

**RESULTS OF WHITE GARDEN SNAIL
ENVIRONMENTAL MONITORING PROGRAM
SPRING AND FALL 1987**

August, 1988

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM



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RESULTS OF WHITE GARDEN SNAIL ENVIRONMENTAL MONITORING PROGRAM

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by

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ABSTRACT

Monitoring undertaken during the first year of the white garden snail suppression program yielded useful information about residue levels and dissipation of metaldehyde and methiocarb in soil. Nonetheless, fall monitoring results though less variable than spring results were unable to accurately reflect the amount of pesticide applied at residential sites more than 65% of the time. Pesticide granule size, application method, and sampling technique most likely contributed to the variable results. In addition, the large range in quality control analytical results from two participating laboratories increased the difficulty of interpreting our data.

PART 1. Spring 1987 White Garden Snail Monitoring Program

Two residential sites and two experimental sites were sampled over nine weeks and 20 days, respectively, to determine residue levels and dissipation rates of metaldehyde and methiocarb following their application to suppress an infestation of white garden snail (Theba pisana Muller). Additionally, home garden vegetables were analyzed for metaldehyde to discern if metaldehyde was absorbed by root systems and translocated to edible plant tissues. Residential residue levels ranged from none detected to 263 mg/sq m for metaldehyde and from none detected to 289 mg/sq m for methiocarb over the 42-day sampling period. The high variability exhibited by the monitoring results led to recommendations for future monitoring programs of increased replication within sites, increased number of sites and additional measurements to ensure treatment and sampling methods were adequate.

Experimental site results showed that 10 to 11 days were required for one-half of applied metaldehyde to dissipate; high variability precluded dissipation estimates for methiocarb. Vegetables from home gardens showed no metaldehyde residues.

PART 2. Fall 1987 White Garden Snail Monitoring Program

Residential monitoring took place at 26 homes during the fall program. Measurements of surface area treated and amount of pesticide applied were collected along with soil samples for residue analysis. Runoff water was collected from one site. Comparison of calculated application rates with mean residue levels of metaldehyde and methiocarb found in soil immediately after application indicated that our sampling results differed significantly from the calculated application rate. Mean residue levels for metaldehyde and methiocarb ranged from 4 to 123 mg/sq m and none detected to 224 mg/sq m, respectively. Since residue levels measured immediately after treatment were not above expected levels, recommendations for future monitoring programs included: measurement of each treatment site (sq. m); documentation of the amount of pesticide applied to each site (mg); and deletion of chemical analysis of soil samples.

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Thank you to all EHAP field crew members who helped conduct this study. The white garden snail suppression crew in San Diego made our task much easier by their assistance, especially Brian Taylor. Additionally, thanks to Sally Powell and Linda Heath who produced our graphics. Finally, we appreciated all of the comments submitted by our reviewers.

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PART 1. SPRING 1987 WHITE GARDEN SNAIL MONITORING PROGRAM

INTRODUCTION

The white garden snail (Theba pisana Muller) is believed to have originated in the coastal areas of the Mediterranean (Baker, 1986) and has invaded California on three separate occasions. Two infestations were successfully eradicated before 1970 and a third occurrence was discovered in 1985 in San Diego County. The potential threat to agriculture and ornamental vegetation posed by the white garden snail (WGS) prompted the California Department of Food and Agriculture (CDFA) to search for control or suppression methods. A Science Advisory Panel was formed, an Environmental Impact Report (EIR) was prepared (CDFA et al., 1987), and public comments of the draft EIR were received at meetings held in potential treatment areas. Accordingly, CDFA developed and implemented a suppression program in early 1987. The program was designed to suppress adult, newly hatched, and immature snails by treating in both fall (before mating) and spring (before aestivation).

CDFA's Environmental Hazard Assessment Program (EHAP) was requested by the Plant Industry Division of CDFA to conduct a white garden snail monitoring program beginning in March, 1987. Objectives of the monitoring program were twofold: To assess metaldehyde and methiocarb residue concentrations in soils, home garden vegetables and rain runoff during and after treatment, and to determine soil dissipation profiles.

MATERIALS AND METHODS

Treatment Materials and Methods

Metaldehyde and methiocarb have been used in the past for snail control in California. Metaldehyde Methiocarb Granules 2-1 (active ingredients: 2 percent metaldehyde and 1 percent methiocarb), manufactured by Amvac Chemical Corporation, was applied to residential yards and experimental plots using a hand-operated granule spreader at a rate of 48.8 kg/ha (1 lb/1000 sq ft). Deadline® Paste (active ingredient: 4 percent metaldehyde), manufactured by Pace National Corporation, was applied near individual home vegetable garden plants as a paste extruded from a tube in 2 cm long segments. Residential treatments occurred at tri-weekly intervals for nine weeks (March 17 through May 19, 1987).

Treatment Areas

Six different locations in San Diego County encompassing 55 ha (135 acres) and 216 residences were treated using 4763 kg (10,500 lb) of product (Figure 1.1). Treatment boundaries of each area included buffer zones which extended beyond each known infestation. All residents within treatment areas received information on the WGS infestation and CDFA suppression program prior to each treatment.

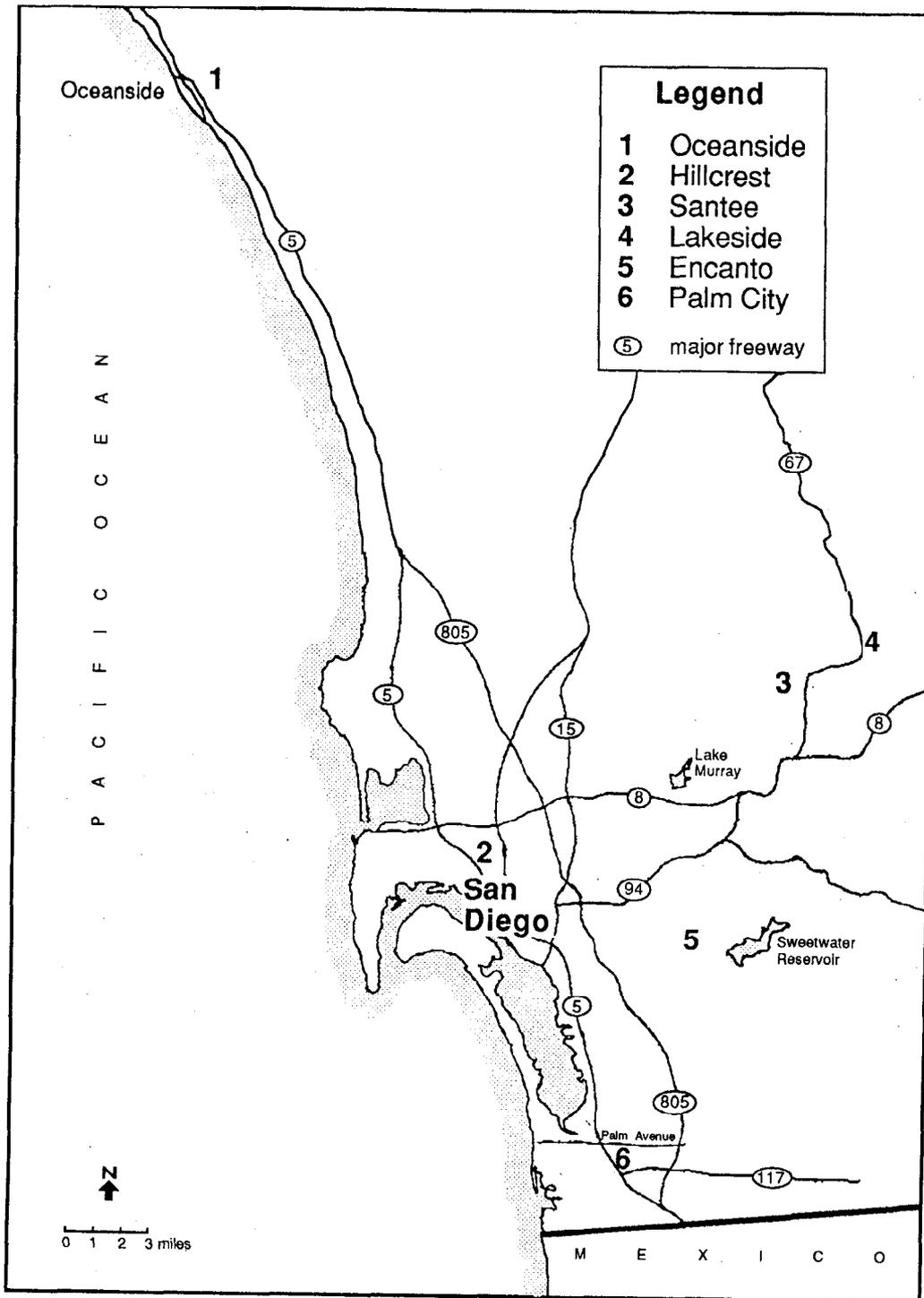


Figure 1.1. White Garden Snail Treatment Areas, Spring 1987

Study Design

During the nine week treatment period, pesticide applications occurred at tri-weekly intervals at Hillcrest and Lakeside treatment areas. The remaining four treatment areas had one or two applications during the study period. Two residences were selected for monitoring (one each from Hillcrest and Lakeside) and two replicate soil samples were collected at weekly intervals at each residence.

Experimental sites adjacent to residential sites were treated once at the beginning of the monitoring program to determine pesticide dissipation rates in soil. Two replicate soil samples were collected randomly on -1, 0, 1, 2, 3, 6, 10, 14, and 20 days after treatment from each 2 m x 10 m grass-covered plot.

Vegetable garden samples from two residences in Palm City were collected and analyzed for metaldehyde residues approximately two weeks after the gardens were treated.

No storm runoff was observed during the monitoring period and, therefore, no runoff samples were collected.

Background soil samples were collected from each residential and experimental site before treatment began. Chain of custody records were completed for all samples documenting activities from sample generation through chemical analysis.

Sampling Methods

Soils -- Soil samples consisted of 40-50 subsample soil cores randomly collected along diagonal transects within treated areas of each residential site; at experimental sites, 50 subsample cores per sample were collected randomly throughout the entire plot. A 1.9 cm diameter Oakfield® sampler was used to extract 4 cm soil plugs for each subsample. Samples were stored in one-quart glass jars with foil-lined lids and transported in ice chests (-70°C) to the Los Angeles County Environmental Toxicology Laboratory for analysis.

Vegetation -- Leaf samples were clipped from yam vines and lettuce plants, and whole onions were collected and stored in one quart glass jars with foil-lined lids on dry ice until analysis. When sufficient vegetation was available, two replicates were collected.

Statistical Methods

Soil concentrations of metaldehyde and methiocarb were reported in parts per million on a dry weight basis (ppm). Additionally, the data were standardized for soil mass and reported in milligrams per square meter (mg/sq m). Samples for which concentrations were not measureable (below the minimum detectable limit), were assigned the value of zero prior to summarization of means.

Residential Sites -- The analysis of variance model applied to the residential data for each application included the following factors:

Analysis of Variance

<u>Source of Variation</u>	<u>Degrees of Freedom</u>	<u>F-test</u>
Site	1	MS_S/MS_{Error}
Replication(Site)	2	-----
Days Post Application	2	MS_D/MS_{Error}
Site * Days Post	2	MS_{SxD}/MS_{Error}
Error	2	-----
<hr/>		
Corrected Total	7	

The monitoring schedule called for sampling on days 0, 7 and 14 following each of the three applications. In order to present a more coherent analysis and avoid the statistical ambiguity subsequent to interpreting results from analyses with differential response patterns for each application, the primary analyses focused on analysis for each application individually.

The main effects of site and days post application were analyzed only if they were not involved in a statistically significant interaction (such as an observed increase in soil residue levels on day 7 at one site while average soil residue levels decreased following application at the other site). The factor or sampling points responsible for the differential response patterns were examined separately.

All analyses were performed using Type III Sums of Squares in the General Linear Models procedures of the SAS system Version 5. 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 ($0.05 < P < 0.10$).

Experimental Sites -- Samples collected at the experimental sites were analyzed by linear regression techniques using days since application as the independent variable and with the same general analysis of variance model as the residential data. The sampling schedule for the experimental sites called for sampling on days 0, 1, 2, 3, 6, 10, 14 and 20 post application. All pairwise comparisons among days were carried out using Fisher's Protected Least Significant Difference t-tests only if the overall F-test for days was significant ($P < 0.05$). Further, the planned comparison of initial (Day 0) versus final (Day 20) soil residue means was performed using the mean square residual term from the overall model.

Analytical Methods

CDFAs Chemistry Lab Services, Sacramento CA, developed methods for metaldehyde analysis. The County of Los Angeles, Environmental Toxicology Laboratory, Downey, CA, conducted primary chemical analysis for both metaldehyde and methiocarb. Soil samples were analyzed for metaldehyde, methiocarb, methiocarb sulfoxide and methiocarb sulfone. Vegetation samples were analyzed for total residues of metaldehyde. Extraction procedures and operating conditions for both gas chromatography (GC) and high pressure liquid chromatography (HPLC) are included in Appendix I. Metaldehyde was quantified on a GC-thermionic-specific detector (GC-TSD) using a DB-5 column and confirmed using a DB-17 column. Methiocarb and its metabolites were

quantified on the HPLC with a fluorescence detector and confirmed on the GC-TSD using a DB-17 column.

Quality Control Procedures

Four soil samples were randomly selected and prepared as interlaboratory control samples. Samples were split and analyzed by both CDFA and Los Angeles County laboratories. For continuous quality control during analysis, a blank matrix and blank matrix spike were analyzed with each extraction set (Appendix I, Tables I-4 through I-7).

RESULTS AND DISCUSSION

Residential Sites

Results from the chemical analysis of the soil residues for metaldehyde and methiocarb from the residential monitoring sites are presented in Table 1.1 as well as in Figures 1.2 through 1.3. No detectable residues were found in the soil at either sampling site prior to the first pesticide application.

Following application, soil residue levels of metaldehyde ranged from 5 to 263 mg/sq m at the Hillcrest site while the corresponding range in methiocarb residues was from none-detected to 193 mg/sq m at Lakeside.

Due to significant two-factor interactions between application number and site for all four dependent variables, the statistical analyses for the residential data focused on each application individually. Further, within each application, the additional variability resulting from inclusion of the Day 7 residue levels yielded significant site by day interactions. For this reason, the analyses discussed below concentrate on Day 0 versus Day 14 residue levels within each application. (Appendix II, Tables II-1A to II-6B).

With respect to the first application, methiocarb and metaldehyde residues decreased substantially for the Lakeside site while residue levels changed only slightly for the Hillcrest site. For example, methiocarb residues decreased from 228 mg/sq m on Day 0 to 46 mg/sq m on Day 14 at the Lakeside site while the corresponding decrease at Hillcrest was from 60 to 58 mg/sq m

Table 1.1. Metaldehyde and Methiocarb Soil Residues (mg/sq m) at Hillcrest and Lakeside Residences, White Garden Snail Monitoring Program, Spring 1987

Application	Days Post Application	Rep. No.	Metaldehyde (mg/sq m)	Mean	Methiocarb (mg/sq m)	Mean	
<u>Hillcrest</u>	0	1	28.6		63.0		
		2	17.4	23.0	57.2	60.1	
	1	7	5.4		ND*		
		2	26.1	15.8	15.7	7.9	
	14	1	32.1		95.6		
		2	7.2	19.7	20.6	58.1	
	2	0	1	263.1		181.9	
			2	67.2	165.2	101.1	141.5
		7	1	76.7		285.5	
			2	51.4	64.1	103.0	194.3
		14	1	25.6		47.6	
			2	85.7	55.7	125.4	86.5
3	0	1	74.3		140.2		
		2	88.8	81.6	288.7	214.5	
	7	1	36.1		113.1		
		2	50.3	43.2	137.8	125.5	
	14	1	5.0		78.8		
		2	6.9	6.0	183.1	131.0	
<u>Lakeside</u>	0	1	192.9		214.4		
		2	102.6	147.9	242.2	228.3	
	1	7	21.0		231.2		
		2	10.9	16.0	174.6	202.9	
	14	1	7.7		64.5		
		2	10.4	9.1	27.4	46.0	
	2	0	1	76.7		145.0	
			2	55.4	66.1	110.7	127.8
		7	1	8.3		118.7	
			2	2.4	5.4	47.0	82.9
		14	1	ND		50.9	
			2	12.1	6.1	82.9	66.9
	3	0	1	66.9		133.0	
			2	30.7	48.8	88.8	110.9
		7	1	ND		105.1	
			2	ND	ND	53.0	79.1
		14	1	23.7		33.3	
			2	ND	11.9	65.1	49.2

*ND = Not detected; minimum detection level = 0.05 and 0.5 ppm for metaldehyde and methiocarb, respectively before transformation to mg/sq m.

Table 1.1 Continued Next Page

Table 1.1 (cont.) Metaldehyde and Methiocarb Soil Residues (ppm dry wt. basis) at Hillcrest and Lakeside Residences, White Garden Snail Monitoring Program, Spring 1987

Application	Days Post Application	Rep. No.	Metaldehyde (ppm, dry)	Mean	Methiocarb (ppm, dry)	Mean	
<u>Hillcrest</u>	0	1	1.34		2.94		
		2	0.87	1.10	2.84	2.89	
	1	7	1	0.25		ND*	
			2	0.97	0.61	0.58	0.29
		14	1	1.70		5.06	
			2	0.47	1.08	1.33	3.20
	2	0	1	13.62		9.41	
			2	3.17	8.39	4.77	7.09
		7	1	4.51		16.80	
			2	3.05	3.78	6.11	11.96
		14	1	1.19		2.21	
			2	3.95	2.57	5.78	4.00
3	0	1	3.67		6.93		
		2	2.92	3.30	9.50	8.22	
	7	1	1.75		5.47		
		2	2.66	2.20	7.28	6.37	
	14	1	0.22		3.49		
		2	0.31	0.26	8.15	5.82	
<u>Lakeside</u>	0	1	5.83		6.48		
		2	2.65	4.24	6.25	6.37	
	1	7	1	0.66		7.22	
			2	0.33	0.50	5.25	6.23
		14	1	0.27		2.26	
			2	0.36	0.31	0.94	1.60
	2	0	1	2.30		4.35	
			2	1.59	1.94	3.18	3.76
		7	1	0.25		3.58	
			2	0.07	0.16	1.37	2.47
		14	1	ND		1.39	
			2	0.25	0.13	1.72	1.55
	3	0	1	2.23		4.44	
			2	1.02	1.62	2.94	3.69
		7	1	ND		2.59	
			2	ND	ND	1.20	1.89
		14	1	0.64		0.90	
			2	ND	0.32	1.49	1.20

*ND = Not detected; minimum detection level = 0.05 and 0.5 ppm for metaldehyde and methiocarb, respectively.

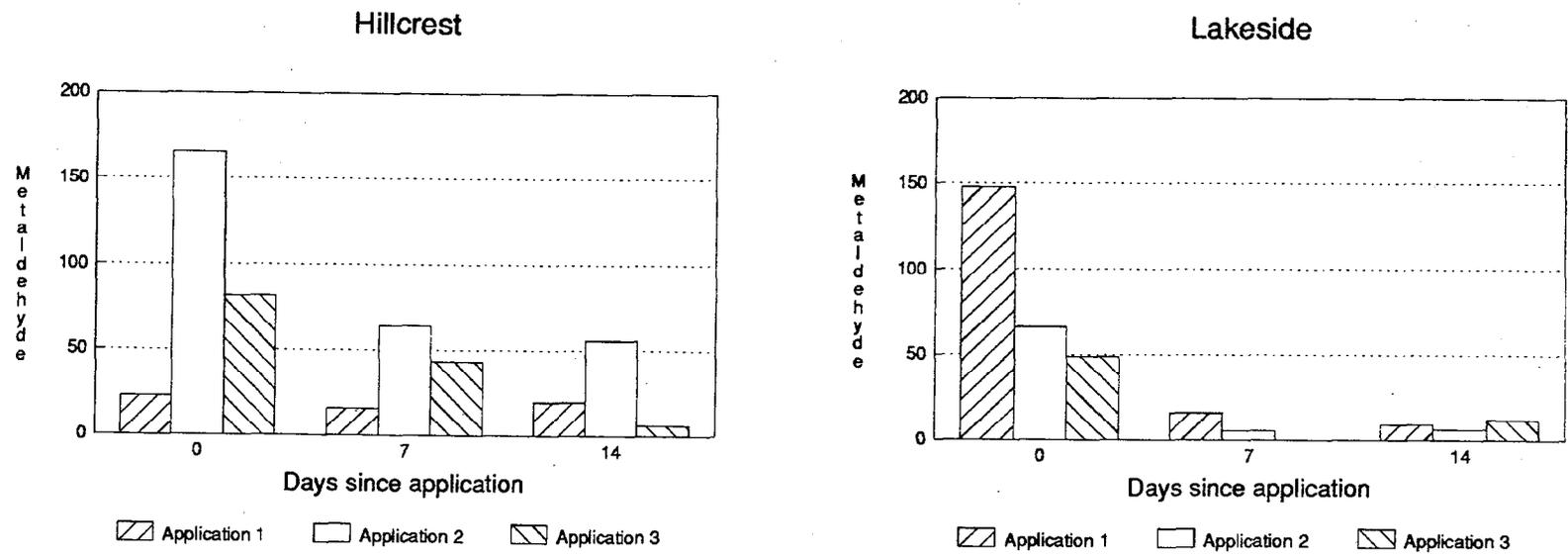


Figure 1.2: Mean Metaldehyde Residues (mg/sq m) in Residential Soil Samples, White Garden Snail Monitoring Program, Spring 1987
(no bar denotes no detectable metaldehyde residues)

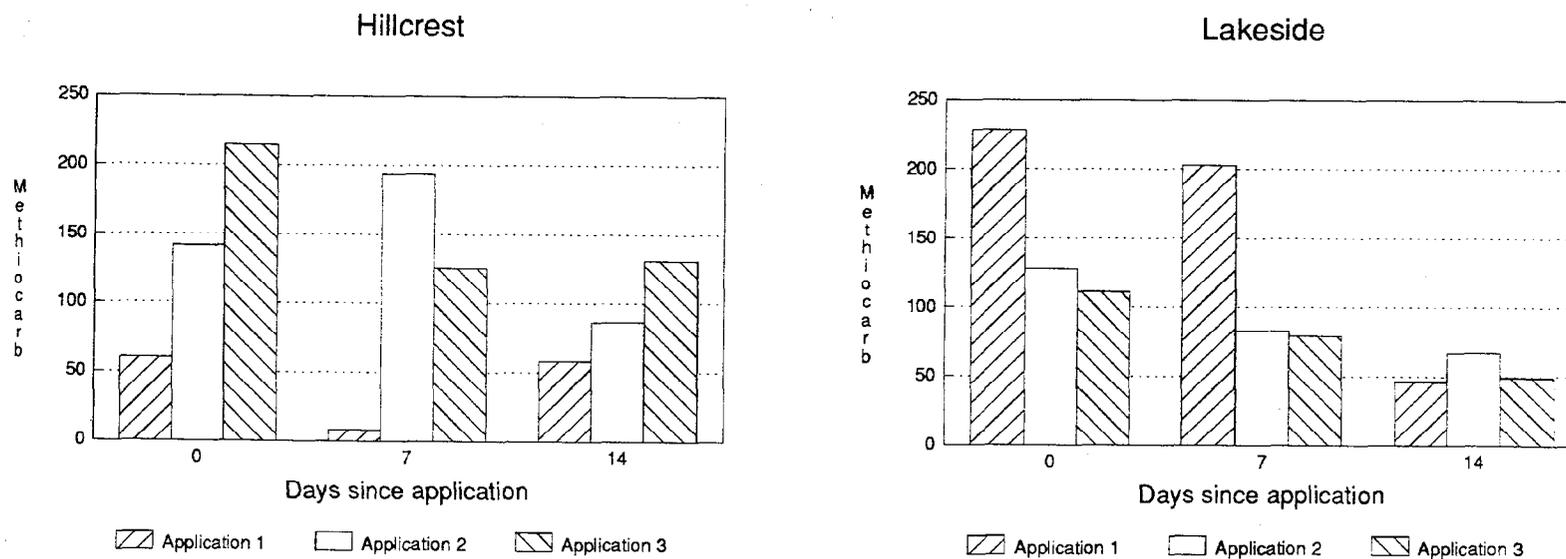


Figure 1.3: Mean Methiocarb Residues (mg/sq m)
in Residential Soil Samples, White Garden Snail
Monitoring Program, Spring 1987

(Table 1.1). These differential rates of change precluded any formal statistical comparisons between Day 0 and Day 14 values across sites.

Within the second application, methiocarb residues were significantly less at the Lakeside versus the Hillcrest site ($P < 0.03$, Appendix II, Tables II-3A through II-4B). Similar trends for metaldehyde were not statistically significant. Examining both sites, methiocarb residues declined from 119 to 97 mg/sq m on Day 0 to Day 14, respectively. An overall metaldehyde residue mean of 116 mg/sq m on Day 0 compared with 31 mg/sq m on Day 14 was observed. The decreases in residue levels from Day 0 to Day 14 were not statistically significant.

Comparison of the two monitoring sites for the third application showed that initial residue levels were approximately twice as high at Hillcrest as compared with Lakeside. However, statistical analyses of methiocarb within the third application did not reveal any significant site differences but the difference between Day 0 and Day 14 was marginally significant (Appendix II, Tables II-5A and II-5B). Averaging over both sites, methiocarb residues decreased from 163 to 90 mg/sq m on Day 0 to Day 14, respectively ($0.05 < P < 0.10$). Due to a significant site by days post application interaction ($P = 0.05$), dissipation of metaldehyde residues from Day 0 to Day 14 were compared within each of the two sites separately. Metaldehyde residues declined from 82 mg/sq m on Day 0 to 6 mg/sq m on Day 14 at Hillcrest while Lakeside metaldehyde residues decreased from 49 to 12 mg/sq m. Both these decreases were statistically significant ($P < 0.01$ and $P < 0.03$, respectively, Appendix II, Tables II-6A and II-6B).

Although many significant interactions were discovered during the course of these analyses, it is difficult to discern whether they may be attributed to a true underlying state. It is more likely that they exist as artifacts of the large degree of variation inherent in data arising from sampling too few within site replicates for a granular pesticide application.

Experimental Sites

Results from the chemical analysis of soil residues for metaldehyde and methiocarb are presented in Table 1.2 and in Figures 1.4 and 1.5. No detectable residues were found in the soil at either site prior to the first pesticide application.

Post-treatment, metaldehyde soil residues levels at the Hillcrest experimental site ranged from 23.7 to 98.8 mg/sq m while the corresponding metaldehyde range for the Lakeside site was 65.0 to 93.4 m/sq m. No site differences were noted for the metaldehyde data with estimates of 10 to 11 days for half of the applied material to dissipate (Appendix II, Tables II-7A, 7B and II-9). Comparison of initial (Day 0) and final (Day 20) residue levels demonstrated significant decreases for metaldehyde residues measured in mg/sq m and ppm ($P < 0.05$). The linear regression model applied to the metaldehyde data (measured in mg/sq m) from which dissipation estimates were derived showed that days since application accounted for approximately 64 to 68 percent of the variation in residue levels.

Post-treatment, methiocarb residues, expressed in mg/sq m, ranged from none-detected to 135.7 mg/sq m at Hillcrest and from 14.2 to 303.3 mg/sq m

Table 1.2. Metaldehyde and Methiocarb Soil Residues (mg/sq m) at Hillcrest and Lakeside Experimental Plots, White Garden Snail Monitoring Program, Spring 1987

Site	Days Post Application	Rep. No.	Metaldehyde (mg/sq m)	Mean	Methiocarb (mg/sq m)	Mean
<u>Hillcrest</u>	0	1	23.7		51.4	
		2	98.8	61.3	26.1	38.8
	1	1	34.8		110.0	
		2	48.1	41.5	29.1	69.5
	2	1	4.6		31.5	
		2	83.6	44.1	104.0	67.8
	3	1	11.0		32.4	
		2	67.8	39.4	30.5	31.5
	6	1	38.7		113.9	
		2	31.4	35.0	24.4	69.1
	10	1	14.7		73.6	
		2	75.5	45.1	ND*	36.8
	14	1	1.7		101.8	
		2	1.7	1.7	70.9	86.3
20	1	2.7		135.7		
	2	21.8	12.2	62.4	99.1	
<u>Lakeside</u>	0	1	65.0		27.2	
		2	93.4	79.2	303.3	165.3
	1	1	132.5		82.6	
		2	68.2	100.3	38.6	60.6
	2	1	95.4		28.3	
		2	91.7	93.6	178.1	103.2
	3	1	206.4		29.0	
		2	35.4	120.8	87.9	58.4
	6	1	18.5		226.3	
		2	22.9	20.7	31.0	128.6
	10	1	23.1		66.9	
		2	34.3	28.7	42.6	54.8
	14	1	20.9		89.4	
		2	33.0	27.0	74.5	82.0
20	1	16.6		14.2		
	2	7.6	12.1	92.5	53.4	

*ND = Not detected; minimum detection level = 0.05 and 0.5 ppm for metaldehyde and methiocarb, respectively, before transformation to mg/sq m.

Table 1.2 Continued Next Page

Table 1.2 (cont.) Metaldehyde and Methiocarb Soil Residues at Hillcrest and Lakeside Experimental Plots (ppm, dry wt. basis), White Garden Snail Monitoring Program, Spring 1987

Site	Days Post Application	Rep. No.	Metaldehyde (ppm, dry)	Mean	Methiocarb (ppm, dry)	Mean
<u>Hillcrest</u>	0	1	0.81		1.76	
		2	3.11	1.96	0.82	1.29
	1	1	1.28		4.04	
		2	1.66	1.47	1.00	2.52
	2	1	0.17		1.13	
		2	2.85	1.51	3.54	2.34
	3	1	0.43		1.26	
		2	2.39	1.41	1.08	1.17
	6	1	1.12		3.30	
		2	1.02	1.07	0.79	2.05
	10	1	0.44		2.21	
		2	2.95	1.70	ND	1.11
	14	1	0.06		3.57	
		2	0.06	0.06	2.51	3.04
	20	1	0.08		4.27	
		2	0.72	0.40	2.05	3.16
<u>Lakeside</u>	0	1	1.86		0.78	
		2	2.72	2.29	8.83	4.81
	1	1	4.07		2.54	
		2	1.84	2.95	1.04	1.79
	2	1	2.93		0.87	
		2	2.81	2.87	5.47	3.17
	3	1	6.55		0.92	
		2	1.49	4.02	3.71	2.32
	6	1	0.56		6.91	
		2	0.67	0.62	0.90	3.91
	10	1	0.85		2.46	
		2	1.09	0.97	1.36	1.91
	14	1	0.67		2.87	
		2	1.01	0.84	2.28	2.57
	20	1	0.49		0.42	
		2	0.19	0.34	2.33	1.38

ND = Not detected; minimum detection level = 0.05 and 0.5 ppm for metaldehyde and methiocarb, respectively.

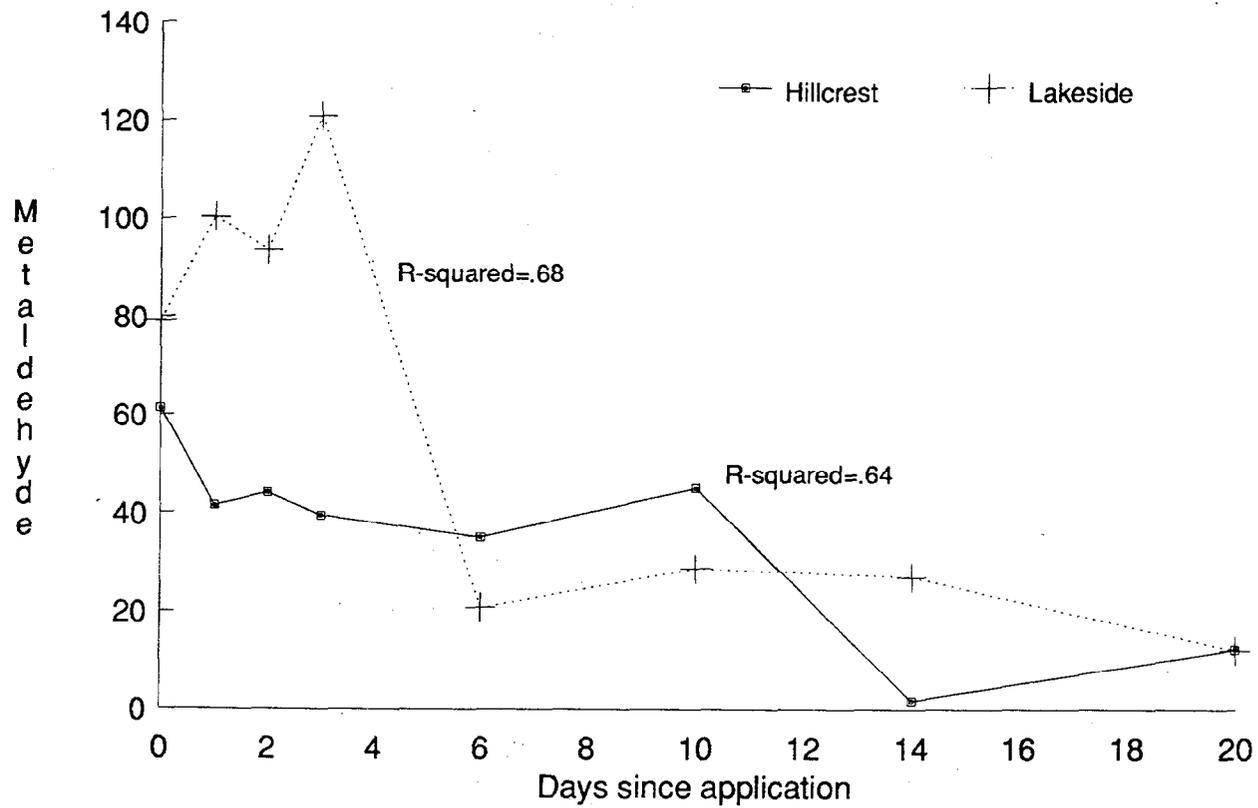


Figure 1.4: Mean Metaldehyde Residues in Soil Samples (mg/sq m) at Two Experimental Sites, White Garden Snail Monitoring Program, Spring 1987

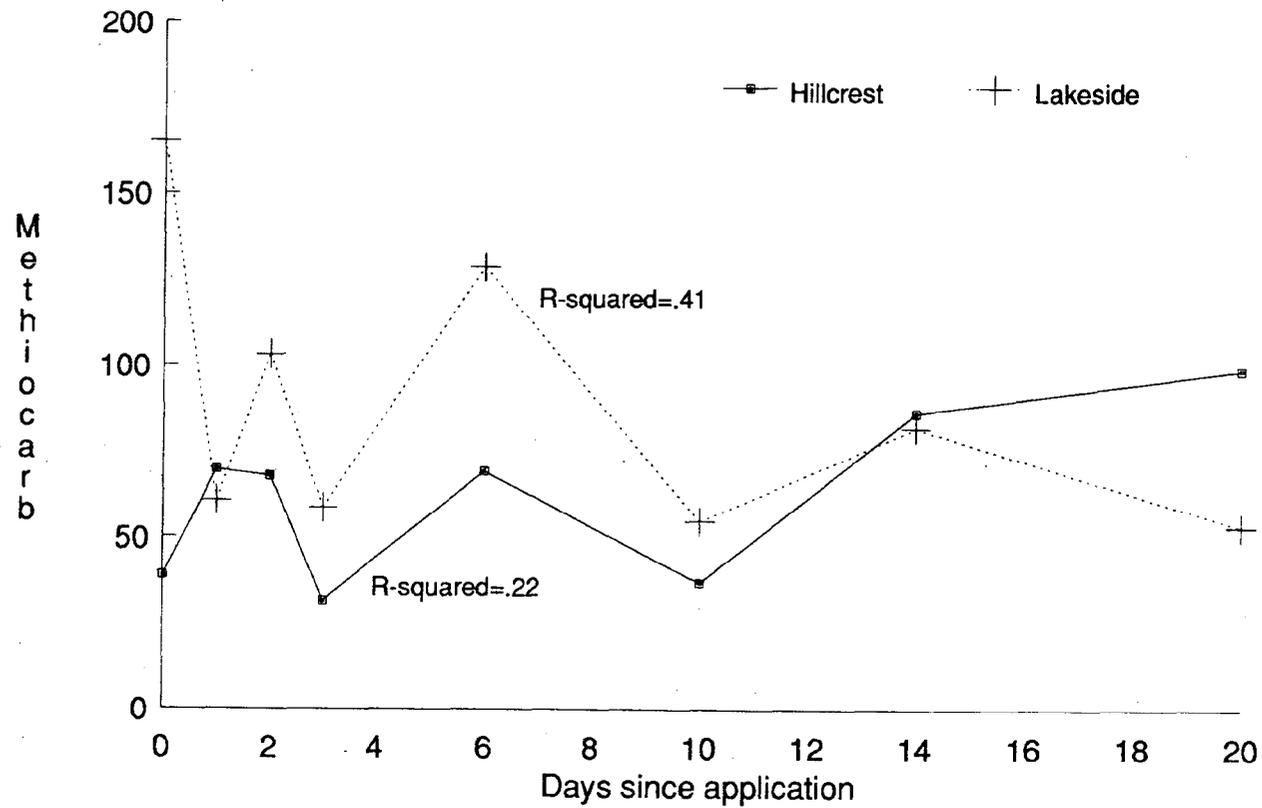


Figure 1.5: Mean Methiocarb Residues in Soil Samples (mg/sq m) at Two Experimental Sites, White Garden Snail Monitoring Program, Spring 1987

at Lakeside. No clear difference between the two experimental sites was observed, however, the large degree of variability among the samples at Lakeside may have masked any underlying trends. Further, regression analyses for this latter site did not show any significant degradation with respect to the analysis of the metaldehyde experimental data ($R^2 = 0.22$, Appendix II, Table II-9). Regression analyses performed on samples collected at the Hillcrest site demonstrated increasing rather than decreasing tendencies for methiocarb over the monitoring period.

Vegetation

No detectable levels of metaldehyde were found in vegetation samples collected from residential gardens during the monitoring program. It appears that Deadline® Paste applied to garden soil was not translocated into above ground (edible) plant tissue.

Metabolites

Methiocarb sulfone was not detected (MDL = 0.5 ppm) in soil throughout the study period. Methiocarb sulfoxide appeared in Hillcrest residential soil approximately 4 weeks after the first application. The amount detected ranged from 0.63 to 0.86 ppm (MDL = 0.5 ppm).

Application Rates

Estimated application rates were calculated by dividing the number of pounds of each active ingredient used per application by the estimated number of acres treated. The rates were then converted from pounds per acre to milligrams per square meter. Comparison of estimated application rates in Table 1.3 with the allowable label application rate of 97.8 and 48.9 mg/sq m for metaldehyde and methiocarb, respectively, shows that 7 out of 11 applications exceeded allowable limits. In addition, while analytical results were highly variable, mean concentrations for methiocarb were consistently higher than estimated application rates.

Quality Control

Continuing quality control spikes of soil samples with 0.5 ppm metaldehyde and methiocarb showed average recovery percentages and standard deviations of 89% and ± 7.0 , and 86% and ± 7.5 , respectively (Appendix I, Tables I-4 and I-5).

Metaldehyde split sample analysis was not completed by the CDFA laboratory due to equipment malfunction. The results of the methiocarb split sample analysis (Appendix I, Table I-8) showed a range of variation between labs of 10 to 77 percent. Part of this may have been due to the difference in detection levels for the laboratories (0.04 ppm for CDFA, and 0.5 ppm for LA County).

Table 1.3 Estimated Application Rates (mg/sq m) for Residential Treatment Areas, White Garden Snail Monitoring Program, Spring 1987

Treatment Area	Application No.	Estimated Application Rate	
		Metaldehyde	Methiocarb
Encanto	1	122	66
Hillcrest	1	99	49
	2	116	58
	3	130	65
Lakeside	1	76	38
	2	134	67
	3	121	60
Oceanside	1	85	42
Palm City	1	83	41
	2	88	44
Santee	1	151	75

The allowable label rate is 97.8 and 48.9 mg/sq m for metaldehyde and methiocarb, respectively.

RECOMMENDATIONS

The variability exhibited in the residue levels found in soil samples collected during the 1987 spring WGS monitoring program lead to several recommendations for future monitoring programs:

1. Increase number of sites to be monitored.
2. Increase number of replicates collected at each site.
3. Calibrate application methods to ensure correct application rates.
4. Measure area (sq m) of treated properties and amount of pesticide applied at each site to ensure that sampling methods are producing results that accurately estimate the actual application rates.

PART 2. FALL 1987 WHITE GARDEN SNAIL MONITORING PROGRAM

INTRODUCTION

The white garden snail poses a serious threat to California agriculture if allowed to become permanently established. CDFA's suppression program was designed to take advantage of the snail's behavior by treatments occurring both in spring and fall (prior to aestivation and mating, respectively). The fall 1987 white garden snail monitoring program was designed after meeting and discussing the spring 1987 monitoring results with CDFA Plant Industry personnel. EHAP's primary objective for the fall season was to monitor pesticide application rates in all treatment areas in order to ensure applications were within allowable label rates. Quantification of pesticide residues in soils immediately after application was required to determine whether sampling methods were adequate to estimate calculated pesticide application rates.

The fall suppression program treated six areas in San Diego County using Metaldehyde-Methiocarb Granules 2-1 (Table 2.1). Oceanside was deleted from fall monitoring while Lemon Grove was added due to a new infestation discovered in the area. The Santee spring treatment location name was changed to Carleton Hills for fall (Figure 2.1). Treatment began during the last week of September and continued through the latter part of November, 1987.

Table 2.1. Treatment Information for White Garden Snail Monitoring Program, Fall 1987

Location	Application		Pounds Product Applied	Number of Residences Treated	Number of Residences Sampled
	No.	Date			
Hillcrest	1	10/14	55	24	2
Carleton Hills	1	11/17	32	16	2
Encanto	1	10/15-11/4	1521	145	15
	2	11/4-11/25	1740	145	0
Lakeside	1	9/29	185	5	0
	2	10/20	285	5	1
	3	11/9	290	5	0
Lemon Grove	1	10/2	94	19	1
	2	10/23-10/26	82	19	1
	3	11/13	91	19	1
Palm City	1	9/30-10/1	51	44	1
	2	10/21-10/22	50	44	1
	3	11/10-11/12	<u>62</u>	<u>44</u>	<u>1</u>
TOTAL:			4538	534	26

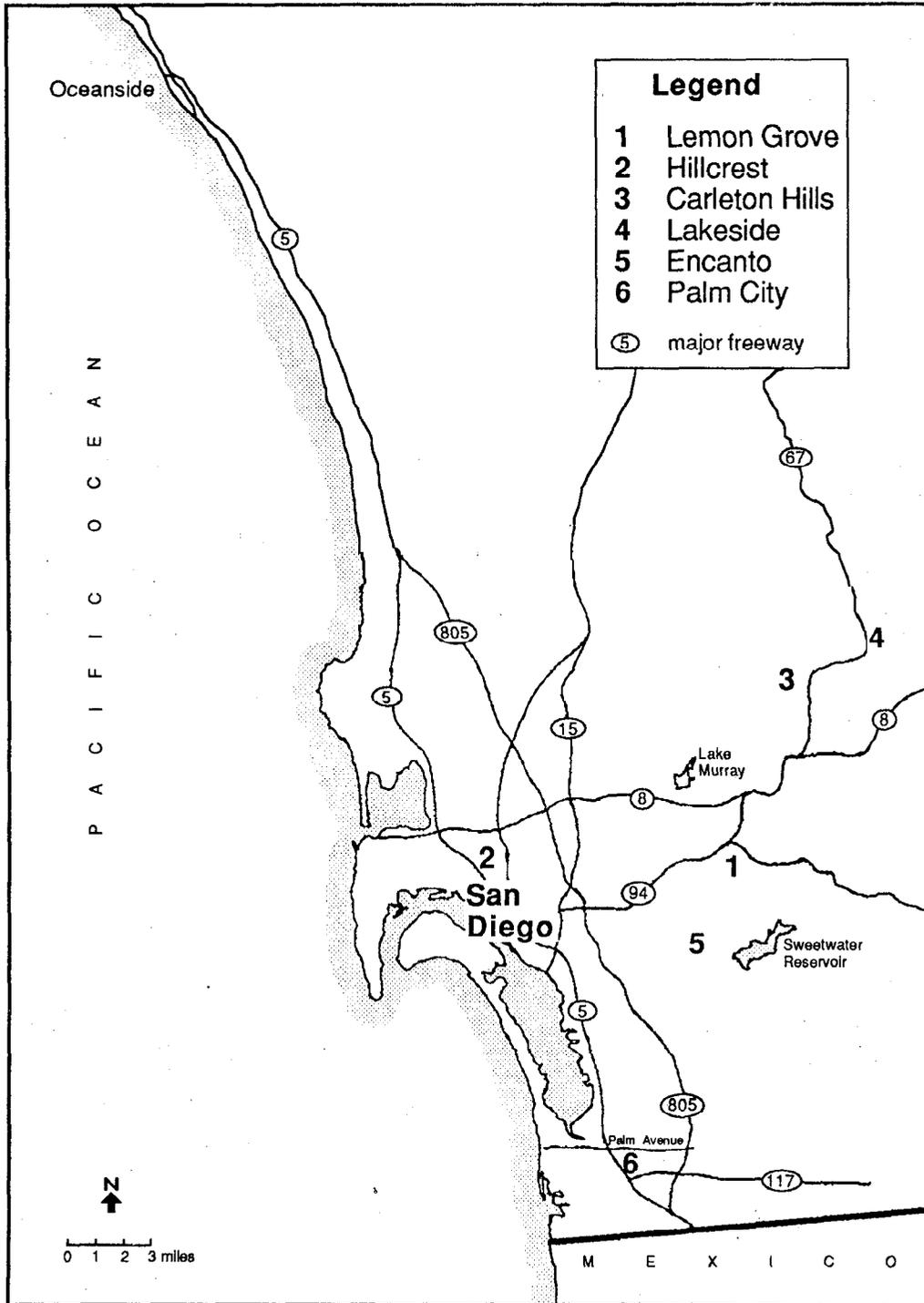


Figure 2.1. White Garden Snail Treatment Areas, Fall 1987

MATERIALS AND METHODS

Treatment Materials and Methods

Just as for the spring suppression program, Metaldehyde Methiocarb Granules 2-1 were applied to all residential sites and an experimental plot; Deadline® Paste was used for home garden vegetables. The same procedures were used to apply the pesticide at a rate of 48.8 kg/ha (1 lb/1000 sq ft).

Treatment Areas

Six locations including 253 residences were treated during the fall program. A total of 2058 kg (4538 lb) of product was applied. Treatment boundaries of each area included buffer zones extending beyond the known infestation of WGS.

Study Design

Three pesticide applications occurred at tri-weekly intervals at Lakeside, Lemon Grove, and Palm City residential treatment locations. Encanto received two applications while Hillcrest and Carleton Hills received one. Approximately 10 percent of the residences receiving pesticide applications were sampled during the eradication program. Four replicate soil samples were collected per residential sampling site within 48 hours after pesticide application.

Immediately following pesticide application to an experimental plot (3 x 12 m), six replicate soil samples were randomly collected in order to evaluate data variability due to sampling methods.

Background soil samples were collected from three treatment areas (Lakeside, Lemon Grove, and Hillcrest) to determine pre-existing levels of metaldehyde and methiocarb. Two replicates were collected from each of three residences. No home garden vegetable samples were collected during this monitoring program. Rain runoff samples were collected from a surface depression and ditch running through a treated vacant lot on November 5, 1987 in the Encanto area.

Chain of custody records were completed for all samples documenting activities from sample generation to chemical analysis.

Sampling Methods

Soils -- Soil samples consisted of 25 subsample soil cores randomly collected along "W"-shaped transects within treated areas of each residential sampling site (usually within a homogeneous vegetation type). The number of subsample cores was reduced from 50 (spring program) to 25 subsamples because the number of replicates per site had been increased and it was felt that 25 subcores per replicate should be sufficient to characterize the site. Similarly, the experimental plot soil samples also consisted of 25 subcores. A 1.9 cm diameter Oakfield® sampler was used to

collect 4 cm soil cores for each subsample. Samples were stored in one-quart glass jars with foil-lined lids at -70°C until transported to the laboratory for analysis.

Runoff -- Water samples were collected using a hand-operated vacuum pump and Teflon[®] tubing. Samples were stored in 1-liter amber glass jars on wet ice (4°C) until transported to the laboratory for analysis.

Application Rates -- All treated areas at each property were measured using measuring tapes (sq m) and the amount of pesticide applied to this area was quantified (mg) in order to calculate application rates.

Statistical Methods

The pesticide concentration for the j^{th} replicate from the i^{th} site may be described using the following linear expression:

$Y_{ij} = \mu + S_i + e_{ij}$ where μ represents an overall mean, $\mu + S_i$ is the mean of the i^{th} site and e_{ij} represents error of measurements associated with a random replicate from the i^{th} site. Errors of measurement include all unknown sources of variability including such factors as soil sampling, storage and laboratory analyses.

With respect to this subsampling plan, the primary objective of the statistical analysis was to construct confidence intervals for the mean

pesticide concentration at each site. This required estimating the variance components σ^2 and σ_s^2 . The analysis of variance table is given below.

<u>Source of Variation</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>Parameters Estimated</u>
Among sites	26-1	MS _{site}	$\sigma_e^2 + 4\sigma_s^2$
Replication (Site)	26(4-1)	MS _{error}	σ_e^2
Corrected total	104-1		

The component of variance for sites is estimated by $\hat{\sigma}_s^2 = ((\hat{\sigma}_e^2 + 4\hat{\sigma}_s^2) - \hat{\sigma}_e^2)/4$. The within site (among replicates) component of variance is estimated by, $\hat{\sigma}_e^2$, the mean square error for replication (site).

Ninety and ninety-five percent confidence intervals for each site were constructed using the t-distribution with three degrees of freedom. The standard error for a particular site was calculated using the pooled components of variance for the overall model.

Analytical Methods

The County of Los Angeles, Environmental Toxicology Laboratory, Downey CA, conducted primary chemical analysis for metaldehyde and methiocarb. Soil and water samples were analyzed for the two active ingredients only since their metabolites did not appear to be significant during the spring monitoring program. Extraction procedures and operating conditions for both

gas chromatography (GC) and high pressure liquid chromatography (HPLC) are included in Appendix I. The methods used were the same as for the spring monitoring program.

Quality Control Procedures

Twelve soil samples were randomly selected and prepared as interlaboratory control samples. Samples were split and were analyzed by CDFA and by L.A. County.

For continuous quality control during analysis, a blank matrix and blank matrix spike were analyzed with each extraction set (Tables I-13 through I-17, Appendix I) .

RESULTS AND DISCUSSION

Residential Monitoring

Tables 2.2 and 2.3 present mean metaldehyde and methiocarb concentrations (mg/sq m) as well as 90 percent confidence intervals for estimating the calculated application concentration from the sample mean. Post-application mean metaldehyde concentrations ranged from 3 mg/sq m to 123 mg/sq m while the corresponding range for methiocarb was from none-detected to 224 mg/sq m.

Examination of the metaldehyde data demonstrated that our mean estimates differed significantly ($P < 0.05$) from the calculated application rate fifteen percent (4/26) of the time and they were marginally different for thirty-five percent (9/26) of the sites ($P < 0.10$). With respect to methiocarb, our estimates of the calculated application rate were significantly greater than the calculated application rate for twelve percent (3/26) of the sites ($P < 0.05$).

The greatest proportion of the total variation is associated with the variability found within sites (between replicates) and not site to site variation as would be anticipated in the general analysis of variance setting (Appendix II, Tables II-10 through Table II-13). For example, the ratio of pure error or variability associated within site replication to the sum of both variance components (within and among sites) was 86 percent for metaldehyde (mg/sq m) and approximately 50 percent for methiocarb (mg/sq m). Future monitoring plans for similarly applied granular substances, if any,

Table 2.2. Application Rates, Mean Concentrations and Confidence Limits for Metaldehyde in Soil Samples, White Garden Snail Monitoring Program, Fall 1987

Location	Property No.	Calculated Application Rate Metaldehyde ^a (mg/sq m)	Mean Concentration Metaldehyde ^b (mg/sq m)	90 Percent Confidence Limits ^c	
				Lower ^c	Upper ^c
Lemon Grove	1	101	86	50	121
	8	81	15	0	51
	24	62	47	11	82
Lakeside	2	51	17	0	52
Palm City	3	84	40	4	75
	7	87	123	87	158
	23	61	6	0	42
Hillcrest	4	50	4	0	40
	5	32	38	2	73
Carleton Hills	25	48	26	0	61
	26	61	4	0	39
Encanto	6	35	28	0	64
	9	23	19	0	55
	10	39	22	0	57
	11	24	50	14	85
	12	25	7	0	43
	13	32	88	52	123
	14	58	18	0	53
	15	38	3	0	38
	16	48	8	0	43
	17	47	61	26	96
	18	66	27	0	63
	19	53	22	0	58
	20	45	11	0	47
21	38	8	0	44	
22	59	58	22	93	

^a Application rate computed from amount of active ingredient applied divided by the area treated.

^b Mean of four composite samples.

^c Mean of four replicates $\pm t_{\alpha/2}(3)$ x standard error of a particular site mean. Confidence limit values below zero were reported as zero.

Table 2.3. Application Rates, Mean Concentrations and Confidence Limits for Methiocarb in Soil Samples, White Garden Snail Monitoring Program, Fall, 1987

Location	Property No.	Calculated Application Rate Methiocarb ^a (mg/sq m)	Mean Concentration Methiocarb ^b (mg/sq m)	90 Percent Confidence Limits ^c	
				Lower	Upper
Lemon Grove	1	51	29	0	94
	8	42	22	0	88
	24	31	13	0	78
Lakeside	2	25	224	159	289
Palm City	3	42	59	0	124
	7	43	188	123	253
	23	31	25	0	90
Hillcrest	4	25	60	0	125
	5	16	33	0	98
Carleton Hills	25	24	8 ^d	0	73
	26	31	ND ^d	0	65
Encanto	6	18	10	0	75
	9	12	ND	0	65
	10	20	11	0	77
	11	12	107	42	172
	12	13	49	0	114
	13	16	30	0	96
	14	29	89	24	154
	15	19	11	0	77
	16	24	19	0	85
	17	24	39	0	104
	18	33	7	0	72
	19	27	15	0	80
	20	22	ND	0	65
21	19	9	0	74	
22	30	20	0	85	

^a Application rate computed from amount of active ingredient applied divided by the area treated.

^b Mean of four composite samples. When value is below minimum detection level, zeros were used to calculate the mean.

^c Mean of 4 reps $\pm t_{\alpha/2}(3)$ x standard error of a particular site mean. Confidence limit values below zero were reported as zero.

^d Not detected.

would be optimized (given a fixed cost) by reducing the number of sites and increasing the number of replicates within each site. Table 2.4 gives the results of the chemical analyses in ppm.

Runoff Results

The two water samples collected within the Encanto treatment area after rainfall show concentrations of both metaldehyde and methiocarb at the minimum detection level, 0.04 and 0.02 ppm, respectively. The runoff was confined to the local field in which it occurred and was finally absorbed there.

Application Rates

Pesticide applications were below allowable label application rates (98 mg/sq m for metaldehyde and 49 mg/sq m for methiocarb) at 25 of the 26 residences monitored. Property No. 1 in Lemon Grove exceeded the allowable rate during application by approximately 3 percent. The remaining residences ranged from 23 to 89 percent of the allowable label rate as determined by our measurements of product applied per property (mg/sq m). Comparison with the spring 1987 monitoring results shows a marked reduction in active ingredients applied during the fall monitoring program and increased compliance with label rate allowances.

Table 2.4. Mean Concentrations of Methiocarb and Metaldehyde in Soil Samples (ppm, dry weight basis) at 26 Residences during White Garden Snail Monitoring Program, Fall 1987

Location	Property No.	Mean Concentration ^a Metaldehyde (ppm)	Mean Concentration ^a Methiocarb (ppm)
Lemon Grove	1	2.34	0.78
	8	0.34	0.51
	24	1.30	0.37
Lakeside	2	0.37	4.76
Palm City	3	1.11	1.70
	7	2.71	4.23
	23	0.18	0.71
Hillcrest	4	0.13	1.97
	5	0.80	0.71
Carleton Hills	25	0.59	0.20
	26	0.11	ND ^b
Encanto	6	0.85	0.19
	9	0.44	ND
	10	0.40	0.20
	11	0.95	2.13
	12	0.14	0.98
	13	1.42	0.46
	14	0.35	1.70
	15	0.05	0.21
	16	0.17	0.40
	17	1.46	0.93
	18	0.65	0.16
	19	0.50	0.40
	20	0.24	ND
21	0.20	0.20	
22	1.28	0.44	

^aMean of four composite samples. When value is less than minimum detection level, zeros were used to calculate the mean.

^bNot detected. (Minimum detection limit: metaldehyde = 0.05 ppm; methiocarb = 0.5 ppm).

Quality Control

The mean percent recovery, SD and CV for metaldehyde and methiocarb continuing quality control spikes were 95%, 3.9 and 4.1, and 91%, 6.8 and 7.5, respectively (Tables I-12 and I-13).

Results for the 12 split soil samples of metaldehyde residues differed markedly between the two laboratories. Regression analyses with CDFA residues as the independent variable and LA lab residues as the dependent variable failed to determine an equation that would successfully predict LA residue results from identical analyses by CDFA ($R^2 = .07$). This trend continued even after the most typical split sample results showing none detected for CDFA and 1.92 ppm for LA were deleted.

CONCLUSIONS AND RECOMMENDATIONS

Fall 1987 monitoring results showed less variability than spring 1987 data. Increasing the number of replicates from two to four per site produced some reduction but, overall, our samples remained too variable to accurately reflect calculated application rates more than 65 percent of the time. The variability may be inherent in the physical nature of granular applications. Granules of different sizes may contain varying amounts of metaldehyde and methiocarb independently of each other; capture of any particular granule by our sampling method was random but did not ensure that either pesticide would be sampled proportionately. Also, the 4 to 5 grams of product applied per square meter by a manual spreader did not guarantee an even distribution of product. In addition, the variability in analytical results (quality control) between the two laboratories increased the difficulty of interpreting the data.

Since the metaldehyde and methiocarb residues in soil measured immediately after treatment were not above expected levels, it is recommended that future white garden snail monitoring programs forego additional chemical analysis of soil. To ensure that applications do not exceed label rates, site visits should be made to measure the treatment area and quantity of metaldehyde and methiocarb applied at residential sites .

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APPENDIX I

ANALYTICAL METHODS AND QUALITY CONTROL PROCEDURE RESULTS

CALIFORNIA DEPT. OF FOOD & AGRIC.
CHEMISTRY LABORATORY SERVICES
ENVIRONMENTAL MONITORING SECTION

Original Date:??
Supercedes: NEW
Current Date:12/21/87

3292 Meadowview Road
Sacramento, CA 95832
(916)+427-4998/4999

Method #:

Metaldehyde in Soils

SCOPE:

This method is for the extraction and the chromatographic analysis of metaldehyde in soils.

PRINCIPLE:

The metaldehyde is extracted from soil with benzene. The extract is treated with sodium metabisulfite to remove the acetaldehyde present in the soil and then cleaned up with florisil. The extract sample is then derivatized with 2-4 dinitrophenylhydrazine and analyzed by gas chromatography.

REAGENTS AND EQUIPMENT:

Tetrahydrofuran (99.5+% Spectrophotometric grade, Aldrich Chem.)
Acetaldehyde (99%, Aldrich Chem.)
Benzene (nanograde)
Hydrochloric acid, conc.
Sodium metabisulfite (Reagent grade)
2,4-dinitrophenylhydrazine (DNPH)(Moist solid with 30% water, Aldrich Chem.)
Florisil, non-activated (PR grade, 60/100 mesh, 6.7% moisture by weight)
Sodium sulfate
Mechanical rotating shaker
Brown jars with lids, 500 ml
Boiling flasks, 125 and 250 ml
Magnetic stirrer
Rotary Evaporator (Buchi-Brinkman, R110)
Test tubes, 15 ml graduate
Separatory funnels, 250 and 500 ml
Glass wool
Pasteur pipets, 9-inch disposable
Chromatographic columns, 10 cm x 2 cm
Drying oven, 105°C(for soils)
Aluminum weighing pans (for soils)

ANALYSIS:

Moisture:

1. Weigh 15-18g of soil into preweighed aluminum weighing pans.
2. Heat pan with soil for 16-24 hours at 105°C until a constant weight is obtained.

EXTRACTION:

1. Weigh 100 g of sample into a 500 ml brown screw top bottle. Add 200 ml of benzene, cap tightly with aluminum foil and screw top, and shake on mechanical rotating shaker for 30 minutes.
2. Decant the benzene through glass wool into a 500 ml separatory funnel.
3. Repeat the extraction of the remaining soil with two 100 ml portions of fresh benzene (total 400 ml), placing each benzene extract in the separatory funnel.
4. Extract the benzene with two portions, 10 ml each, of 2% sodium metabisulfite solution (made fresh daily). (If acetaldehyde analysis is required, save the bisulfite extracts.)
5. Wash the benzene layer with 10 ml water and filter through sodium sulfate into a 500 ml boiling flask.
6. Concentrate the solution to about 5 ml on a rotary evaporator (bath temp.=60°C).
7. Transfer the sample quantitatively to a 10cm x 2 cm chromatographic column containing 13 g florisil previously rinsed with 50 ml benzene.
8. Elute the column with 125 ml of 5% tetrahydrofuran in benzene into a 250 ml boiling flask.
9. Concentrate the eluate to 15 ml on a rotary evaporator (Bath temp=60°C).

Derivatization:**Reagent Preparation:**

1. Preparation of DNPH reagent--Dissolve 0.25 g of 2,4 dinitrophenylhydrazine in a solution of 50 ml water and 30 ml of concentrated HCl by warming on a water bath. Store at room temperature.
2. Preparation of the standard of acetaldehyde DNPH--Add two drops of acetaldehyde solution to 3 ml of DNPH reagent. Filter the precipitate, recrystallize from methanol to give an orange product (m.p. 168°C).

Procedure:

1. Add 15 ml DNPH reagent to the 15 ml benzene solution of metaldehyde in the boiling flasks.
2. Mix the two phases with a magnetic stirrer at room temperature for 20 min.
3. Transfer the mixture to a small separatory funnel, rinsing the reaction flask with 5 to 10 ml benzene. Shake the funnel for about 30 seconds and drain the aqueous phase into another separatory funnel.
4. Drain the benzene layer through a small amount of sodium sulfate into a 125 ml evaporating flask. Extract the aqueous layer again with benzene and place the extract in the 125 ml flask. Concentrate the sample extracts with a rotary evaporator (bath temp=60°C) to 1-2 ml and transfer to a test tube with benzene to a final volume of 5 ml. Analyze by gas chromatography.

EQUIPMENT CONDITIONS:

1. Varian 6000 gas chromatograph with Varian autosampler and Varian 604 Data System; TSD Detector; Column: HP 6000-1767 50% phenylmethyl silicone megabore column, 0.53 mm x 10 mm; Carrier: Helium; Make-up: Helium; Carrier pressure: 15 psi; H2 pressure: 20 psi; Column temperature program: initial temp = 180°C for 0.5 min., final temp=240°C for 1 min.; rate: 6°C/min; Injector Temp=250°C; Detector Temp:300°C

2. Varian 3700 gas chromatograph with HP 7672A Autosampler and HP 3388 Data System TSD Dectector; Column: HP 1 (methyl silicone gum) megabore, 0.53 mm x 10 mm; Carrier: Helium; Make-up: Argon-methane; Carrier flow rate: 15 ml/min; H2 pressure: 20 psi; Column temperature: isothermal, 170°C; Injector Temp: 210°C; Detector Temp: 260°C.

CALCULATIONS:

$$\% \text{ Moisture} = 100 \times \frac{(\text{wt. of undried sample} + \text{pan}) - (\text{wt. of dried sample} + \text{pan})}{(\text{wt. of undried sample} + \text{pan}) - (\text{wt. of pan})}$$

ug metaldehyde=

sample pk hgt	ug std injected	final vol sample(ml)	44
-----x	-----x	-----x	-----
std pk hgt	vol sample injected(ml)		224

PPM metaldehyde= ug metaldehyde
(by dry wt) -----

$$\frac{\text{g sample} \times \% \text{ dry wt}}{(\text{in aliquot})}$$

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3292 Meadowview Road
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Original Date:??
Supercedes: NEW
Current Date:12/18/87
Method #:

METHIOCARB (MESUROL) AND METABOLITES IN SOIL

SCOPE:

This method is for the determination of Methiocarb, Methiocarb sulfoxide, and Methiocarb sulfone in soil.

PRINCIPLE:

Residues of Methiocarb and its sulfoxide and sulfone metabolites are extracted from soil with acetonitrile. The extract is shaken with NaCl and an aliquot taken for analysis by HPLC using a post column reaction and a fluorescence detector.

REAGENTS AND EQUIPMENT:

1. Acetonitrile(HPLC grade)
2. Methanol(HPLC grade)
3. Sodium chloride
4. Mercaptoethanol
5. O-phthaldehyde
6. Fluoraldehyde, Reagent Diluent(1 M Potassium Borate Buffer pH 10.4)
(Pierce Chemical Co.)
7. 0.05 N Sodium hydroxide
8. Jars, amber wide-mouth, 500 or 250 ml
9. Cylinders, mixing, graduated, 100 ml
10. Funnels, glass, stemmed
11. Filter paper (Whatman, #1, 12 cm)
12. Pipets, 50 ml, volumetric
13. Pipets, 9", disposable
14. Flasks, boiling, flat-bottomed, 125 ml
15. Test tubes, graduated, 15 ml
16. Weighing pan, aluminum
17. Rotary Evaporator(Buchi-Brinkman,R110)
18. Mechanical shaker
19. Drying oven, 105°C
20. Syringe filter, nylon, disposable, pore size: 0.45 um, size: 25 mm,
(Schleicher & Schuell)

ANALYSIS

1. Remove soil sample from the freezer and allow it to come to room temperature.
2. Mix sample thoroughly in sample jar.

MOISTURE DETERMINATION

1. Weigh approximately 10 g sample into a preweighed aluminum weighing pan.
2. Heat pan with soil for 16-24 hours at 105°C until a constant weight is obtained.

EXTRACTION

1. Weigh 50 g of well-mixed sample into an amber wide-mouth jar and add 100 ml acetonitrile.
2. Seal jar with aluminum foil and screw-top and place on mechanical shaker for 1 hour.
3. Allow sample to settle 10-15 minutes and filter extract into a 100 ml graduated cylinder containing 10 g NaCl.
4. Shake sample for 2 minutes and allow time for complete phase separation.
5. Pipet a 50 ml sample aliquot from the acetonitrile layer into a 125 ml evaporating flask and reduce volume just to dryness on a Rotoevaporator (Bath temperature = 55°C).
6. Rinse sample into a 15 ml graduated tube with about 10 ml methanol and bring to a final volume of 5 ml on a steam bath under a stream of nitrogen.
7. Filter sample through a 0.45 um filter and analyze by HPLC.

EQUIPMENT CONDITIONS:

Varian 5000 Liquid Chromatograph with autosampler:

Column: Altex "Ultrasphere" ODS, 4.6 mm ID x 15 cm.

Temperature: Ambient ~ 25°

Flow rate: 1 ml/minute.

Solvents and gradient conditions:

- 1.) 10%ACN to 70%ACN in 12 minutes
- 2.) 70%ACN to 10%ACN in 18 minutes.

POST-COLUMN REACTION: Water bath: 92-95°C

Hydrolysis: 0.05 N NaOH; Flow Rate: 0.6 ml/minute.
Reaction coil: 0.75 m x 0.3mm ID tubing in 3" coil.

Derivatization: OPA solution

Preparation: Dissolve 0.5g o-phthaldehyde in 10 ml methanol.
Add 1 ml mercaptoethanol and 50 ml Fluoraldehyde Reagent
Diluent. Dilute to 1 liter with distilled water.

Flow rate: 0.3 ml/min.

Reaction tubing: 0.5 m x 0.3mm ID tubing.

Fluorescent Detection:

Excitation: 350 nm.
Emission: 450 nm.

CALCULATIONS:

% MOISTURE:

$$100 \times \frac{(\text{wt.undried sample\&pan}) - (\text{wt.dried sample\&pan})}{(\text{wt.undried sample\&pan}) - (\text{wt.pan})}$$

ppm METHIOCARB:

$$\frac{\text{Pk hgt sample} \times \text{Std inject}(\mu\text{g}) \times \text{Final vol}(\text{ml})}{\text{Pk hgt Std} \times \text{Vol sample inject}(\text{ml}) \times \text{Sample wt}(\text{g}) \times \% \text{dry wt}}$$

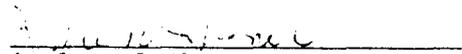
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Klotter, Kevin and Cunico, Robert, *HPLC Post Column Detection of Carbamate Pesticides*, Varian Instrument Group, 2700 Mitchell Dr., Walnut Creek, CA, 94598.

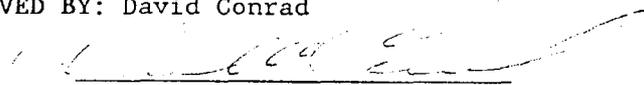
Krause, Richard T., *Jour. Assoc. Anal. Chem.* Vol.63, No.5, 1980, pg. 1114-1124.

Saini, N. *Mesurool (Methiocarb) and its Metabolites: Mesurool Sulfoxide and Mesural Sulfone Residue Analysis by HPLC*, CDFA Worker Health and Safety Method 34.0, 1981.

WRITTEN BY: Karen Hefner


TITLE: Agricultural Chemist II

APPROVED BY: David Conrad


TITLE: Agricultural Chemist III

Method for the Determination of Metaldehyde in Soil and Produce

I. Extraction:

Produce:

1. Finely chop representative sample and weigh 100 grams.
2. Homogenize sample with 200 ml of benzene for 3 min. in blender.
3. Pass resulting mixture through sharkskin filter paper to a 500 ml separatory funnel.
4. Re-extract residue two times with 100 ml each of benzene by shaking on a platform shaker for 20 min., combining all extracts together - continue to 1-5.

Soil:

1. Weigh 100 grams soil into 500 ml erlenmeyer flask.
2. Extract with 200 ml benzene by shaking on a platform shaker for 30 min.
3. Filter through sharkskin filter paper into a 500 ml separatory funnel.
4. Re-extract soil two times with 100 ml each of benzene for 20 min. combining all the extracts together - continue 1-5.

Soil & Produce:

5. Extract benzene layer 2X with 10 ml each of fresh 2% sodium metabisulfite solution.
6. Wash benzene extracts with 10 ml water, then filter through sodium sulfate into a 500 ml round bottom flask.
7. Rotovap in 60°C bath to about 5 ml volume.

II. Clean-up:

1. Prepare florisil column using a 10 X 2 cm chromatographic column with 13 g of florisil.
2. Rinse column with 50 ml benzene.
3. Transfer extract quantitatively to column.
4. Elute column with 125 ml of 5 % tetrahydrofuran in benzene.
5. Collect eluate in 250 ml round bottom flask and concentrate with rotovap (bath temp. 50°C) to about 15 ml volume.

III. Derivatization:

1. Add 15 ml of DNPH reagent to the 15 ml benzene solution in the round bottom flask.
2. Mix two phase at room temperature by shaking on a platform shaker for 20 min.
3. Transfer mixture to a 125 ml separatory funnel.
4. Transfer lower aqueous phase to another 125 ml separatory funnel and drain remaining benzene layer to a 50 ml centrifuge tube.
5. Extract aqueous phase with another 10 ml benzene and combine extracts in the 50 ml tube.
6. Concentrate combined extracts to 1 ml and analyze by G.C.

IV. Gas Chromatographic Analysis:

A. Screening Conditions

Column: DB-5

Col. Dimensions: 8 meters megabore

Col. Temperature: 165°C for 0.5 min. to 185°C for 3.5 min. with
temp. increase at the rate of 6°C/min.

Detector: Thermionic Specific Detector

Detector Temperature: 300°C

Injector Temperature: 250°C

Carrier Gas: Helium

Flow Rate: 15 cc/min.

B. Confirmation Conditions

Column: DB-17

Col. Dimension: 8 meters megabore

Column Temperature: 180°C for 0.5 min. to 185°C for 5 min. with
temperature increase at the rate of 6°C/min.

Detector: Thermionic Specific Detector

Detector Temperature: 300°C

Injector Temperature: 250°C

Carrier Gas: Helium

Flow Rate: 15 cc/min.

Determination of Mesurol in Produce and Soil

I. Mesurol in Produce:

Cut up representative portions of produce sample and weigh 100 grams into a 600 ml beaker. Add 200 ml acetonitrile and homogenize in a 1 quart stainless steel blender cup at high speed for 1-2 min. Filter homogenized produce into a mixing graduated cylinder with 15-20 grams NaCl. Proceed to A.

II. Mesurol in Soil:

In 600 ml erlenmeyer flask, weigh 50 grams of representative portion of the soil sample. Add 100 ml of acetonitrile and shake for 20 min. Filter thru a mixing graduated cylinder with 10 grams NaCl. Proceed to A.

A: Shake the solution for 1 min. and let it settle down for 10 min. Pipet out 20 ml. aliquot portion from the acetonitrile layer into a 100 ml beaker. Blow down the acetonitrile extract to dryness on a water bath under a stream of air. Add 1-3 ml benzene and continue blowing down to drive off residual acetonitrile. Reconstitute with 5 ml MeOH and pass thru C-18 into a 15 ml centrifuge tube.

III. Chromatographic Analysis:

A. HPLC Screening Conditions

Mobile Phase: Isocratic - 0.7 ml/min H₂O and 0.7 ml/min CH₃CN

Column: Ultrashpere - ODS, 25 cm X 4.6 mm I.D., 5 mm.

Precolumn: 4 cm X 3.2 mm I.D. with ultrapack - ODS, 10 um

PCR System Conditions

NaOH Solution Concentration: 0.05 N

Flow Rate: 0.8 ml/min.

OPA Solution Concentration: 0.5 g/l

Detector: Fluorescence

B. G.C. Confirming Conditions

Column: DB-17

Dimension: 8 meters megabore

Cal. Temperature: 150°C

Detector: TSD

Det. Temperature: 300°C

Injector Temperature: 250°C

Carrier Gas: Helium at 20 cc/min.

Method Development

For spring, 1987 method development, replicate blank soil samples were spiked (blank matrix spikes) at different levels with metaldehyde (0.1 and 1 parts per million (ppm)), methiocarb (0.2 and 1 ppm), methiocarb sulfoxide (0.2 and 1 ppm), and methiocarb sulfone (0.2 and 1 ppm). The detection limit, mean percent recovery, and standard deviation (SD) for metaldehyde were 0.05 ppm, 99 and 14.8, respectively (Table I-1). The detection limits, mean percent recoveries and standard deviations for methiocarb, methiocarb sulfoxide and methiocarb sulfone were 0.04 ppm, 89 percent and 7.7, 0.03 ppm, 67 percent and 20, and 0.03 ppm, 39 percent and 33, respectively (Table I-2). For fall 1987 method development, blank matrix spikes were generated by spiking 0.5 ppm of metaldehyde and methiocarb into background soil. The detection limits, mean percent recoveries, and SD for metaldehyde and methiocarb were 0.05 ppm and 0.5 ppm, 96 percent and 91 percent, 3.2 and 5.9, respectively (Table I-11). The mean percent recovery and SD were used to calculate the spring and fall warning limits (± 2 SD from mean) and control (± 3 SD from mean) for accuracy. The spring 1987 method validation study data generated by CDFA laboratory were used as guidelines by L.A. County laboratory for spring 1987 continuing quality control analysis.

To measure repeatability, three DNPH-acetaldehyde standard injections were prepared during the beginning of the spring 1987 analyses at three levels (10, 50 and 100 nanograms (ng)) and replicated 5 times. The mean recovery for all 3 samples was 100 percent with the SD ranging from 3.2 to 4.5 (Table I-3).

Quality Control Results

In the spring 1987 analyses, all matrix spike recoveries for each chemical fell within the warning and control limits set by the method validation study (Tables I-4 to I-7). In the fall 1987 analyses, one blank matrix spike fell outside the lower control limit set for metaldehyde at 86% and one fell outside the lower control limit set for methiocarb at 73% (Tables I-12 to I-13). Only 1 out of 21 matrix spikes for each compound fell outside the control limits, therefore no corrective action was taken.

Split Sample Analyses

The spring 1987 data for quality control samples split between laboratories showed positive levels for metaldehyde, methiocarb and methiocarb sulfoxide. Metaldehyde levels ranged from 0.07 ppm to 1.03 ppm with the detection limit set by L.A. Co. laboratory at 0.05 ppm. CDFA laboratory split sample analysis for metaldehyde was not completed due to problems encountered with the gas chromatograph injector. Methiocarb was found in all split samples by both laboratories. The mean methiocarb level, SD and coefficient of variation (CV) between the 2 laboratories ranged from 1.61 ppm to 3.84 ppm, 0.4 to 1.46, and 10 percent to 77 percent, respectively (Table I-8). Positive methiocarb sulfoxide levels were found by CDFA laboratory only, ranging from 0.04 ppm to 0.27 ppm (Table I-9). The detection limits set by CDFA and L.A. Co. laboratories at 0.04 ppm and 0.5 ppm, respectively, might have accounted for the positive methiocarb sulfoxide levels found by CDFA

and not by L.A. Co. laboratory. Methiocarb sulfone split sample analysis showed non-detected levels by both laboratories (Table I-10).

The fall 1987 data for quality control samples split between laboratories showed positive levels for both methiocarb and metaldehyde. Methiocarb was found in six out of the twelve samples analyzed by L.A. Co. laboratory, while CDFA analysis showed all positive methiocarb levels (Table I-14). The detection limits set by CDFA and L.A. Co. laboratories at 0.04 ppm and 0.5 ppm, respectively, might have accounted for the positive methiocarb levels found by CDFA and not by L.A. Co. laboratory. All metaldehyde split samples showed positive levels except one sample analyzed by L.A. Co. laboratory that showed non-detected. The mean metaldehyde level, SD and CV between the 2 laboratories ranged from 0.12 ppm to 0.67 ppm, 0 to 0.36 and 0 percent to 92 percent, respectively (Table I-15).

Table I-1. Metaldehyde Method Validation Study for Soil, Spring 1987

Analyte: Metaldehyde
Matrix: Soil
Detection Limit: 0.05 ppm

Lab: CDFA
Chemist: Karen Hefner
Date: 12/16/87

<u>Study Sample #</u>	<u>Lab Sample #</u>	<u>Results (ppm)</u>	<u>Spike Level (ppm)</u>		<u>Recovery %</u>	
001	441	0.088	0.1		88	
002	442	0.124	0.1		124	
003	443	0.084	0.1		84	
004	444	0.071	0.1		71	
005	445	0.108	0.1		108	
006	435	1.084	1.0		108	
007	436	1.067	1.0		107	
008	437	0.993	1.0		99	
009	438	0.993	1.0		99	
010	439	0.977	1.0		98	
<u>Matrix</u>	<u>\bar{X}</u>	<u>SD</u>	<u>LWL*</u>	<u>UWL*</u>	<u>LCL**</u>	<u>UCL**</u>
Soil	99	14.8	69	129	55	143

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

* = UWL and LWL = $\bar{X} \pm 2 \text{ SD}$
 ** = UCL and LCL = $\bar{X} \pm 3 \text{ SD}$

Table I-2. Methiocarb and Metabolites Method Validation Study for Soil, Spring 1987

Analyte: Methiocarb
Matrix: Soil
Detection Limit: 0.04 ppm

Lab: CDFA
Chemist: Karen Hefner
Date: 12/16/87

<u>Study Sample #</u>	<u>Lab Sample #</u>	<u>Results (ppm)</u>	<u>Spike Level (ppm)</u>	<u>Recovery %</u>
001	1152	0.176	0.2	88
002	1151	0.2	0.2	100
003	1150	0.81	1	81
004	708	0.834	1	83
005	707	0.93	1	93

Analyte: Methiocarb sulfoxide
Matrix: Soil
Detection Limit: 0.03 ppm

Lab: CDFA
Chemist: Karen Hefner
Date: 12/16/87

001	1152	0.18	0.2	90
002	1151	0.162	0.2	81
003	1150	0.704	1	70
004	708	0.478	1	48
005	707	0.444	1	44

Analyte: Methiocarb sulfone
Matrix: Soil
Detection Limit: 0.03 ppm

Lab: CDFA
Chemist: Karen Hefner
Date: 12/16/87

001	1152	0.14	0.2	70
002	1151	0.136	0.2	68
003	1150	0.5	1	50
004	708	0.046	1	5
005	707	0.032	1	3

	\bar{X}	SD	LWL *	UWL *	LCL **	UCL **
Methiocarb	89	7.7	74	104	66	112
M. sulfoxide	67	20	27	107	7	127
M. sulfone	39	33	-27	105	-60	138

* = UWL and LWL = $\bar{X} \pm 2 \text{ SD}$

** = UCL and LCL = $\bar{X} \pm 3 \text{ SD}$

Table I-3. Metaldehyde/Methiocarb Replicate Injection Analyses, Spring 1987

<u>Analyte:</u> DNPH-acetaldehyde <u>Matrix:</u> Standard <u>Detection Limit:</u> 0.05 ppm			<u>Lab:</u> CDFA <u>Chemist:</u> Karen Hefner <u>Date:</u> 12/16/87		
Lab Sample #	Results (Ng)	Spike Level (Ng)	Concentration		
			%	\bar{X}	SD
448	9.93	10	99		
448	10.3	10	103		
448	10.5	10	105		
448	9.69	10	97		
448	9.53	10	95	100	4.1
447	51.0	50	102		
447	51.3	50	103		
447	52.6	50	105		
447	46.8	50	94		
447	48.2	50	97	100	4.5
446	100	100	100		
446	101	100	101		
446	104	100	104		
446	95.1	100	95		
446	99.9	100	100	100	3.2

Table I-4. Metaldehyde Quality Control Data, Spring 1987

<u>Analyte:</u> Metaldehyde <u>Matrix:</u> Soil <u>Detection Limit:</u> 0.05 ppm			<u>Lab:</u> L.A. Co. <u>Chemist:</u> Mimi S. <u>Date:</u> 12/16/87		
Extraction Set Sample Nos.	Spike Level (ppm)	Recovery %			
			\bar{X}	SD	
37-40,43-44	0.5	100			
87-88,91-93, 94-96	0.5	81			
62-66,71-72, 77-84,61	0.5	84			
73-76,103-8	0.5	80			
11-12,25-6	0.5	91			
97-102	0.5	90			
119-120,5-10	0.5	93			
111-118	0.5	95	89	7.0	

Table I-5. Methiocarb Quality Control Data, Spring 1987

<u>Analyte:</u> Methiocarb <u>Matrix:</u> Soil <u>Detection Limit:</u> 0.5 ppm			<u>Lab:</u> L.A. Co. <u>Chemist:</u> Mimi S. <u>Date:</u> 12/16/87	
<u>Extraction Set</u> <u>Sample Nos.</u>	<u>Spike Level</u> <u>(ppm)</u>	<u>Recovery</u> <u>%</u>	<u>\bar{X}</u>	<u>SD</u>
37-40,43-44	0.5	81		
87-88,91-93, 94-96	0.5	91		
62-66,71-72, 77-84,61	0.5	81		
73-76,103-8	0.5	85		
11-12,25-6 97-102	0.5	78		
119-120,5-10	0.5	100		
111-118	0.5	92	86	7.5
		81		

Table I-6. Methiocarb Sulfoxide Quality Control Data, Spring 1987

<u>Analyte:</u> Methiocarb sulfoxide <u>Matrix:</u> Soil <u>Detection Limit:</u> 0.5 ppm			<u>Lab:</u> L.A. Co. <u>Chemist:</u> Mimi S. <u>Date:</u> 12/16/87	
<u>Extraction Set</u> <u>Sample Nos.</u>	<u>Spike Level</u> <u>(ppm)</u>	<u>Recovery</u> <u>%</u>	<u>\bar{X}</u>	<u>SD</u>
43-44	0.5	96		
37-40,87-88, 91-92,94-96	0.5	88		
62-66,71-72, 93	0.5	78		
77-84,61	0.5	86		
73-76,103-8	0.5	97	89	7.8

Table I-7. Methiocarb Sulfone Quality Control Data, Spring 1987

Analyte: Methiocarb sulfone
Matrix: Soil
Detection Limit: 0.5 ppm

Lab: L.A. Co.
Chemist: Mimi S.
Date: 12/16/87

<u>Extraction Set Sample Nos.</u>	<u>Spike Level (ppm)</u>	<u>Recovery %</u>	<u>\bar{X}</u>	<u>SD</u>
37-40, 43-44	0.5	82		
87-88, 91-93, 94-96	0.5	98		
62-66, 71-72, 77-84, 61	0.5	81		
73-76, 103-8	0.5	109	94	12.1
		100		

Table I-8. Methiocarb Split/Confirmation Analyses, Spring 1987

<u>Analyte: Methiocarb</u> <u>Matrix: Soil</u> <u>Detection Limit (CDFA): 0.04 ppm</u> <u>Detection Limit (L.A. Co.): 0.5 ppm</u>			<u>Lab: CDFA</u> <u>Chemist (CDFA): Karen Hefner</u> <u>Chemist (L.A. Co.): Mimi S.</u> <u>Date: 12/16/87</u>			
<u>Study Sample #</u>	<u>Lab Sample #</u>	<u>L.A. Co. (ppm)</u>	<u>CDFA (ppm)</u>	<u>\bar{X}</u>	<u>SD</u>	<u>CV (%)</u>
0001	S013	3.03				
0002	352		1.30	2.17	1.22	56
0003	S014	0.73				
0004	353		2.48	1.61	1.24	77
0067	S056	3.56				
0068	354		4.12	3.84	0.40	10
0069	S057	1.36				
0070	355		3.42	2.39	1.46	61

Table I-9. Methiocarb Sulfoxide Split/Confirmation Analyses, Spring 1987

<u>Analyte: Methiocarb sulfoxide</u> <u>Matrix: Soil</u> <u>Detection Limit (CDFA): 0.04 ppm</u> <u>Detection Limit (L.A. Co.): 0.5 ppm</u>			<u>Lab: CDFA</u> <u>Chemist (CDFA): Karen Hefner</u> <u>Chemist (L.A. Co.): Mimi S.</u> <u>Date: 12/16/87</u>		
<u>Study Sample #</u>	<u>Lab Sample #</u>	<u>L.A. Co. (ppm)</u>	<u>CDFA (ppm)</u>		
0001	S013	<0.5			
0002	352		.05		
0003	S014	<0.5			
0004	353		.04		
0067	S056	<0.5			
0068	354		.24		
0069	S057	<0.5			
0070	355		.27		

Table I-10. Methiocarb Sulfone Split/Confirmation Analyses, Spring 1987

<u>Analyte:</u> Methiocarb Sulfone	<u>Lab:</u> CDFA
<u>Matrix:</u> Soil	<u>Chemist (CDFA):</u> Karen Hefner
<u>Detection Limit (CDFA):</u> 0.04 ppm	<u>Chemist (L.A. Co.):</u> Mimi S.
<u>Detection Limit (L.A. Co.):</u> 0.5 ppm	<u>Date:</u> 12/16/87

<u>Study Sample #</u>	<u>Lab Sample #</u>	<u>L.A. Co. (ppm)</u>	<u>CDFA (ppm)</u>
0001	S013	<0.5	
0002	352		<0.04
0003	S014	<0.5	
0004	353		<0.04
0067	S056	<0.5	
0068	354		<0.04
0069	S057	<0.5	
0070	355		<0.04

Table I-11. Metaldehyde/Methiocarb Method Validation Study for Soil, Fall 1987

Analyte: Metaldehyde
Matrix: Soil
Detection Limit: 0.05 ppm

Lab: L.A. Co.
Chemist: Mimi S.
Date: 12/6/87

<u>Lab Sample #</u>	<u>Results (ppm)</u>	<u>Spike Level (ppm)</u>	<u>Recovery %</u>
001	0.48	0.5	96
002	0.505	0.5	101
003	0.465	0.5	93
004	0.47	0.5	94
005	0.47	0.5	94

Analyte: Methiocarb
Matrix: Soil
Detection Limit: 0.5 ppm

Lab: L.A. Co.
Chemist: Mimi S.
Date: 12/6/87

<u>Lab Sample #</u>	<u>Results (ppm)</u>	<u>Spike Level (ppm)</u>	<u>Recovery %</u>
001	0.475	0.5	95
002	0.44	0.5	88
003	0.475	0.5	95
004	0.475	0.5	95
005	0.41	0.5	82

<u>Matrix</u>	<u>\bar{X}</u>	<u>SD</u>	<u>LWL *</u>	<u>UWL *</u>	<u>LCL **</u>	<u>UCL **</u>
<u>Metaldehyde:</u>						
Soil	96	3.2	90	102	86	106
<u>Methiocarb:</u>						
Soil	91	5.9	79	103	73	109

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

* = UWL and LWL = $\bar{X} \pm 2 \text{ SD}$
 ** = UCL and LCL = $\bar{X} \pm 3 \text{ SD}$

Table I-12. Metaldehyde/Methiocarb Continuing Quality Control Data, Fall 1987:
Blank Matrix Spikes (Soil)

<u>Analyte: Metaldehyde</u> <u>Matrix: Soil</u> <u>Detection Limit: 0.05 ppm</u>				<u>Lab: L.A. Co.</u> <u>Chemist: Mimi S.</u> <u>Date: 12/6/87</u>		
<u>Extraction Set</u> <u>Sample Nos.</u>	<u>Results</u> <u>(ppm)</u>	<u>Spike Level</u> <u>(ppm)</u>	<u>Recovery</u> <u>%</u>	<u>\bar{X}</u>	<u>SD</u>	<u>CV</u> <u>%</u>
001-006	0.46	0.5	92			
007-012	0.46	0.5	92			
017-024	0.46	0.5	92			
037-039	0.47	0.5	94			
040-048	0.47	0.5	94			
026	0.465	0.5	93			
028	0.465	0.5	93			
25,27,29-31,						
033-036	0.465	0.5	93			
032	0.465	0.5	93			
181-182	0.415	0.5	83			
089-098	0.099	0.1	99			
113-120	0.096	0.1	96			
121-128	0.099	0.1	99			
129,131-						
136	0.097	0.1	97			
130	0.097	0.1	97			
53-56	0.1	0.1	100			
57-62	0.1	0.1	100			
63-80	0.09	0.1	90			
99-102,107	0.096	0.1	96			
103-108	0.097	0.1	97			
81-88	0.098	0.1	98	95	3.9	4.1

* Extraction set sample nos. 181-182 fell outside the lower control limit set for metaldehyde at 86%.

Table I-13. Metaldehyde/Methiocarb Continuing Quality Control Data, Fall 1987:
Blank Matrix Spikes (Soil)

Analyte: Methiocarb
Matrix: Soil
Detection Limit: 0.5 ppm

Lab: L.A. Co.
Chemist: Mimi S.
Date: 12/6/87

<u>Extraction Set Sample Nos.</u>	<u>Results (ppm)</u>	<u>Spike Level (ppm)</u>	<u>Recovery %</u>	<u>\bar{X}</u>	<u>SD</u>	<u>CV %</u>
001-006	0.485	0.5	97			
007-012	0.495	0.5	99			
017-024	0.455	0.5	91			
037-039	0.44	0.5	88			
040-048	0.4	0.5	80			
026	0.455	0.5	91			
028	0.355	0.5	71*			
25,27,29-31,						
033-036	0.445	0.5	89			
032	0.475	0.5	95			
181-182	0.435	0.5	87			
089-098	1.8	2.0	90			
113-120	2.0	2.0	100			
121-128	1.9	2.0	95			
129,131-,						
136	1.9	2.0	95			
130	1.76	2.0	88			
53-56	1.89	2.0	95			
57-62	1.82	2.0	91			
63-80	1.88	2.0	94			
99-102,107	1.92	2.0	96			
103-108	1.92	2.0	96			
81-88	1.67	2.0	84	91	6.8	7.5

* Sample no. 28 fell outside the lower control limit set for methiocarb at 73%.

Table I-14. Metaldehyde/Methiocarb Split/Confirmation Analyses, Fall 1987

<u>Analyte: Methiocarb</u> <u>Matrix: Soil</u> <u>Detection Limit (CDFA): 0.04 ppm</u> <u>Detection Limit (L.A. Co.): 0.5 ppm</u>			<u>Lab: CDFA</u> <u>Chemist (CDFA): Karen Hefner</u> <u>Chemist (L.A. Co.): Mimi S.</u> <u>Date: 12/21/87</u>			
<u>EHAP</u> <u>Sample #</u>	<u>Lab</u> <u>Sample #</u>	<u>L.A. Co.</u> <u>(ppm)</u>	<u>CDFA</u> <u>(ppm)</u>	<u>\bar{X}</u>	<u>SD</u>	<u>CV</u> <u>(%)</u>
0045 0049	S118 971	<0.5	1.07			
0046 0050	S119 972	0.83	0.76	0.80	0.05	6.3
0047 0051	S120 973	0.87	0.17	0.52	0.49	94
0048 0052	S121 974	<0.5	0.08			
0069 0073	S134 975	<0.5	0.52			
0070 0074	S135 976	0.54	0.18	0.36	0.25	69
0071 0075	S136 977	0.62	0.16	0.39	0.33	85
0072 0076	S137 978	2.33	0.15	1.24	1.54	124
0101 0109	S162 979	<0.5	0.19			
0102 0110	S163 980	1.18	0.99	1.09	0.13	11.9
0103 0111	S164 981	<0.5	0.07			
0104 0112	S165 982	<0.5	0.19			

Table I-15. Metaldehyde/Methiocarb Split/Confirmation Analyses, Fall 1987

<u>Analyte: Metaldehyde</u> <u>Matrix: Soil</u> <u>Detection Limit (CDFA): 0.04 ppm</u> <u>Detection Limit (L.A. Co.): 0.05 ppm</u>			<u>Lab: CDFA</u> <u>Chemist (CDFA): Karen Hefner</u> <u>Chemist (L.A. Co.): Mimi S.</u> <u>Date: 12/21/87</u>			
<u>EHAP</u> <u>Sample #</u>	<u>Lab</u> <u>Sample #</u>	<u>L.A. Co.</u> <u>(ppm)</u>	<u>CDFA</u> <u>(ppm)</u>	<u>\bar{X}</u>	<u>SD</u>	<u>CV</u> <u>(%)</u>
0045 0049	S118 971	0.14	0.65	0.39	0.36	92
0046 0050	S119 972	0.37	0.51	0.44	0.10	23
0047 0051	S120 973	0.41	0.33	0.37	0.06	16
0048 0052	S121 974	0.2	0.2	0.2	0	0
0069 0073	S134 975	0.13	0.63	0.38	0.35	92
0070 0074	S135 976	<0.05	1.92			
0071 0075	S136 977	0.10	0.14	0.12	0.03	25
0072 0076	S137 978	0.28	0.22	0.25	0.04	16
0101 0109	S162 979	0.59	0.74	0.67	0.11	16
0102 0110	S163 980	0.45	0.38	0.41	0.05	12
0103 0111	S164 981	0.31	0.28	0.30	0.02	6.7
0104 0112	S165 982	0.14	0.42	0.28	0.20	71

APPENDIX II

**Statistical Tables for Spring and Fall White Garden
Snail Monitoring Results**

Table II-1A. Analysis of Variance Results for Metaldehyde (mg/sq m) at White Garden Snail Residential Monitoring Sites, Application No. 1, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	1831.698	1.63
Replication (Site)	2	1122.121	--
Days Post	1	10089.101	9.13
Site X Days Post	1	9159.811	8.29 ¹
Residual	2	1104.586	--

Table II-1B. Analysis of Variance Results for Metaldehyde (ppm) at White Garden Snail Residential Monitoring Sites, Application No. 1, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	0.990	0.64
Replication (Site)	2	1.554	--
Days Post	1	7.781	5.52
Site X Days Post	1	7.624	5.41 ¹
Residual	2	1.394	--

1. Although not statistically significant ($P=.10$ and $P=.14$, respectively), evidence of differential response patterns may affect validity of all other statistical tests.

Table II-2A. Analysis of Variance Results for Methiocarb (mg/sq m) at White Garden Snail Residential Monitoring Sites, Application No. 1, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	119.072	0.14
Replication (Site)	2	826.891	--
Days Post	1	16992.461	15.10
Site X Days Post	1	16263.061	14.46
Residual	2	1125.081	--

Table II-2B. Analysis of Variance Results for Methiocarb (ppm) at White Garden Snail Residential Monitoring Sites, Application No. 1, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	0.118	0.06
Replication (Site)	2	2.133	--
Days Post	1	9.946	5.54
Site X Days Post	1	12.852	7.16
Residual	2	1.796	--

1. Strong indications of interactions or differential response patterns (P=0.06 and P=0.11, respectively) may affect validity of all other statistical tests.

Table II-3A. Analysis of Variance Results for Metaldehyde (mg/sq m) at White Garden Snail Residential Monitoring Sites, Application No. 2, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	5732.498	2.48
Replication (Site)	2	2315.785	--
Days Post	1	14365.125	1.72
Site X Days Post	1	1225.125	0.15
Residual	2	8331.445	--

Table II-3B. Analysis of Variance Results for Metaldehyde (ppm) at White Garden Snail Residential Monitoring Sites, Application No. 2, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	19.483	2.63
Replication (Site)	2	7.418	--
Days Post	1	29.223	1.33
Site X Days Post	1	8.020	0.37
Residual	2	21.928	--

Table II-4A. Analysis of Variance Results for Methiocarb (mg/sq m) at White Garden Snail Residential Monitoring Site, Application No. 2, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	58.824	32.93**
Replication (Site)	2	1.786	--
Days Post	1	6722.201	1.82
Site X Days Post	1	17.701	<0.10
Residual	2	3693.706	--

Table II-4B. Analysis of Variance Results for Methiocarb (ppm) at White Garden Snail Residential Monitoring Sites, Application No. 2, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	1.867	8.07**
Replication (Site)	2	0.231	--
Days Post	1	14.071	1.73
Site X Days Post	1	0.392	0.03
Residual	2	8.707	--

Table II-5A. Analysis of Variance Results for Metaldehyde (mg/sq m) at White Garden Snail Residential Monitoring Sites, Application No. 3, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	383.688	0.80
Replication (Site)	2	482.121	--
Days Post	1	6333.751	160.85**
Site X Days Post	1	746.911	18.97
Residual	2	39.376	--

Table II-5B. Analysis of Variance Results for Metaldehyde (ppm) at White Garden Snail Residential Monitoring Sites, Application No. 3, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	0.001	0.01
Replication (Site)	2	0.482	--
Days Post	1	9.396	72.94**
Site X Days Post	1	1.488	11.55
Residual	2	0.129	--

1. Strong indications of interactions or differential response patterns (P=.05 and P=.08, respectively) may affect validity of all other statistical tests.
2. Significance at the 5% and 1% level denoted * and **, respectively.

Table II-6A. Analysis of Variance Results for Methiocarb (mg/sq m) at White Garden Snail Residential Monitoring Sites, Application No. 3, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	2257.812	0.28
Replication (Site)	2	8007.700	--
Days Post	1	10541.520	10.90 ¹
Site X Days Post	1	237.620	0.25
Residual	2	966.205	--

Table II-6B. Analysis of Variance Results for Methiocarb (ppb) at White Garden Snail Residential Monitoring Sites, Application No. 3, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	0.468	0.07
Replication (Site)	2	6.637	--
Days Post	1	11.956	10.95 ¹
Site X Days Post	1	0.005	<0.01
Residual	2	1.092	--

1. Differences between days were marginally significant ($0.05 < P < 0.10$)

Table II-7A. Analysis of Variance Results for Metaldehyde (ppm) at White Garden Snail Experimental Sites, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	10932.488	2.80
Replication (Site)	2	3903.620	--
Days Post	7	3103.122	2.26 ¹
Site X Days Post	7	1269.051	0.92
Residual	14	1369.727	--

Table II-7B. Analysis of Variance Results for Metaldehyde (ppm) at White Garden Snail Experimental Sites, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	3.458	0.77
Replication (Site)	2	4.503	--
Days Post	7	3.209	2.46 ¹
Site X Days Post	7	1.249	0.96
Residual	14	1.302	--

1. Differences between days were marginally significant ($.05 < P < .10$).

Table II-8A. Analysis of Variance Results for Methiocarb (mg/sq m) at White Garden Snail Experimental Sites, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	5676.765	1.0
Replication (Site)	2	5398.299	--
Days Post	7	1914.234	0.34
Site X Days Post	7	2666.301	0.47
Residual	14	5706.015	--

Table II-8B. Analysis of Variance Results for Methiocarb (ppm) at White Garden Snail Experimental Sites, Spring 1987

Source of Variation	Degrees Freedom	Mean Square	F
Site	1	3.220	0.64
Replication (Site)	2	5.057	--
Days Post	7	1.374	0.26
Site X Days Post	7	2.710	0.51
Residual	14	5.323	--

Table II-9. Summary of Regression Analysis Results for Metaldehyde and Methiocarb at Experimental Monitoring Sites, Spring 1987

Site	Variable	Units	Intercept	Slope	R ²	Root Mean Square
Hillcrest	Metaldehyde	mg/sq m	50.54	-2.22	.68	11.70
	Metaldehyde	ppm	1.71	-0.07	.64	0.42
	Methiocarb	mg/sq m	46.93	2.20	.41	20.39
	Methiocarb	ppm	1.70	0.08	.54	2.35
Lakeside	Metaldehyde	mg/sq m	93.58	-4.79	.64	27.72
	Metaldehyde	ppm	2.88	-0.14	.59	0.9349
	Methiocarb	mg/sq m	107.40	-2.73	.22	39.102
	Methiocarb	ppm	3.90	-0.10	.12	2.12

Table II-10. Analysis of Variance Results on Metaldehyde (mg/sq m), White Garden Snail Monitoring Program, Fall 1987

Source of Variation	Degrees Freedom	Mean Square	Parameters Estimated
Among Sites	25	3,639.602 ¹	$\sigma_e^2 + 4\sigma_s^2$
Replication (Site)	78	2,205.520	σ_e^2

¹The estimated component of variance for sites is 358.521.

Table II-11. Analysis of Variance Results for Metaldehyde (ppm), White Garden Snail Monitoring Program, Fall 1987

Source of Variation	Degrees Freedom	Mean Square	Parameters Estimated
Among Sites	25	1.881	$\sigma_e^2 + 4\sigma_s^2$
Replication (Site)	78	1.251	σ_e^2

¹The estimated component of variance for sites is 0.158.

Table II-12. Analysis of Variance Results for Methiocarb (mg/sq m), White Garden Snail Program, Fall 1987

Source of Variation	Degrees Freedom	Mean Square	Parameters Estimated
Among Sites	25	12,275.501	$\sigma_e^2 + 4\sigma_s^2$
Replication (Site)	78	2,382.645	σ_e^2

¹The estimated component of variance for sites is 2,473,214.

Table II-13. Analysis of Variance Results for Methiocarb (ppm), White Garden Snail Program, Fall 1987

Source of Variation	Degrees Freedom	Mean Square	Parameters Estimated
Among Sites	25	5.870	$\sigma_e^2 + 4\sigma_s^2$
Replication (Site)	78	1.204	σ_e^2

¹The estimated component of variance for sites is 1.167.