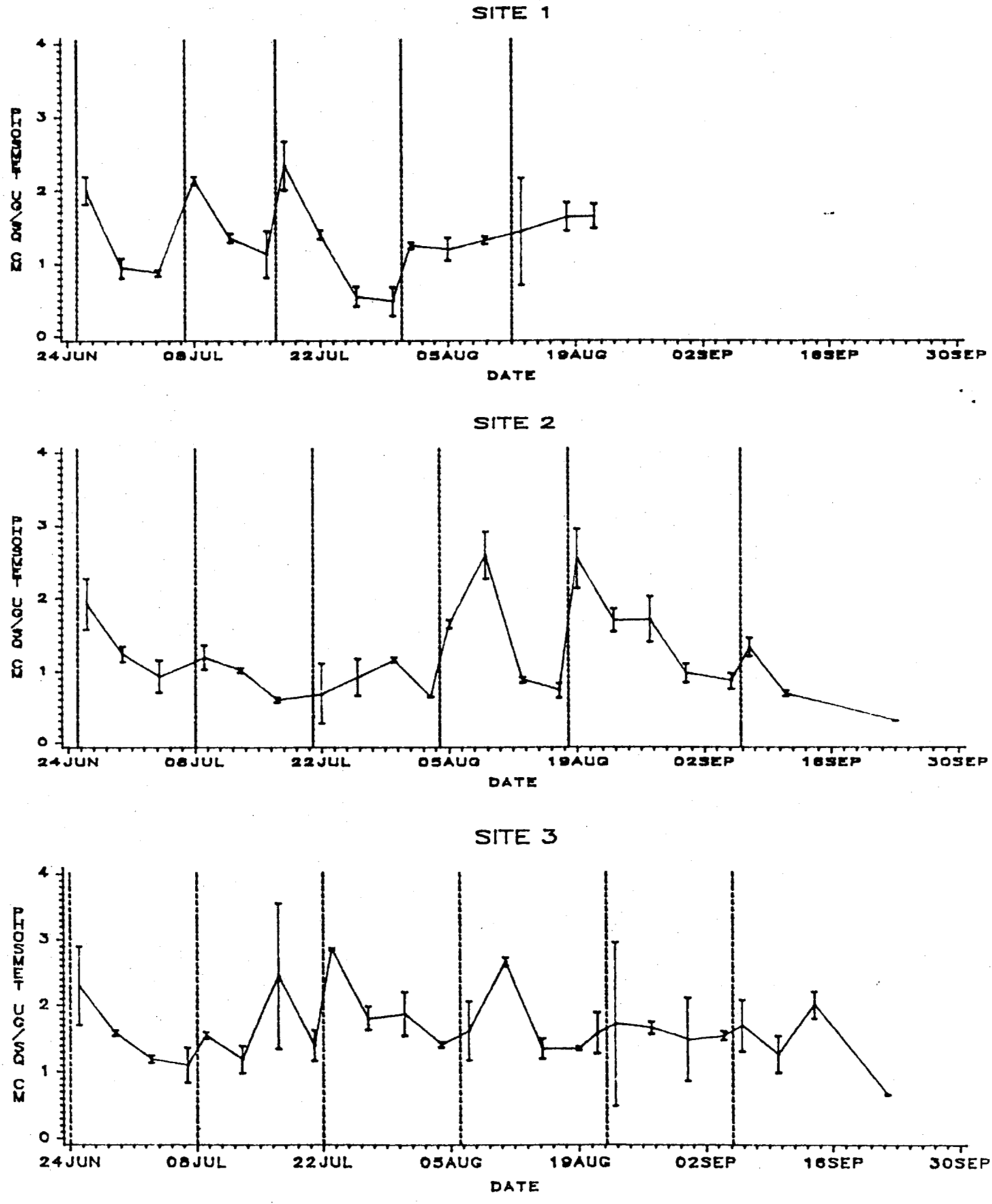

FIGURE 3. MEAN PHOSMET CONCENTRATION IN FOLIAGE SAMPLES. BARS INDICATE PLUS AND MINUS ONE STANDARD ERROR. DOTTED VERTICAL LINES INDICATE DATES OF SPRAYING.

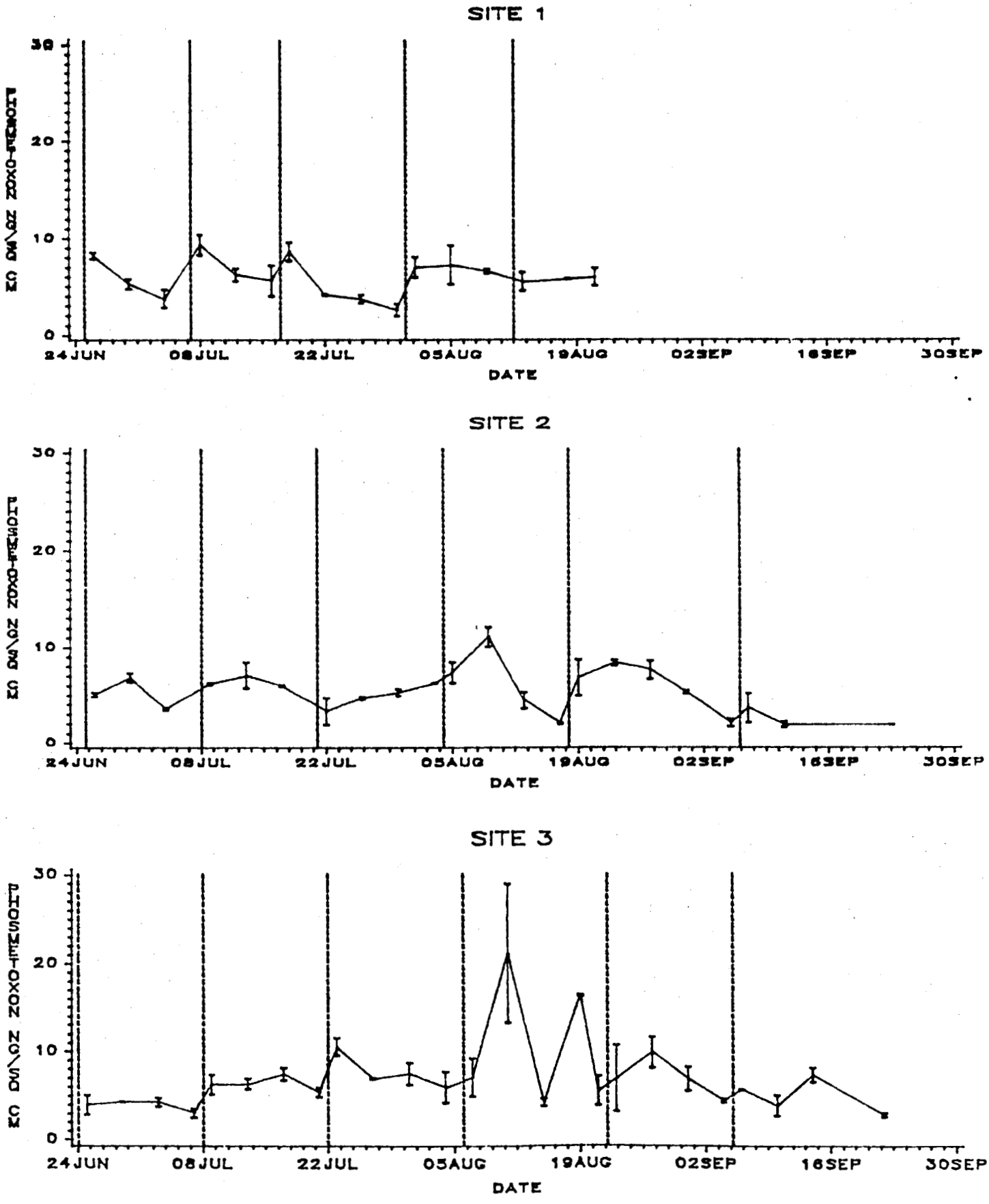

FIGURE 4. MEAN PHOSMETOXON CONCENTRATION IN FOLIAGE SAMPLES. BARS INDICATE PLUS AND MINUS ONE STANDARD ERROR. DOTTED VERTICAL LINES INDICATE DATES OF SPRAYING.

amount of phosmet detected in foliage samples was approximately three orders of magnitude greater than phosmetoxon.

The analysis of variance (ANOVA) for dislodgeable foliar residues of phosmet and phosmetoxon indicated that there was a significant difference between sprays for the amount of phosmetoxon detected but not for the phosmet parent (Appendix II, Table II-5). For both chemical species, there was a highly significant difference between Humboldt and Del Norte County sites but not between two sites in Del Norte County. With respect to degradation, there was a highly significant linear decline in phosmet and phosmetoxon over time. The absence of a significant site x day interaction indicated that the slope of the dissipation curve was similar between sites.

Half-life estimates for phosmet and phosmetoxon on foliage were 15.1 days and 19.4 days, respectively. These estimates were based on regression analyses computed for the overall mean including significant factors as determined by ANOVA in the regression model. Predicted site specific half-lives for phosmet and phosmetoxon ranged from 13.3 days to 16.9 days and 13.6 days to 29.2 days, respectively.

Soil

Results for soil sampling are presented in Appendix II, Table II-6. The means and standard errors of the mean for the milligrams phosmet per kg soil (parts per million) are presented in Figure 5. Levels of phosmet in soil above the detection limit ranged from 0.27 ppm to 2.61 ppm at site 1, 0.91 ppm to 5.6 ppm at site 2 and 0.16 ppm to 1.81 ppm at site 3.

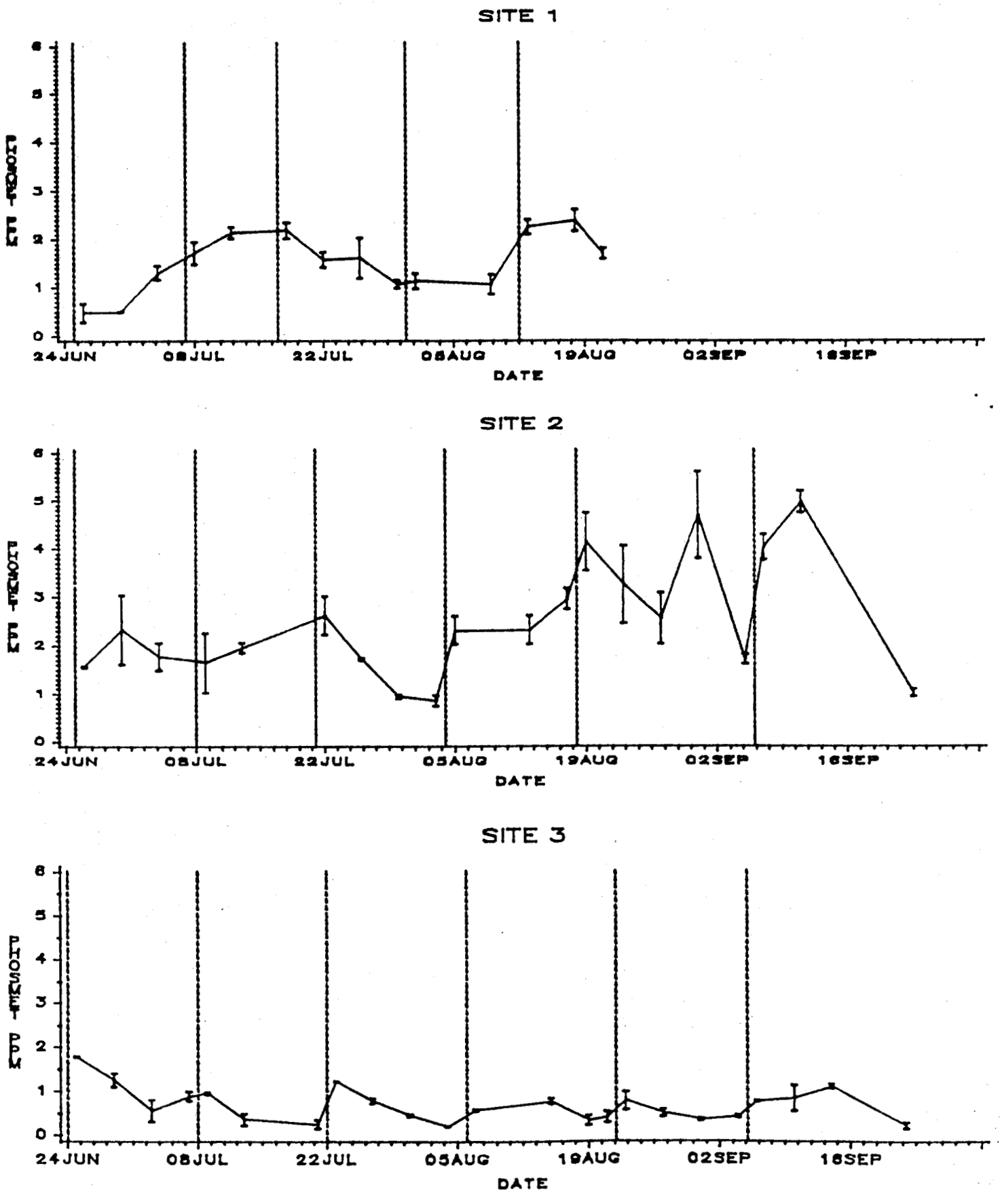

FIGURE 5. MEAN PHOSMET CONCENTRATION IN SOIL SAMPLES. BARS INDICATE PLUS AND MINUS ONE STANDARD ERROR. DOTTED VERTICAL LINES INDICATE DATES OF SPRAYING.

The ANOVA for residues of phosmet in soil indicated that there was a highly significant effect of site (Appendix II, Table II-7). Significant differences in the amount deposited were measured between sites in different counties as well as between the two sites in Del Norte County. Even though there was a difference in the amount of material deposited at each site, the linear contrast was significant.

The half-life estimate for phosmet in soil was 19.5 days. This estimate was based on regression analysis computed for the overall mean of phosmet in soil including significant factors as determined by ANOVA in the regression model. Predicted site specific half-lives for phosmet in soil ranged from 11 days to 29.4 days.

Fruit

Results for fruit sampling are shown in Appendix II, Table II-8. The means and standard error of the means for the milligrams of phosmet per kg fruit (parts per million) are presented in Figure 6. In all cases, concentrations of phosmet in fruit were below the tolerance level set at 10 parts per million. Phosmet concentrations above the detection limit in fruit ranged from 0.11 ppm to 2.5 ppm.

The ANOVA indicated that there was a significant difference between sprays for the amount of phosmet detected in fruit and that there was a highly significant difference in the amount of phosmet detected in fruit from sites in different counties (Appendix II, Table II-9) Again, even though site and

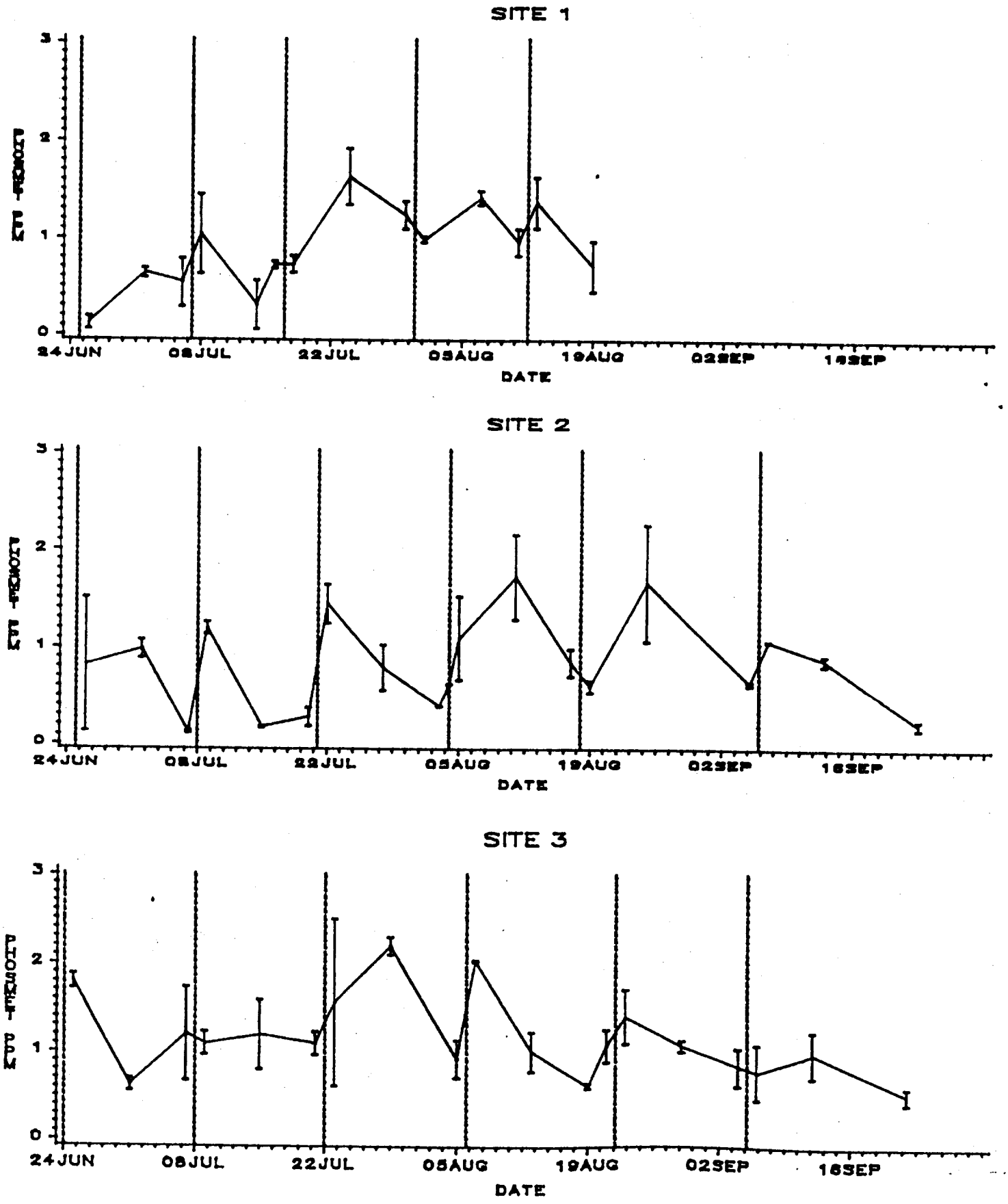

FIGURE 6. MEAN PHOSMET CONCENTRATION IN FRUIT SAMPLES. BARS INDICATE PLUS AND MINUS ONE STANDARD ERROR. DOTTED VERTICAL LINES INDICATE DATES OF SPRAYING.

spray effect were significant, a highly significant linear decline in the concentration of phosmet in fruit was measured over time. The lack of a site x day interaction indicates that the slopes of the dissipation curves were similar between sites.

The half-life estimate for concentration of phosmet in fruit was 17.2 days. This estimate was based on regression analysis computed for the overall mean of phosmet in fruit including significant factors as determined by ANOVA in the regression model. Predicted site specific half-life for phosmet in fruit ranged from 12 days to 23 days.

Surface Waters

No phosmet was detected in either background surface water samples or in 175 samples taken subsequent to phosmet applications. During the period of sampling from June to September, 1986, stream flows for the Smith River, Mad River and Lindsay Creek ranged from 240 to 1200, 106 to 910, and 1.9 to 15.6 cubic feet per second, respectively. The pH values for the Smith River, Mad River and Lindsay Creek ranged from 6.4 to 7.4, 6.8 to 8.3 and 6.1 to 7.4, respectively, during the sampling period.

Ground Water Samples

No phosmet or phosmetoxon were detected in either of two wells sampled before or subsequent to pesticide application.

Air Samples

Concentrations of phosmet in air samples collected at two monitoring locations are shown in Table 1. No phosmet was detected in background air samples collected using high volume or low volume air samplers. Phosmet was not detected in low volume air samples during the first three spray events. Concentrations of phosmet detected in high volume air samples ranged during the spray period from none detected to 285 ng per cubic meter; during the period immediate post spray from none detected to 8.3 ng per cubic meter; and during the 24 hour post spray period from none detected to 5.6 ng per cubic meter. No phosmetoxon was detected in air samples.

Tank Samples

Tank sample results were highly variable (Table 2). Percentages of active ingredient of phosmet in tank samples taken at three monitoring locations prior to each treatment ranged from 0.046% to 0.088%. After initial samples showed low tank concentrations, additional sampling was conducted by Project personnel. The eleven supplemental samples ranged from 0.064% to 0.099%. A tank dissipation study was conducted to observe the stability of tank formulation concentration over time to determine acceptable mixture tank life. After a three day storage period, a small loss of 3.1 to 5.6% of the initial amount of phosmet was detected. This study is presented in Appendix III.

Blank Matrix Spikes

Dislodgeable residue recovered from spiked foliage samples averaged 98.72% for phosmet and 97.43% for phosmetoxon. Using a paired comparison t-test procedure, it was determined that there was a significant difference between the

Table 1. Concentrations of phosmet in air samples collected for Apple Maggot Project, 1986. Results are expressed in nanograms per cubic meter (ng/m^3).

		TIME INTERVAL OF SAMPLE							
		Background		During Spray[a/]		Immediate Post		24 Hour Post	
Spray	Site	Rep #1	Rep #2	Rep #1	Rep #2	Rep #1	Rep #2	Rep #1	Rep #2
1[b/]	2	<49.6[c/]		<331		<49.6		<49.6	
	3	<49.6		<144		<49.6		<49.6	
2	2	<49.6		<330		<49.6		<49.6	
	3	<49.6		<114		<49.6		<49.6	
3[d/]	2	<49.6	<2.78	<194	170	<49.6	<2.78	<49.6	<2.78
	3	<49.6	<2.78	<198	37	<49.6	15	<49.6	3.9
4[e/]	2	NA[f/]	<1.39	43.8	<15.6	5.6	8.3	<2.78	
	3	<1.39		12.9	<8.06	2.8	2.2	4.4	5.6
5	2	<1.39		6.67	<3.30	2.8	3.3	1.7	1.7
	3	<1.39		<11.9		<1.39	1.7	4.4	<1.39
6	2	<2.78		285	210	4.40	6.70	<2.78	
	3	<2.78		<27.8	27.8	2.80	<2.78	<2.78	

a/ Detection limits of spray samples vary due to changing time duration of sprays. Sprays ranged from 16 to 78 minutes.
b/ Spray 1 and 2 samples collected using low volume air sampler calibrated at 28 l/min.
c/ Single column figure represents two replicates having same detection limit.
d/ Two types of samplers were used for the third spray. Rep #1 samples collected using low volume samplers calibrated at 28 l/min. Rep #2 samples collected using high volume samplers calibrated at 1 m^3/min.
e/ All remaining samples collected using high volume samplers calibrated at 1 m^3/min.
f/ NA - Not analyzed; sample broken.

Table 2. Percentages of active ingredient of phosmet in tank samples taken at three locations prior to each monitored treatment. Optimum theoretical composition is 0.0904% active ingredient.

	LOCATIONS		
Treatments	1	2	3
1	0.0603%	0.0553%	0.0886%
2	0.061%	0.0570%	0.0590%
3	0.072%	0.0603%	0.0798%
4	0.046%	0.08%	0.082%
5	0.0749%	0.088%	0.073%
6	--	0.08%	0.081%

amount of both chemical species applied and the amount recovered. Given the very high recovery rates, the significant differences were statistical in nature and not of practical importance.

Recoveries from spiked soil samples averaged 98% (range of 90% to 110%) for phosmet and 99.6% (range of 94% to 110%) for phosmetoxon. Using a paired t-test procedure, no significant differences between amounts of both chemical species applied and recovered could be discerned.

Recoveries from apple samples spiked with phosmet and phosmetoxon averaged 98% for both species. Using a paired t-test procedure, it was determined that there were no significant differences between amounts of both chemicals applied and recovered. Recoveries of phosmet and phosmetoxon from XAD-2 resin used with high volume air samplers averaged 94% (range of 90% to 102%) and 108% (range of 101% to 118%), respectively. There were no significant differences between the amount of phosmet or phosmetoxon applied and recovered as determined by a paired t test procedure.

Split Matrix

The amount of phosmet detected from split fruit samples by the NCL and the CDFA laboratories were not significantly different as determined by a paired t-test (Appendix II, Table II-10). There was a significant difference ($p>0.027$) between the amount of phosmet detected in split soil samples by the NCL and the CDFA laboratories. This difference was due to discrepancies among two sets of samples (Appendix II, Table II-11). Seven sets of split water

samples were submitted for analysis. No phosmet or phosmetoxon residue were detected by either laboratory.

Split Spiked Matrix

There were no significant differences between the amount of phosmet added to split water samples and the amount detected by both the NCL and the CDFA chemistry laboratories. Recoveries of phosmet from spiked split water samples averaged 91% (range of 50% to 160%) and 116% (range of 94% to 177%) for NCL and CDFA laboratories, respectively (Appendix II, Table II-12). No significant differences could be detected between the amount of phosmetoxon added to split water spikes and the amount recovered for the water samples analyzed by the NCL or samples analyzed by the CDFA. Recoveries averaged 64% (range of 40% to 114%) and 96% (range of 61% to 156%) for the NCL and the CDFA, respectively.

To enhance the confidence in quality control results, additional studies were conducted to evaluate the efficacy of water sample treatment methods in maintaining phosmet concentrations over time. Details of these water dissipation studies are presented in Appendix III.

IV. DISCUSSION

This study required the collection of extensive numbers of environmental samples over a three month period. Due to the complexity of factors inherent in environmental samples, a high degree of variability was observed in the

results for specific site and media. General trends in the overall environmental behavior of phosmet in each media could be observed. However, no specific trends by site were obvious in fruit or soil.

Previous studies (3,4,5,6) indicated that phosmet was relatively short lived in the environment. The major pathways of degradation were hydrolysis and oxidation. Photodegradation was another route of degradation but data on this subject is not yet available.

The soil half-life for phosmet and phosmetoxon have been reported to range from 3 days at pH 7.2 to 19 days at pH 5.1 (3). Degradation rates can increase with increasing values of soil moisture, soil temperature, microbial activity and soil organic content. The hydrolysis rate of aqueous phosmet solutions increases with pH values. Half-lives of phosmet at pH 5, 7 and 9 were 225, 18 and 16 hours, respectively (4). Photodegradation, hydrolysis and oxidation are all contributing factors in foliar degradation.

Our field data indicated that while there was a high degree of variability from site to site and within specific media, there was in general a significant linear decrease in phosmet and phosmetoxon concentrations over time. The foliage data was the only media that provided useful information on phosmetoxon. These data indicate that phosmetoxon represents only a small fraction of phosmet's degradation pathway under the environmental conditions present at the sites. Phosmet and phosmetoxon residues detected on leaves 18 days post application exhibited degradation rates within the expected norm at site 2 while at site 3, residue concentrations at 15 days post application

were slightly more persistent. The phosmet half-life on foliage observed in this study were similar to the findings of MacNeil and Hikichi (5). Local weather conditions probably contributed to the different degradation rates at the two sites.

The wide range of site specific phosmet soil half-lives indicated differences in the conditions existing at each site. The differences between counties in the amount of phosmet detected in soil could reflect the type of trees and amount of use the sites received. Site 3 in Humboldt County had extensive residential use and received regular watering. The trees at this site also had dense foliage which retained more of the spray preventing it from reaching the soil. The sites in Del Norte County had very little use, more infrequent waterings and the trees had much thinner foliage allowing more of the spray to be deposited on the ground under the tree canopy. An increased phosmet degradation rate could be expected in soil having a higher moisture content as stated by Freed et. al (6). Lamoreaux and Newland (7) also stress the importance of soil organic matter content and microbial action as factors influencing the degradation rate.

The high degree of variation present in the fruit results can be attributed in part to the changing number and size of the apples represented in each sample collected during the three month study. The fruit concentrations are expressed on a weight basis, micrograms of phosmet per gram of apples. In contrast, the amount of phosmet applied to apples is a function of surface area, and there is much more variation in apple weight when compared to apple

surface area. The apple weight is proportional to the cube of the apple radius, while the surface area is proportional to the square of the radius.

The absence of detectable amounts of phosmet in the low volume air samples and the small concentrations of residue detected in the high volume air samples reflects the low volatility characteristic of phosmet at low ambient temperatures.

Since no phosmet was detected in any of the water samples, it can be assumed that any phosmet present was below the detection limit due to hydrolytic degradation, high dilution ratio or a combination of both. Considering the pH range represented by the surface water samples, it is unlikely that the half-life would exceed 48 hours. In addition, the AMEP application methods greatly stressed the importance of preventing spray material from entering surface waters. These preventative practices were an important contributive factor in phosmet not being detected in any surface water samples.

Considering the wide range in the percent active ingredient present in the tank mixtures as listed in Table 2 and the variety of application practices employed by the various spray crews, the variation observed in the field results were expected.

The recovery rates of blank matrix spikes for soil, leaf, and air provided a satisfactory average range of 94% to 99.6% for both chemical species. The analytical methods utilized on these media adequately provided results with the degree of accuracy this study required. The results of the split matrix

can be explained in part by incomplete mixing of the soil prior to analysis. A more complete explanation would have to include the possibility of laboratory error. As the only detected phosmet and phosmetoxon in field water samples was a result of the split spiked matrix samples, much importance was placed on the confidence in the laboratory results. There was acceptable overall agreement between the laboratories on the results of split water samples (Appendix II, Table 12).

The water storage dissipation studies compared water at four pH values without toluene, and water at two pH values with toluene added for ability to maintain phosmet and phosmetoxon concentrations over time. The data showed that in water at pH 2 and 4, phosmet concentrations were maintained for up to 80 hours with only minimal degradation occurring (Appendix III, Figure 1). As expected, the degradation rate also increased with increasing pH values. The increased phosmet half-life observed in this dissipation study was probably due in part to the storage of samples in dark refrigerated conditions. Data suggested that phosmetoxon may start to break down immediately at all pH values tested (Appendix III, Figures 1 and 2). However, after the initial drop in concentration during the first five hours, phosmetoxon then exhibited the pH dependent behavior similar to the parent compound. Toluene in water was efficient in the extraction of both chemical species at the two pH levels and in holding the concentration over time. This reinforced the confidence in the method used in treating the field samples.

The tank dissipation results confirmed that buffered tank mixtures, if left in spray rigs overnight or over a weekend, could maintain an effective concentration of active ingredient.

The water used to wash apple fruit accounted for most of the phosmet detected in the dislodgeable fraction in the apple dissipation study. The high phosmet concentrations detected in the internal fraction imply that either the water and sur-ten wash did not completely remove the dislodgeable residue, or that phosmet moved into the fruit tissue. Although the high phosmet concentration detected in the internal fraction was not expected, it was not possible in this study to fully account for the total possible amount of dislodgeable fraction. After 7 days, 74.1% of the total phosmet detected in fruit on day 0 still remained. The total phosmet concentration detected on day 7 of the dissipation study was within the range of phosmet concentrations detected on day 7 in the field fruit samples.

Overall, the results of this study did not detect any significant unexpected behavior of phosmet and phosmetoxon under the environmental conditions studied. These results reflect the fate of the chemical species under the environmental conditions specific to the north coast counties monitored. As the AMEP covered six counties, additional data on the environmental behavior of phosmet and phosmetoxon under different environmental conditions represented in the spray area would be useful.

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APPENDIX I

LABORATORY ANALYTICAL METHODS

TABLE OF CONTENTS

SCOPE: This method is for the determination of Phosmet or Phosmetoxon in water samples.

Phosmet/Imidoxone Method Outline

1. Place 50 ml sample into 125 ml separatory funnel
2. Add 5 ml toluene
3. Cap and shake for 2 minutes
4. Let phases separate for 5 minutes
5. Drain lower aqueous phase and decant toluene into a 1.5 ml storage vial
6. Inject 2 or 3 ul

GC Conditions

Varian: 6000 with 402 data system

Detector: TSD M.V. between 8-15

Column: J&W DB1 + Megabore

Column Temp.: 200

Inf Temp.: 205

Ion Oven: 210

Flow: 550 on flow control valve (approx. 55 ml/min.)

Note for Sample Analysis:

When a sample tests positive for Phosmet or Imidoxone a standard is made at the same level that was found in the sample. A standard compaired with a sample at the same level gives better accuracy.

6/26/86

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Original Date:??
Supercedes: NEW
Current Date:7/14/86
Method #:

IMIDAN/IMIDOXONE

SCOPE:

This method is for the determination of Imidan and Imidoxone from apple commodities.

PRINCIPLE:

Chopped portions of apple samples are blended with Acetonitrile and then salted out with NaCl. An aliquot is taken down to near dryness and exchanged into Acetone. A final volume is made with Ethyl Acetate. The extract is dried with Na2SO4 and is then ready for analysis by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Acetonitrile.
2. Acetone.
3. Ethyl Acetate, nanograde. Check for interferences.
4. NaCl.
5. Sorval blender, cup and blade.
6. Graduated mixing cylinders, 100 ml capacity with glass stoppers.
7. Glass wool.
8. Sodium Sulfate, anhydrous.
9. Filter funnel.
10. Volumetric pipet, 20 ml T.D.
11. Glass beakers, 150 mls.
12. Analytical standards of Imidan and Imidoxone.
    a) Stock standards - 1 mg/ml.
    b) Working standards - Dilute stock standards to several working standards covering the linear range of the gas chromatograph and detector used, e.g. 0.1 to 10 ng/ul.
13. A gas chromatograph equipped with a Nitrogen-phosphorus detector.
14. A 10m x 0.53 mm I.D. megabore column coated with 50% Phenyl Methyl Silicone.

ANALYSIS:

1. Chop the entire apple sample into small pieces.
2. Blend in a cuisinart for 30 seconds.
3. Stir contents to mix thoroughly and weigh out 50 grams into a metal Sorval blender cup.
4. Add 100 mls of Acetonitrile to the blender cup and blend on high speed for 2 minutes.
5. Decant Acetonitrile through glass wool and Na2SO4 into a 100 ml graduated mixing cylinder.
6. Add 10 grams of NaCl to the cylinder, stopper and shake for 1 minute.
7. Allow the aqueous and organic layers to separate for 5 minutes.
8. Pipet 20 mls of the Acetonitrile into a 150 ml beaker.
9. Place on a steam bath and take down to near dryness.
10. Add 10 mls of Acetone to the beaker and take down to near dryness again.
11. Repeat step 10.
12. Quantitatively transfer Acetone to a volumetric test tube with Ethyl Acetate.
13. Bring to a final volume of 5 mls.
14. Add 1 gram of Na2SO4 to the test tube and shake for 30 seconds.
15. Extract is ready for analysis by gas chromatography.

EQUIPMENT CONDITIONS:

1. Gas Chromatograph - HP 5880A.
   a) Oven temperature - 240 C.
   b) Injector temperature - 275 C.
   c) Detector temperature - 300 C.
   d) Helium carrier gas flow - 15 mls/min.
   e) NPD make-up gas flow - 5mls/min.

Using these conditions, Imidan has a retention time of 4.54 minutes and Imidoxone has a retention time of 3.70 minutes.

CALCULATIONS:

Results are reported as ppm Imidan (and/or Imidoxone) on both a wet and dry basis for each sample.

For this study, a moisture analysis was also performed for each sample.

DISCUSSION:

Recoveries:		
	1 ug Imidan - 97%.	10 ug Imidoxone - 95%.
	10 ug Imidan - 98%.	100 ug Imidoxone - 99%.

REFERENCES:

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Original Date:??
Supercedes: NEW
Current Date:7/14/86
Method #:

IMIDAN/IMIDOXONE

SCOPE:

This method is for the determination of Imidan and Imidoxone in soil samples.

PRINCIPLE:

Soil samples are mixed thoroughly and then subsampled. Distilled water is added to the subsample and mixed. Ethyl Acetate is added to the sample and mixed for 30 minutes. The EtAc is dried with Sodium Sulfate and the extract is then ready for analysis by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Distilled water.
2. Ethyl Acetate, nanograde. Check for interferences.
3. Sodium Sulfate, anhydrous.
4. Large, wide-mouth, brown bottles with teflon lined screw caps.
5. Volumetric test tubes with glass stoppers.
6. Analytical standards of Imidan and Imidoxone.
   a) Stock standards - 1 mg/ml.
   b) Working standards - Dilute stock standards to several working standards covering the linear range of the gas chromatograph and the detector used, e.g. 0.1 to 10 ng/ul.
7. A New Brunswick G10 Gyrotator.
8. A gas chromatograph equipped with a Nitrogen-phosphorus detector.
9. A 10m x 0.53 mm I.D. megabore column coated with 50% Phenyl Methyl Silicone.

ANALYSIS:

1. Shake jar containing the soil plugs until they are broken up into small pieces.
2. Place on a roller and rotate for 30 minutes at 40-80 rpm.
3. Weigh out 50 grams of soil into a large, wide-mouth, brown bottle.
4. Add 10mls of distilled water to the sample and shake manually to mix.
5. Add 100 mls of Ethyl Acetate to the sample and cap tightly.
6. Place sample jar on Gyrotator for 30 minutes set at 275 rpm.
7. Allow sample to set for 15 minutes.
8. Draw off 10 mls of solvent into a volumetric test tube.
9. Add 1 gram of Na_2SO_4 to the test tube and shake for 30 seconds.
10. Extract is ready for analysis by gas chromatography.

EQUIPMENT CONDITIONS:

1. Gas Chromatograph - HP 5880A.
   a) Oven temperature - 240 C.
   b) Injector temperature - 275 C.
   c) Detector temperature - 300 C.
   d) Helium carrier gas flow - 15 mls/min.
   e) Detector make-up gas flow - 5 mls/min.

Using these conditions, Imidan has a retention time of 4.54 minutes and Imidoxone has a retention time of 3.70 minutes.

CALCULATIONS:

Results are reported as ppm Imidan (and/or Imidoxone) per sample.

DISCUSSION:

Recoveries:	1 ug Imidan - 98%.	10 ug Imidoxone - 96%.
	10 ug Imidan - 99%.	100 ug Imidoxone - 99%.

For this study, a moisture analysis was also performed for each soil sample.

REFERENCES:

WRITTEN BY: Sheila Margetich

Sheila Margetich

TITLE: Agricultural Chemist I

APPROVED BY: David Conrad

TITLE: Agricultural Chemist III

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Original Date:??
Supercedes: NEW
Current Date: 7/14/86
Method #:

IMIDAN/IMIDOXONE

SCOPE:

This method is for the determination of dislodgeable residues of Imidan and Imidoxone from leaf surfaces.

PRINCIPLE:

The surfaces of leaves are rinsed with a distilled water and surfactant solution to remove the pesticide. The aqueous solution is then extracted with Methylene Chloride. The Methylene Chloride is exchanged into Ethyl Acetate. The extract is then ready for analysis by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Distilled water.
2. Sur-ten solution, 2%.
3. Methylene Chloride.
4. Ethyl Acetate, nanograde. Check for interferences.
5. NaCl.
6. Glass wool.
7. Sodium Sulfate, anhydrous.
8. Separatory funnel, 1000 ml capacity with glass stoppers and teflon stopcocks.
9. Glass filter funnels.
10. Boiling flask, 500 ml capacity.
11. Rotoevaporator.
12. Analytical standards of Imidan and Imidoxone.
    a) Stock standards - 1 mg/ml.
    b) Working standards - Dilute stock standards to several working standards covering the linear range of the gas chromatograph and detector used, e.g. 0.1 to 10 ng/ul.
13. A gas chromatograph equipped with a Nitrogen-phosphorus detector.
14. A 10m x 0.53 mm I.D. megabore column coated with 50% Phenyl Methyl Silicone.

ANALYSIS:

1. To the sample jar containing the leaves, add 200 mls of distilled water and 10 drops of sur-ten.
2. Rotate the sample jar on a roller set at 80 rpm for 20 minutes.
3. Decant the aqueous solution through a glass funnel into a 1000 ml separatory funnel.
4. Repeat steps 1-3 twice more.
5. Add 40 grams of NaCl to the sep. funnel and shake to dissolve.
6. Extract aqueous portion with 100 mls of Methylene Chloride, draining the extract through glass wool and Na2SO4 into a 500 ml boiling flask.
7. Extract aqueous portion twice more with 100 mls, then 50 mls of Methylene Chloride, combining all extracts in the boiling flask.
8. Roto-evaporate the Methylene Chloride down to about 1 ml.
9. Add 10 mls of Ethyl Acetate to the flask and roto-evaporate down to about 1 ml.
10. Repeat step 9.
11. Quantitatively transfer the Ethyl Acetate to a volumetric test tube with EtAc.
12. Bring to a final volume of 10 mls.
13. Extract is ready for analysis by gas chromatography.

EQUIPMENT CONDITIONS:

1. Gas Chromatograph - HP 5880A.
   a) Oven temperature - 240 C.
   b) Injector temperature - 275 C.
   c) Detector temperature - 300 C.
   d) Helium carrier gas flow - 15 mls/min.
   e) NPD make-up gas flow - 5 mls/min.

Using these conditions, Imidan has a retention time of 4.54 minutes and Imidoxone has a retention time of 3.70 minutes.

CALCULATIONS:

Results are reported as micrograms of Imidan (and/or Imidoxone) per sample.

DISCUSSION:

Recoveries:	1 ug Imidan - 99%.	10 ug Imidoxone - 99%.
	10 uf Imidan - 100%.	100 ug Imidoxone - 100%.

For this study, a fresh weight was obtained for each leaf sample.

REFERENCES:

WRITTEN BY: Sheila Margetich

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Original Date:??
Supercedes: NEW
Current Date: 7/14/86
Method #:

IMIDAN/IMIDOXONE

SCOPE:

This method is for the determination of Imidan and Imidoxone from lo-vol resin tubes.

PRINCIPLE:

Lo-vol resin tubes are desorbed with Ethyl Acetate. The extract is ready for anaysis by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl Acetate, nanograde. Check for interferences.
2. Boiling flasks, 250 or 500 ml capacity.
3. Separatory funnels, 125 ml capacity.
4. Volumetric test tubes with glass stoppers.
5. Roto-evaporator.
6. A gas chromatograph equipped with a Nitrogen-phosphorus detector.
7. A 10m x 0.53 mm I.D. megabore column coated with 50% Phenyl Methyl Silicone.

ANALYSIS:

1. Remove rubber stoppers from ends of resin tube.
2. Clamp in a vertical position over a boiling flask with the last 3 inches of the tube inserted into the neck of the flask.
3. Clamp a separatory funnel over the the top of the resin tube with the tip of the funnel about 2 inches above the resin bed.
4. Fill the sep. funnel with 100 mls of Ethyl Acetate.
5. Open the stopcock of the sep. funnel and adjust the flow of the solvent so that the it elutes out the bottom of the resin tube at about 1 drop per second.
6. Add another 100 mls of Ethyl Acetate to the sep. funnel above the resin tube just before the first 100 mls has passed through.(Do not let the resin bed dry out between additions of solvent.)
7. Collect all of the solvent in the boiling flask.
8. Reduce the volumn of the EtAc in the boiling flask to 5mls using a roto-evaporator.
9. Quantitively transfer the EtAc to a volumetric test tube.
10. Bring the final volumn up to 10mls.
11. Extract is readay for analysis.

DESORPTION COEFFICIENT:

Recovery:	1 ug Imidan - 100%	10 ugs Imidoxone - 99%
	10 ugs Imidan - 100%	100 ugs Imidoxone - 100%

EQUIPMENT CONDITIONS:

1. Gas Chromatograph - HP 5880A
   a) Oven temperature - 240 C.
   b) Injector temperature - 275 C.
   c) Detector temeperature - 300 C.
   d) Helium carrier gas flow - 15 mls/min.
   e) NPD make-up gas flow - 5 mls/min.

Using these conditions, Imidan has a retention time of 4.54 minutes and Imidoxone has a retention time of 3.70 minutes.

CALCULATIONS:

Results are reported as micrograms of Imidan (and/or Imidoxone) per sample.

REFERENCES:

WRITTEN BY: Sheila Margetich

TITLE: Agricultural Chemist I

APPROVED BY: David Conrad

TITLE: Agricultural Chemist III

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Original Date: December 10, 1986
Supercedes: New
Current Date: December 10, 1986
Method #: ??

APPLE MAGGOT - IMIDAN AND IMIDOXONE IN HIGH VOLUME AIR SAMPLER RESIN SAMPLES

SCOPE:
The analysis of the organophosphate pesticide Imidan and its oxone in high volume air sampler resin samples from the Apple Maggot study is discussed.

PRINCIPLE:
Pesticide residues were extracted from XAD-2 resin samples with ethyl acetate. The solvent was rotary evaporated to dryness and the residues were brought back up to volume in ethyl acetate for gas chromatographic analysis.

REAGENTS AND EQUIPMENT:
Solvents - pesticide grade (Burdick and Jackson)
Rotary evaporator - Buchi
Sodium Sulfate - Mallinkrodt #8024
Ultrasonic bath - Branson B72
Chromatographic columns (19 mm by 500mm) - Kimble #17810-19500
500 ml wide-mouth amber bottles - Qorpak

ANALYSIS:
1.) The resin from the high volume air sampler was emptied into a 500 ml wide mouth amber bottle.

2.) The resin was covered with ethyl acetate (approx. 150 ml), foil lined capped and placed into an ultrasonic bath for thirty minutes.

3.) The solvent and most of the resin was then poured into a 19 mm diameter by 500 mm long chromatography column with a glass wool plug at the outlet end.

4.) The solvent was allowed to flow from the column at 2-3 ml/minute into a 500 ml flat bottomed boiling flask.

5.) The 500 ml bottle from step #1 was rinsed with 100 ml ethyl acetate; the solvent and remaining resin was poured into the resin column.

6.) The solvent was allowed to elute into the same flask as before.

7.) The column was eluted with a further 50 ml of the same solvent.

8.) The solvent was rotary evaporated just to dryness at 65 degrees centigrade at approximately 20 mm Hg vacuum.

9.) The sample residues were brought up in ethyl acetate to 10 ml final volume and stored in the freezer at -20 degrees centigrade until analysis by gas chromatography.

EQUIPMENT CONDITIONS:
Varian 3700 with TSD:

Column: Hewlett Packard; HP-1 (#19015Z-121)
10 meter x 0.53mm; 2.65um film thickness methyl silicone megabore capillary.

Oven: Isothermal 200 C.

Carrier Gas: Helium - 30 ml/minute; 12 psig.

Injector: 200 C

Detector: 220 C; Bead Current Setting - 775.
Hydrogen Flow Pressure = 21 psig.

WRITTEN BY: Jim Echelberry

TITLE: Laboratory Technician (Chemical Analysis)

APPROVED BY: David Conrad

TITLE: Agricultural Chemist III

State of California
DEPARTMENT OF FOOD AND AGRICULTURE

Pesticide Formulations Laboratory

PHOSMET ANALYSIS IN TANK MIX

SAMPLE PREPARATION

Sample is shaken to mix and 50 ml pipetted out into 100 ml volumetric flask. This is made up to volume with HPLC grade acetonitrile and shaken to mix. An aliqout is clarified thru 0.2 microns filter prior to injection in the HPLC instrument.

HIGH PERFORMANCE CHROMATOGRAPHY PARAMETERS

Standard concentration: 0.5 mg/ml

Column: Ubondapak C18 30 cm, 4mm i.d.
Mobile Phase: 60:40 Acetonitrile:Water
Flowrate: 1.0 ml/min
Detection: UV 292 nm
Absorbance: 0.2 AUFS

Retention time: 4.62 minutes

APPENDIX II

TABLES OF ANALYTICAL RESULTS

LIST OF TABLES

Table II-1. Concentrations of phosmet on apple leaves sampled for Apple Maggot Project, 1986. Expressed in micrograms per square centimeter (ug/cm^2) of leaf surface area.

		Days Post Spray Spray									
		1		5		9		13		>13[b]	
Spray	Site	$\bar{x}$[a]	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
1	1	2.00	0.27	0.94	0.20	0.87	0.06	NS[c]			
	2	1.92	0.49	1.23	0.15	0.92	0.32	NS			
	3	2.30	0.85	1.58	0.06	1.19	0.08	1.10	0.37		
2	1	2.14	0.07	1.35	0.08	1.13	0.45	NS			
	2	1.19	0.24	1.01	0.05	0.60	0.06	NS			
	3	1.50	0.14	1.19	0.30	2.45	1.56	1.39	0.33		
3	1	2.34	0.47	1.39	0.09	0.55	0.30	0.48	0.28		
	2	0.69	0.59	0.91	0.36	1.16	0.04	0.64[d]			
	3	2.84	0.02	1.81	0.25	1.87	0.47	1.41	0.06		
4	1	1.24	0.06	1.19	0.22	1.31	0.08	NS			
	2	1.64	0.08	2.58	0.46	0.88	0.06	0.72	0.15		
	3	1.61	0.63	2.65	0.09	1.34	0.22	1.34	0.05	1.58	0.44
5	1	1.44	1.03	1.63[e]	0.28	1.64	0.23	NS			
	2	2.54	0.58	1.69	0.22	1.70	0.45	0.97	0.18	0.86	0.16
	3	1.72	1.74	1.65	0.13	1.48	0.88	1.54	0.10		
6	1	NS		NS		NS		NS			
	2[f]	1.32	0.18	0.69	0.06	NS		NS		0.30[d]	
	3[f]	1.69	0.55	1.26	0.40	2.00	0.30	NS		0.66	0.01

a/ Concentrations are the mean of two samples of approximately 30 leaves each. MDL 0.5 ug/sample.
b/ Spray 4, site 3 represents a 15 day post sample; spray 5, site 2 represents an 18 day post sample; spray 6, site 2 and 3 represent a 17 day post sample.
c/ NS= Not Sampled; conditions did not require collection of samples.
d/ Replicate sample lost. No standard deviation.
e/ Represents 6 day post sample.
f/ Dry weight of samples estimated by regression.

Table II-2. Concentrations of phosmetoxon on apple leaves sampled for Apple Maggot Project, 1986. Expressed in nanograms per square centimeter (ng/cm^2) of leaf surface area.

		Days Post Spray									
		1		5		9		13		>13[b]	
Spray	Site	$\bar{x}$[a]	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
1	1	8.22	0.49	5.30	0.74	3.73	1.31	NS[c]			
	2	5.10	0.32	6.86	0.67	3.55	0172	NS			
	3	3.98	1.60	4.33	0.07	4.28	0.74	3.04	0.79		
2	1	9.34	1.46	6.19	0.92	5.60	2.23	NS			
	2	6.25	0.18	7.11	1.94	6.03	0.12	NS			
	3	6.27	1.58	6.32	0.89	7.43	0.98	5.39	0.74		
3	1	8.64	1.36	4.16	0.04	3.70	0.64	2.60	0.90		
	2	3.31	2.03	4.70	0.25	5.30	0.49	6.31[d]			
	3	1.05	1.41	6.94	0.04	7.48	1.77	5.94	2.49		
4	1	7.02	1.48	7.21	2.84	6.57	0.34	NS			
	2	7.38	1.59	11.1	1.49	4.46	1.22	2.05	0.11		
	3	7.10	3.02	21.1	11.2	4.20	0.59	16.3	0.16	5.51	2.30
5	1	5.53	1.36	5.82[e]	0.03	6.03	1.27	NS			
	2	6.85	2.69	8.39	0.39	7.64	1.35	5.35	0.28	2.13	0.57
	3	6.88	5.34	9.85	2.49	6.86	1.92	4.43	0.28		
6	1[f]	NS		NS		NS		NS			
	2[f]	3.65	2.24	1.92	0406	NS		NS		1.86[d]	
	3	5.72	0.04	3.88	1.68	7.31	1.15	NS		2.80	0.33

a/ Concentrations are the mean of two samples of approximately 30 leaves each. MDL 0.5 ug/sample.
b/ Spray 4, site 3 represents a 15 day post sample; spray 5, site 2 represents an 18 day post sample; spray 6, site 2 and 3 represent a 17 day post sample.
c/ NS - Not sampled; conditions did not require collection of samples.
d/ Replicate sample lost. No standard deviation.
e/ Represents 6 day post sample.
f/ Dry weight of samples estimated by regression.

Table II-3. Concentrations of phosmet on apple leaves sampled for Apple Maggot Project, 1986. Expressed in parts per million (ppm).

		Days Post Spray									
		1		5		9		13		>13[b]	
Spray	Site	$\bar{x}$[a]	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
1	1	502.8	27.7	251.1	42.6	206.1	16.7	NS[c]			
	2	397.5	97.9	247.8	17.5	152.4	49.5	NS			
	3	513.8	230.4	359.4	17.8	256.8	26.9	225.9	75.7		
2	1	518.9	11.2	398.4	55.6	333.7	180.2	NS			
	2	202.8	37.4	191.8	1.41	108.2	2.2	NS			
	3	273.1	10.0	246.2	68.1	479.3	300.7	274.1	66.5		
3	1	561.6	51.2	329.2	10.4	132.1	46.2	112.0	63.3		
	2	115.0	97.6	165.9	47.4	223.0	11.4	112.1	d/		
	3	540.3	4.8	351.7	47.1	379.7	91.5	265.8	25.8		
4	1	277.9	16.0	232.2	31.0	322.2	31.0	NS			
	2	315.2	37.9	433.1	64.8	158.4	7.6	123.3	21.5		
	3	313.5	106.8	445.0	27.6	276.7	45.5	259.0	16.9	297.6	65.5
5	1	336.2	227.7	417.0[e]	29.0	429.1	63.4	NS			
	2	504.0	141.0	309.2	45.2	289.7	74.0	158.4	33.8	177.3	33.2
	3	322.0	339.8	347.2	20.9	283.8	159.5	337.7	19.8		
6	1	NS		NS		NS		NS			
	2[f]	289.0	49.7	139.4	4.6	NS		NS		61.03[d]	
	3[f]	351.9	124.0	265.0	92.1	462.6	65.9	NS		136.7	1.08

a/ Concentrations are the mean of two samples of approximately 30 leaves each. MDL 0.5 ug/sample.
b/ Spray 4, site 3 represents a 15 day post sample; spray 5, site 2 represents an 18 day post sample; and spray 6, site 2 and 3 represent a 17 day post sample.
c/ NS = Not sampled; conditions did not require collection of samples.
d/ Replicate sample lost. No standard deviation.
e/ Represents 6 day post spray sample.
f/ Dry weight of samples estimated by regression.

Table II-4. Concentrations of phosmetoxon on apple leaves sampled for Apple Maggot Project, 1986. Expressed in parts per million (ppm).

		Days Post Spray									
		1		5		9		13		13[b/]	
Spray	Site	$\bar{x}$[a/]	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
1	1	2.07	0.035	1.41	0.141	0.88	0.302	NS[c/]			
	2	1.08	0.014	1.29	0.163	0.59	0.013	NS			
	3	0.89	0.425	0.93	0.026	0.92	0.126	0.37	0.522		
2	1	2.27	0.332	1.80	0.014	1.66	0.891	NS			
	2	1.07	0.014	1.35	0.424	1.08	0.099	NS			
	3	1.12	0.372	1.31	0.219	1.46	0.177	1.06	0.144		
3	1	2.08	0.106	1.03	0.017	0.89	0.152	0.61	0.189		
	2	0.55	0.327	0.87	0.523	1.02	0.003	1.11[d/]			
	3	1.99	0.260	1.35	0.016	1.52	0.336	1.11	0.406		
4	1	1.57	0.318	1.40	0.488	1.61	0.021	NS			
	2	1.06	0.120	1.86	0.198	0.80	0.212	0.35	0.028		
	3	1.37	0.516	3.63	2.22	0.87	0.120	3.14	0.057	1.04	0.375
5	1	1.30	0.255	1.50[e/]	0.134	1.58	0.346	NS			
	2	1.37	0.601	1.53	0.042	1.30	0.219	0.88	0.064	0.44	0.127
	3	1.28	1.07	2.06	0.481	1.33	0.318	0.97	0.057		
6	1	NS		NS		NS		NS			
	2[f/]	0.80	0.523	0.39	0.099	NS		NS		0.38[d/]	
	3[f/]	1.19	0.021	0.82	0.382	1.69	0.255	NS		0.59	0.078

a/ Concentrations are the mean of two samples of approximately 30 leaves each. MDL 0.5 ug/sample.
b/ Spray 4, site 3 represents a 15 day post sample; spray 5, site 2 represetns an 18 day post sample; spray 6, sites 2 and 3 represent a 17 day post sample.
c/ NS = Not sampled; conditions did not require collection of samples.
d/ Replicate sample lost. No standard deviation.
e/ Represents 6 day post sample.
f/ Dry weight of samples estimated by regression.

Table II-5. Analysis of variance mean squares of phosmet and phosmetoxon on apple foliage.

Source of Variation	df	Mean Square Phosmet	Mean Square[a/] Phosmetoxon x 10^4
Spray	5	0.472	2.419**[b/]
Site	2		
Humboldt vs Del Norte Co. (C1)	1	5.660**	0.786**
Del Norte vs Del Norte (C2)	1	0.408	0.057
Days Post	2		
Days post linear (DL)	1	12.080*	1.220**
Days post quadratic (DQ)	1	0.003	0.199
Site x Days Post	4		
C1 x DL	1	0.603	0.121
C1 x DQ	1	0.179	0.137
C2 x DL	1	0.108	0.014
C2 x DQ	1	0.001	0.045
Residual	37	0.386	0.079

a/ Mean squares derived from Type I sums of square for sequential fit of terms in a General Linear Model (SAS).

b/ Mean squares that would give F values greater than the tabulated value for the F distribution of α=.05 and α=.01 are denoted * and **, respectively.

Table II-6. Concentrations of phosmet in surface soil samples for Apple Maggot Project, 1986. Expressed in parts per million (ppm). MDL= 10 ppb.

		Days Post Spray									
		1		5		9		13		>13[b]	
Spray	Site	$\bar{x}$[a]	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
1	1	0.48	0.27	0.05	0.01	1.31	0.21	NS[c]			
	2	1.57	0.02	2.33	1.00	1.78	0.41	NS			
	3	1.79	0.03	1.26	0.23	0.57	0.36	0.90	0.15		
2	1	1.72	0.33	2.14	0.17	1.46	0.09	NS			
	2	1.65	0.87	1.96	0.16	1.41	0.11	NS			
	3	0.97	0.04	0.37	0.20	d/		0.25	0.14		
3	1	2.19	0.23	1.58	0.22	1.61	0.59	1.07	0.11		
	2	2.62	0.56	1.73	0.04	0.95	0.60	0.86	0.16		
	3	1.23	0.00	0.79	0.08	0.46	0.40	0.20	0.01		
4	1	1.14	0.23	1.33	0.06	1.06	0.30	NS			
	2	2.31	0.41	4.88	0.93	2.32	0.41	2.96	0.30		
	3	0.48	0.17	1.19	0.30	0.78	0.09	0.34	0.17	0.41	0.18
5	1	2.25[e]	0.21	2.38[f]	0.32	1.70	0.15	NA[g]			
	2	4.14	0.85	3.25	1.14	2.56	0.74	4.70	1.28	1.72	0.15
	3	0.78	0.29	0.50	0.12	0.36	0.05	0.43	0.04		
6	1	NA		NA		NA		NA			
	2	4.03	0.37	4.98	0.33	no sample/rain		no sample/rain		1.03	0.11
	3	0.77	0.01	0.84	0.42	1.11	0.07	no sample/rain		0.23	0.10

a/ Concentrations are the mean of two samples.
All samples analyzed for phosmet (MDL=10 ppb) and the oxygen analog phosmetoxon (MDL= 50 ppb).

b/ Spray 4, site 3 represents a 15 day post sample; spray 5, site 2 represents an 18 day post sample; and spray 6, site and 3 represent a 17 day post sample.

c/ NS= Not Sampled; next application occurred before 13 day post sample day.

d/ Sample lost.

e/ Only sample to detect phosmet OA (MDL= 50 ppb) x = 0.12 ppm SD = 0.14

f/ Represents 6 day post sample.

g/ NA= No Access; site not available for monitoring purposes.

Table II-7. Analysis of variance mean squares of phosmet in soil.

Source of Variation	df	Mean Square Phosmet[a/]
Spray	5	2603787
Site	2	
Humboldt vs Del Norte Cos (C1)	1	54058124**[b/]
Del Norte vs Del Norte (C2)	1	11100524**
Days Post	2	
Days post linear (DL)	1	8169906*
Days post quadratic (DQ)	1	1704389
Site x Days Post	4	
C1 x Dl	1	107922
C1 x DQ	1	237034
C2 x DL	1	416723
C2 x DQ	1	30624
Residual	34	1240414

a. Means squares derived from Type I sums of square for sequential fit of terms in a General Linear Model (SAS).

b. Means squares that would give F values greater than the tabulated value for the F distribution of α=.05 and α=.01 are denoted * and **, respectively.

Table II-8. Concentrations of phosmet on apple samples collected for Apple Maggot Project, 1986. The results are means of two replicate samples reported in parts per million (ppm, fresh weight basis).

		Days Post Spray 1		Days Post Spray 7		Day Before Next Treatment	
Spray	Site	$\bar{x}$[a/]	SD	$\bar{x}$	SD	$\bar{x}$	SD
1	1	0.13	0.09	0.64	0.07	0.11 11 day post	0.35
	2	0.82	0.97	0.99	3.55	0.13 12 day post	0.02
	3	1.80	0.12	0.63	0.10	1 20 13 day post	0.76
2	1	1.04	0.58	0.31	0.35	0.72 9 day post	0.05
	2	1.20	0.09	0.18	0.01	0.29 12 day post	0.13
	3	1.10	0.18	1.19	0.56	1.10 13 day post	0.18
3	1	0.73	0.13	1.63	0.41	1.24 13 day post	0.20
	2	1.45	0.28	0.80	0.33	0.51 13 day post	0.17
	3	1.56	1.32	2.20	0.14	0.93 14 day post	0.30
4	1	0.99	0.04	1.42	0.11	0.96 11 day post	0.20
	2	1.10	0.61	1.73	0.62	0.85 13 day post	0.19
	3	2.03	0.01	1.01	0.32	0.62 13 day post	0.04
5	1	1.37	0.37	0.71	0.37	NS[b/]	
	2	0.60	0.09	1.67	0.85	0.64 18 day post	0.03
	3	1.40	0.43	1.07	0.09	0.84 13 day post	0.30
6	1	NS		NS		NS	
	2	1.08	0.01	0.88	0.07	0.22 17 day post	0.06
	3	0.70	0.45	0.99	0.37	0.53 17 day post	0.13

a/ Samples analyzed for phosmet - MDL 0.005 ppm (fresh weight basis) and the oxygen analog, phosmetoxon - MDL 0.025 ppm (fresh weight basis). Phosmetoxon was not detected in any of the samples.

b/ Not sampled. Site not available for monitoring purposes.

Table II-9. Analysis of variance mean squares of phosmet in fruit.

Source of Variation	df	Mean Square[a/] phosmet
Spray	5	0.815*[b/]
Site	2	
Humboldt vs Del Norte Cos (C1)	1	2.212**
Del Norte vs Del Norte (C2)	1	
Days Post	2	
Days post linear (DL)	1	3.392**
Days post quadratic (DQ)	1	.285
Site x Days Post	4	
C1 x DL	1	.147
C1 x DQ	1	.542
C2 x DL	1	.020
C2 x DQ	1	.001
Residual	36	.327

a/ Mean squares derived from Type I sums of square for sequential fit of terms in a General Linear Model (SAS).

b/ Mean squares that would give F values greater than the tabulated value for the F distribution of α=.05 and α=.01 are denoted * and **, respectively.

Table II-10. Split matrix fruit samples for Apple Maggot Project, 1986. Concentrations of phosmet in parts per million (ppm), fresh weight basis. MDL=0.1 ppm.

Sample #	Phosmet Concentration Reported	
	CDFA	NCL
1	2.57	1.7
2	1.54	1.7
3	1.63	0.9
4	1.36	1.4

Table II-11. Split matrix soil samples for Apple Maggot Project, 1986. Concentrations of phosmet in parts per million (ppm), dry weight basis. MDL=0.1 ppm.

Sample #	Replicate #	Phosmet Concentration Reported	
		CDFA	NCL
1	1	1.49	0.72
	2	1.34	0.71
2	1	1.40	1.71
	2	1.53	2.63
3	1	1.28	0.36
	2	1.37	0.21
4	1	5.54	3.34
	2	4.22	3.50
5	1	1.40	0.25
	2	0.97	0.33

Table II-12. Split spiked water samples for Apple Maggot Project, 1986. Concentrations of phosmet and phosmetoxon (OA) expressed in parts per billion (ppb). MDL= 1 ppb.

			CONCENTRATIONS REPORTED BY LAB											
Sample #	Concen. of Spike		CDFA		% Recov.		NCL							
	Phosmet	Phosmetoxon	Phosmet	Phosmetoxon	Phos.	OA	Phosmet	Phosmetoxon	% Recov. Phos.	OA	Phosmet	Phosmetoxon	% Recov. Phos.	OA
1	25	25	44.4	34.3	178	137	26	19	104	76	27	15	108	60
2	50	50	53.4	37.6	107	75	50	57	100	114	49	34	98	68
3	6.25	6.25	9.0	9.8	144	157	4	3	64	48	4	3	64	48
4	25	25	24.4	18.8	98	75	14	10	56	40	14	10	56	40
5	10	10	9.4	8	94	80	5	4	50	40	5	5	50	50
6	20	20	21	12.3	105	62	19	11	95	55	22	14	110	70
7	5	5	4.9	5.3	98	106	5	2	100	40	5	3	100	60
8	30	30	32.8	23.6	109	79	48	31	160	103	42	34	140	113

APPENDIX III

PHOSMET DISSIPATION STUDIES IN WATER, TANK MIXTURE AND APPLES

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DISSIPATION STUDIES

A. Quality Control Dissipation

Two water dissipation studies were conducted by the personnel of the CDFA laboratory and the NCL. One study was done to better assess the effectiveness of toluene in extracting and stabilizing the concentration of phosmet and phosmetoxon in water over time during storage, and the other to evaluate the degradation of phosmet and phosmetoxon in water over time at different pH values.

In the study conducted by the CDFA lab, six 500 ml water samples at pH 6 and six at pH 9 (twelve total) in one liter amber glass bottles were spiked with 50 ppb phosmet and 50 ppb phosmetoxon. Each bottle had 50 ml toluene added and was shaken for two minutes. The toluene layer was removed from two replicate samples at each pH value for analysis after sample preparation on day 0. The remaining samples were stored in the dark and refrigerated throughout the study to duplicate conditions of field samples. Replicate toluene samples at each pH value were again collected for analysis on days 3 and 6. Due to laboratory problems, one of the samples at pH 9 was analyzed on day 6 and one on day 7.

The study conducted by the NCL consisted of 10 one liter amber glass bottles with 500 ml distilled-deionized water at each pH value of 2, 4, 6 and 8 (40 total) and each was spiked with 100 ppb phosmet and 100 ppb phosmetoxon. No toluene was added to the sample bottles. Two samples at each pH value were collected for duplicate analysis at intervals of 6, 12, 20, 24, 48, 72, 96,

120, 144 and 168 hours post prepration time. The samples were stored in dark refrigeration for the duration of the study.

Dissipation in Toluene and Water - There were no significant decreases in the concentration of phosmet and its oxygen analog from day 0 to day 7 as determined by Tukey's method for all pairwise means comparisons. The analytical values are presented in Table III-1. There was a large amount of variability in concentrations of phosmetoxon, however, which may mask an actual decrease. It should also be noted that the initial concentration placed in each bottle was 50 ppb for each chemical species, yet the day 0 concentrations of phosmetoxon were 32.25 and 23.30 ppb, for pH 6 and 9, respectively. There appeared to be a drop in concentration of phosmetoxon between the time the spiked samples were created and the time analysis occurred on day 0.

Water Dissipation - For each pH and each of ten sampling periods, concentrations of phosmet and phosmetoxon in duplicate samples were averaged. The best fitting polynomial regression models selected by stepwise regression for the relationship between time and concentration of phosmet or its oxygen analog at each of four pH levels are presented in Table III-2 and Figures III-1 and III-2. Since the best fitting regression models were in general non-linear and were of different orders, it was not possible to compare them statistically. However, observation of plots of the fitted regression curves suggests an apparent relationship between dissipation rate and pH.

While each sample received an initial dose of 100 ppb of both phosmet and phosmetoxon, in all cases there was a relatively sharp drop in concentration

Table III-1. Degradation of phosmet and phosmetoxon over time in toluene water at two pH values. Expressed in parts per billion (ppb).

	CONCENTRATION REPORTED							
	pH 6				pH 9			
Time Days	Replicate 1		Replicate 2		Replicate 1		Replicate 2	
	Phosmet	Phosmetoxon	Phosmet	Phosmetoxon	Phosmet	Phosmetoxon	Phosmet	Phosmetoxon
Spike conc.	50	50	50	50	50	50	50	50
0	49.7	32.7	49.4	31.8	41.4	23.4	40.4	23.2
3	48.4	13.3	48.3	30.4	44.6	14.3	46.2	18.6
6	45.8	24.5	45.3	24.3	45.4	12.2	--	--
7	--	--	--	--			42.0	12.3

Table III-2. Best polynomial models selected by stepwise regression.

Phosmet	Best Model[a/]	R^2[b/]
pH 2	$C = 78.78 + .06T - .000006\ T^3$	.895
pH 4	$C = 81.86 - .000004\ T^3$	.817
pH 6	$C = 83,`.71 - .001\ T^2$	.966
pH 8	$C = 55.36 - 1.05\ T + .008\ T^2 - .00002\ T^3$	.985
Phosmetoxon		
pH 2	$C = 34.17 + .29\ T - .000006\ T^3$	.847
pH 4	$C = 31.51 + .83\ T - .008\ T^2 + .00002\ T^3$	.908
pH 6	$C = 40.07 - .00000\ T^3$	.361[c/]
pH 8	$C = 18.33 - .14\ T$	.902

a/ C= Concentration ppb; T= time in hours
b/ p>.05 p= probability value
c/ Coefficient of determination; amount of variation accounted for by the regression line.

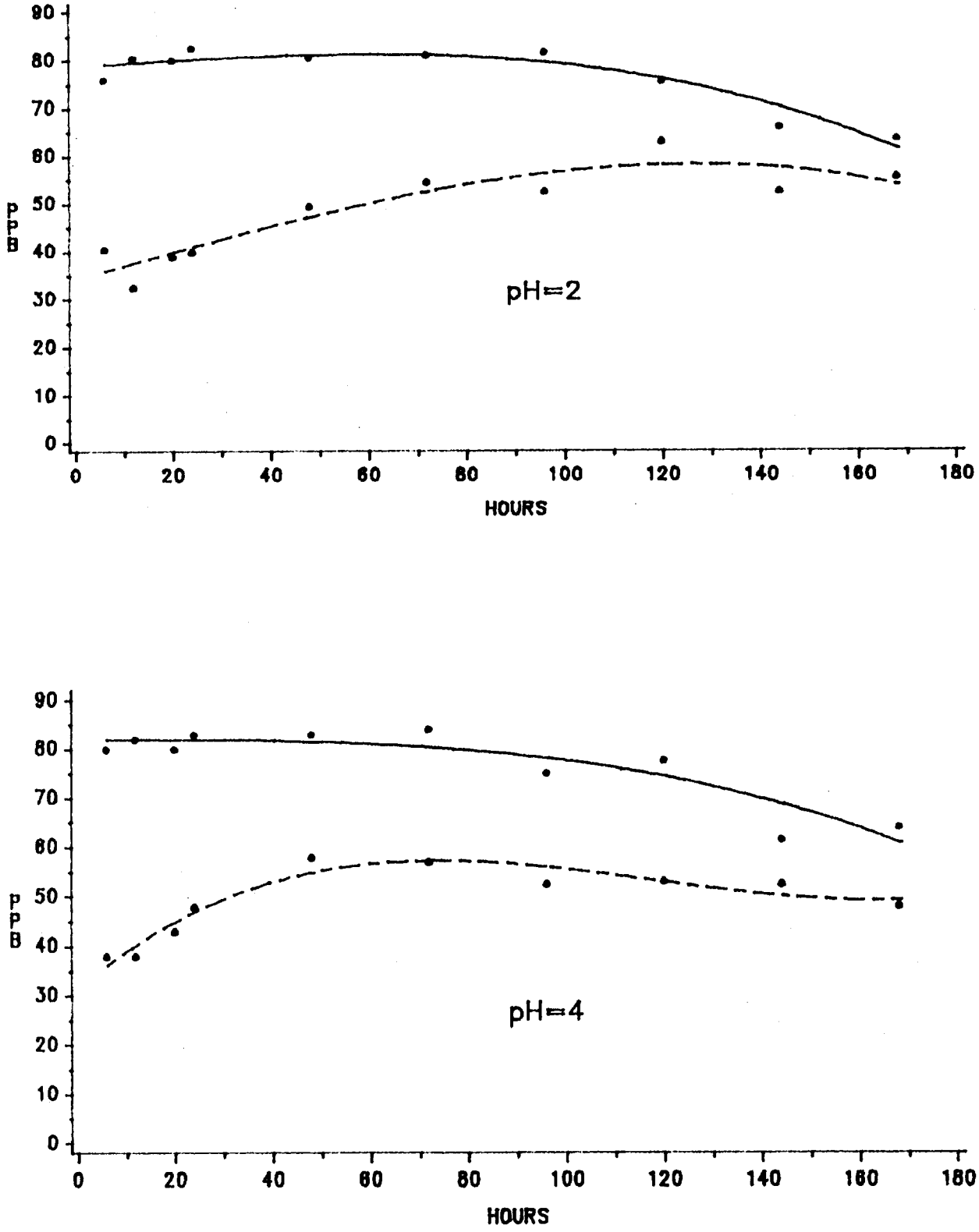

FIGURE III–1. DEGRADATION OF PHOSMET (SOLID CURVE) AND PHOSMETOXON (BROKEN CURVE) IN WATER AT PH LEVELS 2 AND 4. CURVE INDICATES BEST–FITTING POLYNOMIAL MODEL.

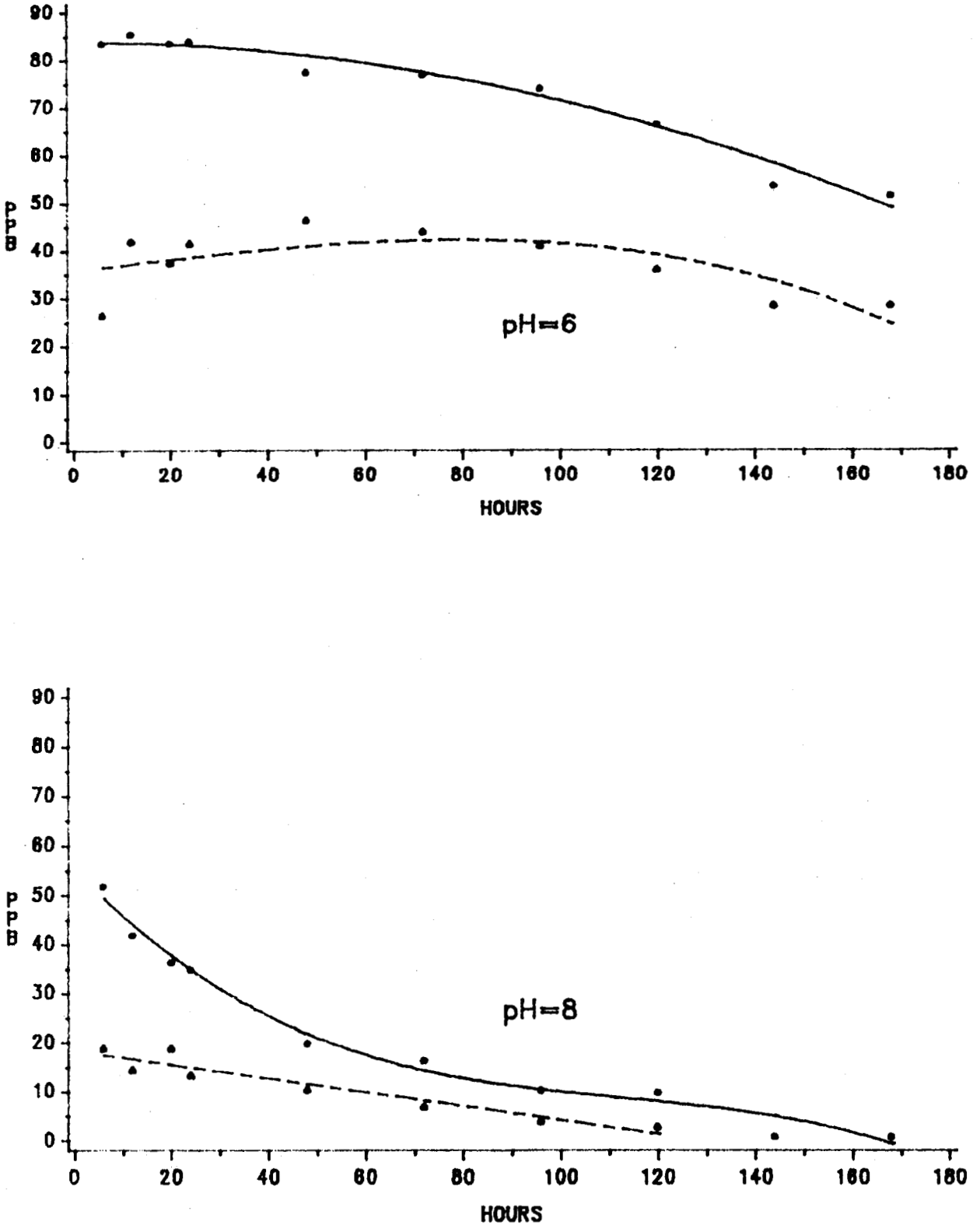

FIGURE III–2. DEGRADATION OF PHOSMET (SOLID CURVE) AND PHOSMETOXON (BROKEN CURVE) IN WATER AT PH LEVELS 6 AND 8. CURVE INDICATES BEST–FITTING POLYNOMIAL MODEL.

of both species after six hours. This initial drop in concentration was greater for phosmetoxon than phosmet regardless of pH.

Decreasing hydrogen ion concentration from pH 2 to pH 6 produced only a small increase in dissipation of phosmet in water after 168 hours, with residual concentrations of phosmet ranging from 48% to 61% of the initial concentration levels. At pH 8, there was an increase in the dissipation rate of phosmet in water. After 144 hours at pH 8, phosmet could not be detected in water samples analyzed. Phosmet half-life at pH 2, 4 and 6 was not within the range of the observed study so valid extrapolation could not be made. The half-life would be in excess of 180 hours. At pH 8 however, the phosmet half-life was 35.5 hours.

Following a drop from initial dosage levels, concentrations of phosmetoxon gradually increased over time in water at pH 2 to pH 6, and then began to gradually decrease. This increase in the concentration of phosmetoxon is most likely the result of the breakdown of phosmet and the concomitant increase in its breakdown product, phosmetoxon. The final predicted concentrations of phosmetoxon after seven days were 54%, 49%, 28% and 0% of the original concentrations for pH 2, 4, 6, and 8, respectively. At pH 8, an increase in the dissipation rate of phosmetoxon may explain why no build up of phosmetoxon occurred.

There was concern that a significant loss of toluene could result from its evaporation into the head space of the water bottles during storage. This would contribute a factor of error to the laboratory's ability to accurately

calculate chemical concentrations. To evaluate this possibility, nine 500 ml distilled-deionized water samples at pH 6, and nine at pH 9 were put in one liter amber glass bottles. Six bottles at each pH (12 total) were spiked with 100 ppb phosmet and 100 ppb phosmetoxon, and three bottles at each pH value (6 total) were left blank. Each bottle had 50 ml ≈43.1530 gr. toluene added and shaken for two minutes. On day 0, a designated weight of toluene aliquot was removed from one blank bottle and two spiked bottles at each pH value. The weight of toluene in each bottle after the aliquot was removed was determined. This weight was compared to the theoretical toluene weight that should have remained and any possible toluene loss could be calculated from the difference. This procedure was repeated three days post and six days post on the remaining sets of samples. The mean amount of toluene recovered from the initial amount of toluene on days 0, 3, and 6 was 98.9, 98.8 and 98.4%, respectively. These results indicate that toluene loss to bottle head space should not significantly impact laboratory results.

B. **Field Dissipation**

A dissipation study was conducted on buffered tank mixture to better evaluate the Imidan® concentration stability over time. Additionally, in response to a request by the CDFA Medical Toxicology Branch, an apple dissipation study was initiated by the EHAP to determine the maximum amount of phosmet that would occur as residue on apples under laboratory conditions. The tank and apple studies were conducted by personnel of the EHAP.

Tank Mixture Dissipation - Four replicate tank samples were collected from a truck-mounted spray rig just after a fresh formulation had been mixed for use

in Humboldt County. The samples were collected in one quart wide mouth glass jars using the rig's spray gun after flushing the hose system for 60 seconds. Tank sample containers were sealed, stored, and transported to the CDFA lab in Sacramento under ambient conditions and maintained at ambient conditions in the laboratory during the three day study period before analysis. Subsamples from the four containers were analyzed on days 0, 1, 2, and 3 post mix (16 total). However, two of the one day post and one of the two day post samples were lost due to laboratory problems.

Tank Dissipation Results - A one way repeated measure analysis of variance was performed using the average percent active ingredient of six subsample measurements as the dependent variable, and day as the repeated factor. The main effect of day was not significant ($F= 2.12$; $df= 3,6$; $p=0.20$). After 3 days from 94.4% to 96.9% of initial levels of active ingredient remained.

Apple Dissipation Study - Apples dipped in Imidan® were sampled according to a schedule that coincided with the pre-harvest interval, and analyzed for phosmet and phosmetoxon. The residue analysis consisted of three fractions:

* H_2O used to rinse the apples
* Sur-ten solution used to strip the remaining surface residue
* Analysis of whole apples

Materials and Methods - One-hundred and sixty pesticide free apples, provided by the AMEP were each labeled with their individual weights and a letter (A-P) which corresponded to a particular sample. The apples were dipped for one

minute in a five gallon container of Imidan® 50 WP at a 1-1/2 lbs/100 gal concentration. They were removed with tongs and allowed to drain briefly, then placed on drying racks stem side up within a cool, shady, well ventilated area. Immediately after drying, replicate samples A through E, which consisted of 10 apples per sample, were collected and deposited into pre-numbered polyethylene bags. Samples F through J and K through O were collected on post days 1 and 7, respectively. Sample P was used as a back up. The study facility temperature was recorded at collection time and noted on the chains of custody. All samples were immediately cooled on wet ice and shipped with their corresponding chains of custody to the CDFA laboratory in Sacramento for analysis.

Apple Dissipation Results - The results for the dissipation of phosmet from apples are presented in Table III-3 and Figure III-3. Phosmet was consistenly recovered from water, surfactant and internal fractions. While the amount contained in the internal fraction was more than expected, the total residue was much less than the 10 ppm tolerance. Phosmetoxon was detected in the water fraction only, with mean concentrations ranging from 1.0 to 1.2 ppb. Phosmet was present in concentrations approximately three orders of magnitude greater than those for its oxygen analog. Results from means comparison tests (LSD,SAS) indicated that there were no significant differences in the concentration of phosmet between days for the water and surfactant fractions, but a significant decline occurred between days 1 and 7 for the internal fraction. There were no significant differences between days for phosmetoxon in the water fraction. Additional data representing 234 apples produced a mean weight of 102.97 grams per apple with a standard deviation of 18.2.

Table III-3. Dissipation of phosmet in apples over time for the 1986 Apple Maggot Project. Expressed in parts per million (ppm) phosmet.

		DAY 0		DAY 1		DAY 7	
		$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
Dislodgeable	water	0.609[a/]	0.145	0.522	0.056	0.637	0.106
Fraction in:	Sur-ten	0.154	0.041	0.152	0.064	0.242	0.122
Total Dislodgeable		0.763	0.119	0.674	0.100	0.879	0.129
Internal		1.42	0.41	1.75	0.60	0.67	0.14
Total (Dislodgeable + Internal)		2.183	0.491	2.424	0.668	1.549	0.230

a/ Concentrations are the mean of five samples.

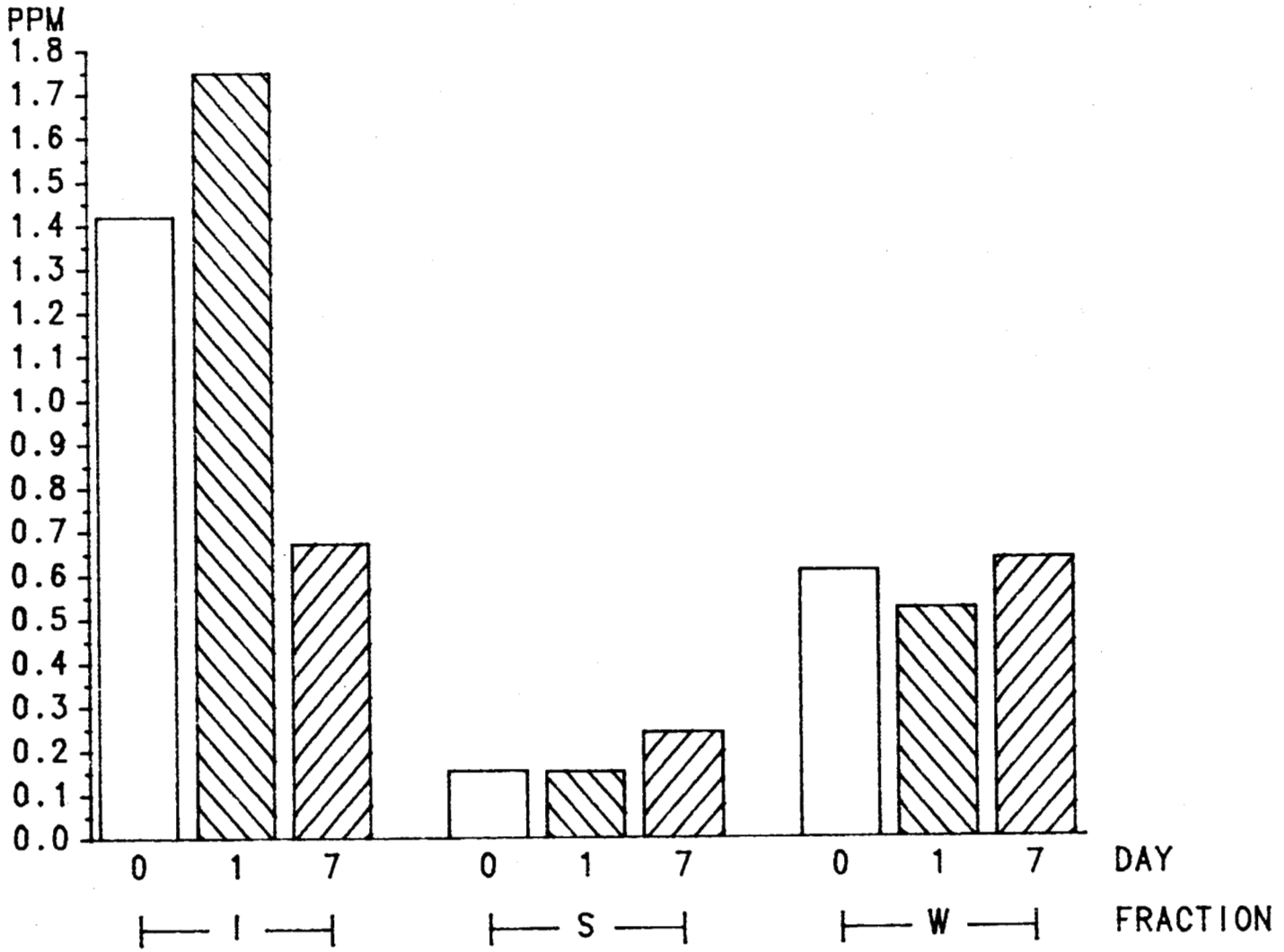

FIGURE III–3. MEAN PHOSMET CONCENTRATION IN WATER (W), SURFACTANT (S) AND INTERNAL (I) FRACTIONS FROM APPLES, DAYS 0 TO 7.