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EXECUTIVE SUMMARY
of Report EH 92-04 Entitled
**"Estimation of the Contribution from Offsite Aerial Deposition
to Methyl Parathion Residues
in Agricultural Drains in the Sacramento Valley"**

Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulation

PURPOSE

The Department of Pesticide Regulation's Environmental Hazards Assessment Program (EHAP) monitored water from agricultural drainage ditches to determine whether offsite deposition from aerial applications of methyl parathion was a significant factor contributing to residues in the Sacramento River.

BACKGROUND

Methyl parathion is a pesticide with many uses in California, including rice, where it is used to control the tadpole shrimp (*Triops longicaudatus*). Residues, presumably from applications on rice, have been detected in water samples from the Colusa Basin Drain in the Sacramento Valley at levels that are toxic to aquatic organisms.

Water quality objectives are limits or levels of water quality constituents or characteristics which are established for the reasonable protection of beneficial uses of water or the prevention of nuisance within a specific area (Water Code Section 13050 (h)). There is no numerical water quality objective for methyl parathion. There are a number of narrative objectives, including the following:

"Inland surface water communities and populations, including vertebrate, invertebrate, and plant species, shall not be degraded as a result of the discharge of waste" (Inland Surface Waters Plan, April, 1991).

The Central Valley Regional Water Quality Control Board has prohibited the discharge of irrigation water from rice fields containing methyl parathion unless the discharger is following a management practice, consisting of specific rice pesticide handling activities, approved by the Board. To receive approval, the management practice must be expected to meet a performance goal, defined as concentrations of water quality constituents established for receiving waters that a discharger must make best efforts to meet. They serve as a measure of success in improving water quality.



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To promote dissipation and meet the performance goal, water management practices have been implemented that prohibit the discharge of irrigation water from rice fields treated with methyl parathion until the 25th day following application.

Since observed concentrations in 1990 exceeded performance goals, additional measures appeared necessary to meet performance goals in subsequent years. Accordingly, an investigation was conducted to determine whether the contribution from offsite deposition during aerial application is a significant contributor to pesticide residues in the River.

STUDY METHODS

Water sampled from irrigation drainage ditches adjacent to four rice fields in Colusa County was analyzed for methyl parathion residues during and following the aerial application period. Deposition during application was also measured with mass deposition cards distributed along the drain.

RESULTS

The amount of offsite movement from aerial applications of pesticide was calculated in two ways, using water samples and mass deposition cards. The amount of pesticide found in the entire drain was calculated from the water samples. Assuming all the pesticide came from an aerial application, the amount of pesticide falling on the surface of the drain would have been from 1.2 to 11.1 milligrams per square meter. This is equivalent to between 1.7% and 15.9% of a normal aerial application at the label rate of 70 milligrams per square meter.

The mass deposition cards also allowed a calculation of the offsite movement. However, these values, 0.25 to 2.00 milligrams per square meter, are 78.5% to 82.0% lower than levels calculated from water samples. Further investigation is required to determine the cause of the discrepancy between mass deposition cards and water samples.

CONCLUSIONS

This study shows that offsite deposition may result in significant levels of methyl parathion in agricultural drains adjacent to the application site. Patterns of deposition also implicated aerial application.

The Regional Water Quality Control Board has approved the discharge of irrigation water from rice fields for the 1992 season with

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management practices which include control of drift during aerial application.

A handwritten signature in cursive script that reads "John Sanders".

John Sanders
Acting Branch Chief

5/6/92

**ESTIMATION OF THE CONTRIBUTION FROM OFFSITE AERIAL DEPOSITION
TO METHYL PARATHION RESIDUES
IN AGRICULTURAL DRAINS IN THE SACRAMENTO VALLEY**

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ABSTRACT

The presence of methyl parathion (*O,O*-dimethyl-*O*-*p*-nitrophenyl phosphorothioate; MeP) in waterways of the Sacramento Valley of California is associated with its use in rice fields. Since observed concentrations in 1990 (up to 0.66 µg/L) exceeded the target levels (0.26 µg/L for 1991) established by the California Regional Water Quality Control Board - Central Valley Region, an investigation was conducted to determine whether the contribution from offsite deposition during aerial application is a significant factor. Water sampled from agricultural drainage ditches adjacent to four rice fields in Colusa County was analyzed for MeP during and following the aerial application period. Maximum concentrations at the four sites were 5.3, 16.7, 2.8, and 4.7 µg MeP/L; background levels, measured upstream, did not exceed the experimental limit of detection (0.5 µg/L) prior to application. Mean offsite deposition levels calculated from the aqueous concentrations and the volume of water conveyed by the drains ranged from 1.2 to 11.1 mg/m², which is equivalent to 1.7% to 15.9% of a direct application to the drain at the label rate of 70 mg active ingredient/m². Deposition during application was also measured with mass deposition (MD) cards distributed along the drain. The MD card residues ranged from 0.25 to 2.00 mg MeP/m², which is 82.0% to 78.5% lower than the levels calculated from aqueous sampling; further investigation is required to determine why this rate was less than expected. This study shows that offsite deposition may result in significant levels of MeP in agricultural drains adjacent to the application site. Patterns of deposition revealed by MD samples showed increased levels where an application leg of the flight pattern lay parallel to the drain, suggesting that swath misalignment may be a factor. Some mitigation could result from conservative flight path practices around agricultural drains.

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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

The Department of Pesticide Regulation cooperates with other State agencies to monitor and control the discharge of pesticide residues into surface waters of the Sacramento Valley. During monitoring in 1990, levels of the pesticide methyl parathion sufficient to adversely affect aquatic life were detected in the Colusa Basin Drain, which is a major return path for irrigation water from the rice growing areas of Glenn and Colusa Counties to the Sacramento River (Department of Fish and Game, 1991; California Department of Food and Agriculture, 1991c).

Methyl parathion (*O,O*-dimethyl-*O-p*-nitrophenyl phosphorothioate; MeP) is a restricted-use organophosphate pesticide used primarily for control of tadpole shrimp, leafhoppers, armyworms, cutworms, rice caseworms, rice bugs, and leaf-folders in rice cultivation (Cheminova, 1985-90). In 1990 MeP was applied to 78,601 acres in California; in 1991 it was used on 58,286 acres in the Sacramento Valley, where the majority of California rice is grown (California Department of Food and Agriculture, 1991a,b).

The water quality control plan of the California Regional Water Quality Control Board - Central Valley Region - for the Sacramento Valley specified a daily maximum performance goal for MeP of 0.26 $\mu\text{g/L}$ for 1991; the 1992 performance goal will be 0.13 $\mu\text{g/L}$ (California Regional Water Quality Control Board, 1991). During the 1990 season, the MeP concentration at a Colusa Basin Drain monitoring site in Yolo County exceeded the 1991 performance goal between May 12-21, peaking at 0.66 $\mu\text{g/L}$ on May 17, significantly in excess of the proposed standard (California Department of Food and Agriculture, 1991a). The 48-hour

MeP LC₅₀ is 2.6 µg/L for the invertebrate *Ceriodaphnia dubia* (Norberg-King, et al., 1991). Accordingly, studies were undertaken to identify the MeP sources in order to develop effective management strategies to ameliorate the levels.

MeP residues in aquatic systems may be due to contributions from several sources:

- a) release of water from treated fields into drains following post-application discharge moratoriums (3 days prior to 1991; 24 days during the 1991 season)
- b) offsite aerial deposition during application
- c) "other events" (e.g. early emergency release, leaky drop boxes, etc.)
- d) "illegal uses"
- e) leaching of residual contamination into agricultural drains
- f) seepage through levees of treated fields ("subbing")
- g) volatilization with subsequent offsite movement and deposition

The study reported herein was undertaken to examine the effect of offsite deposition during aerial application, and to estimate its contribution to the levels of MeP observed in agricultural drains that serve rice fields in the Sacramento Valley. Offsite deposition may lead to significant amounts of MeP being deposited into agricultural drains and thus returned directly to major waterways (Domagalski and Kuivila, 1991; Foe and Connor, 1989).

This study was designed to obtain typical estimates of the extent of contributions from offsite deposition to agricultural drains; we purposely chose sites with diverse field conditions so that our range of results would be realistic. Factors that might affect the extent of offsite deposition include weather conditions (especially temperature inversions and wind); application pattern,

release height, and nozzle design; and site characteristics (Akesson and Yates, 1984; Draper and Street, 1981; MacCollom et al., 1985; Maksymiuk, 1972; Moore, 1990; Seiber, et al., 1980, 1989; Steinke and Yates, 1989).

II. MATERIALS AND METHODS

Study Sites

Four commercial rice fields located in Colusa County were selected for measurement of offsite deposition during aerial application of methyl parathion. The primary criteria for site selection were that the rice field be bordered by a drainage ditch along at least one side, and that the drain be suitable for sampling at the time of application. Other criteria included the cooperation of the grower and the aerial applicator as well as site accessibility. Over 20 fields were originally identified as potential study sites. During the two week post-planting period when tadpole shrimp infestation is most prevalent, close contact was maintained with the growers, pest control advisors (PCAs) and flying services for notice of possible MeP application; County Agriculture Department Notices of Intent were also polled daily. Four of the 20 fields that were followed were ultimately used as study sites; Figure 1 depicts their locations. The site characteristics and agricultural drain data are summarized in Table 1.

Figure 1. Locations of four rice field sites in Colusa County where offsite aerial deposition studies for methyl parathion applications were conducted in 1991.

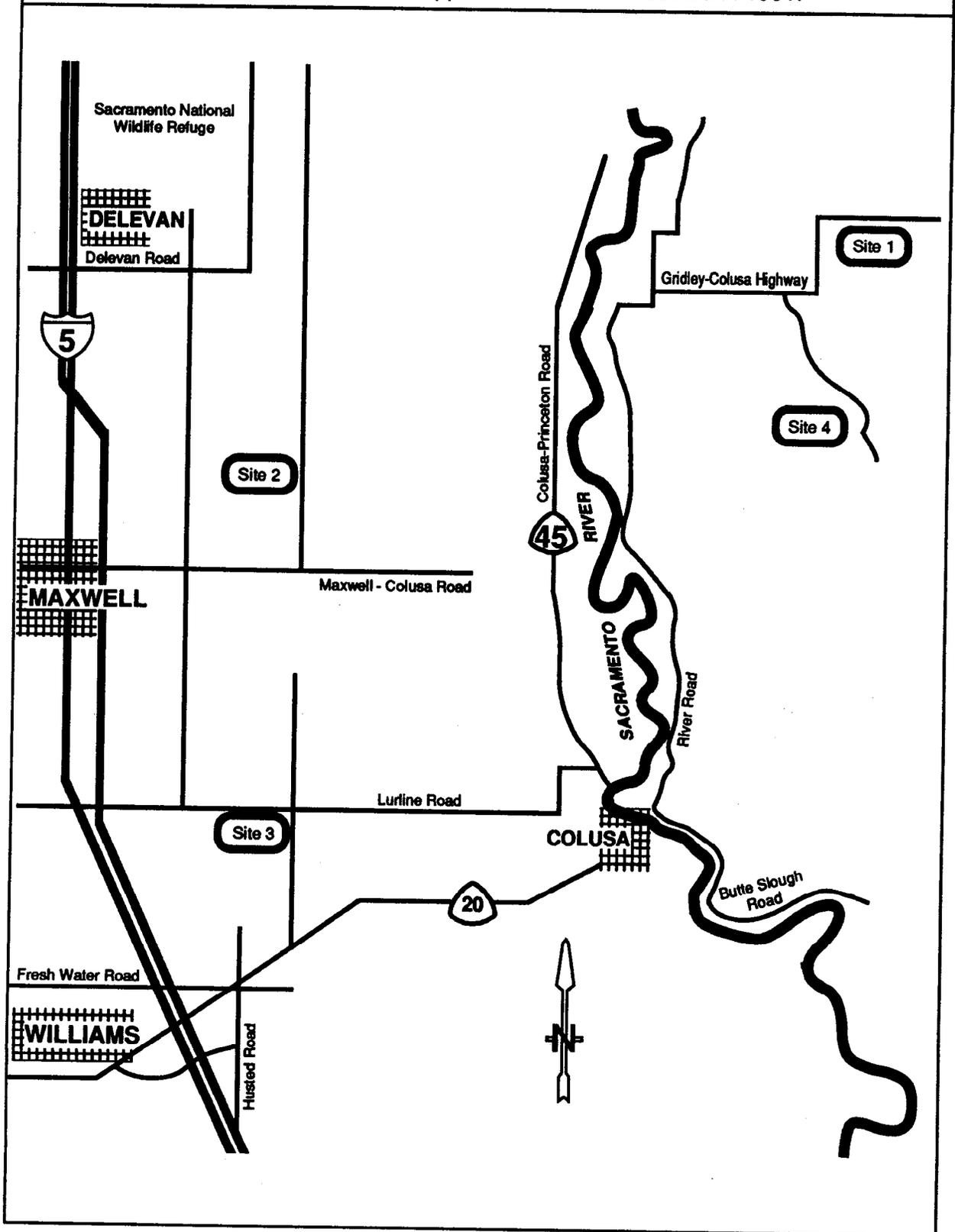


Table 1. Location data and physical characteristics of four rice-field sites in Colusa County where offsite deposition studies for methyl parathion were conducted in 1991.

Site	1	2	3	4
<u>General site information</u>				
County	Colusa	Colusa	Colusa	Colusa
Field area (ha)	174	30	38	55
Irrigation water system	RD1004 ^a	GCID ^b	GCID	RD1004
Field length (m)	1,448	762	774	955
Field width (m)	1,219	382	645	617
<u>Drain length parameters</u>				
Upstream station distance ^c (m)	207	61	0	0
Upstream segment length ^d (m)	1,219	382	774	308
Downstream segment length ^d (m)	1,448	762	645	309
Downstream station distance ^c (m)	70	2	7	170
Sampling length ^e (m)	2,738	1,146	1,426	787
<u>Drain flow parameters</u>				
Mean width (m)	7.01	2.84	2.84	3.44
Mean depth (m)	1.34	0.13	0.14	0.37
Cross-section (m ²)	9.39	0.36	0.40	1.27
Surface area (m ²)	19,193	3,255	4,050	2,707
Velocity (m/s)	0.20	0.27	0.41	0.37
Discharge (m ³ /s)	1.85	0.42	0.34	0.46

a. RD1004 = Reclamation District 1004.

b. GCID = Glenn Colusa Irrigation District.

c. measured from edge of field to autosampler location.

d. for sites where the drain lay on one side, each segment was half the length of the field;
for sites where the drain tracked two sides, each segment was the length of a side.

e. sampling length includes the two field segments and the downstream station distance.

Sampling Methods

Two methods of sampling methyl parathion residues were utilized: a) agricultural drain water was sampled for the aqueous MeP concentration, and b) mass deposition (MD) cards were used to sample the aerial MeP deposition on drain banks. It was anticipated that if the results of the aqueous sampling and MD cards were in agreement, the simpler MD card method might suffice for future investigations. However, there is no report to date that demonstrates this for methyl parathion, and both methods were used for this study.

The organization of the aqueous and mass deposition sampling stations with respect to the field and the agricultural drain is depicted for each of the four sites in Figures 2-5.

Aqueous Samples: Sampling stations were established upstream and downstream from each selected field. The upstream station was used to assess the background MeP concentration attributable to upstream sources. Samples collected downstream from the field were used to determine the direct contribution of offsite deposition of airborne residues. Sheet metal or wooden stake baffles were set in the drain to promote adequate aqueous mixing where needed.

Isco Model 2700 refrigerated automatic samplers were used at the upstream and downstream stations to collect eight composite aqueous samples in 1.8-L bottles; the samples were composed of 75- to 100-mL subsamples collected at 2- or 3-minute intervals. The subsample volume and time interval were calculated from the total sampling period as estimated from the drain velocity. Field blanks of distilled deionized water were also collected at a rate of one for

Figure 2. Physical layout of Site 1; location and sizes of field and agricultural drain; locations of aqueous mass deposition sampling stations; flight pattern and windrose for application period on 5/12/91. 174 Ha.

Drain:

Sampling Length - 2,738 m
 Mean Width - 7.0 m
 Mean Depth - 1.3 m
 Discharge - 1.85 m³/s

Legend:

- Mass Deposition Cards
- ☒ Autosampler Location
- ▶ Direction of Drain Flow

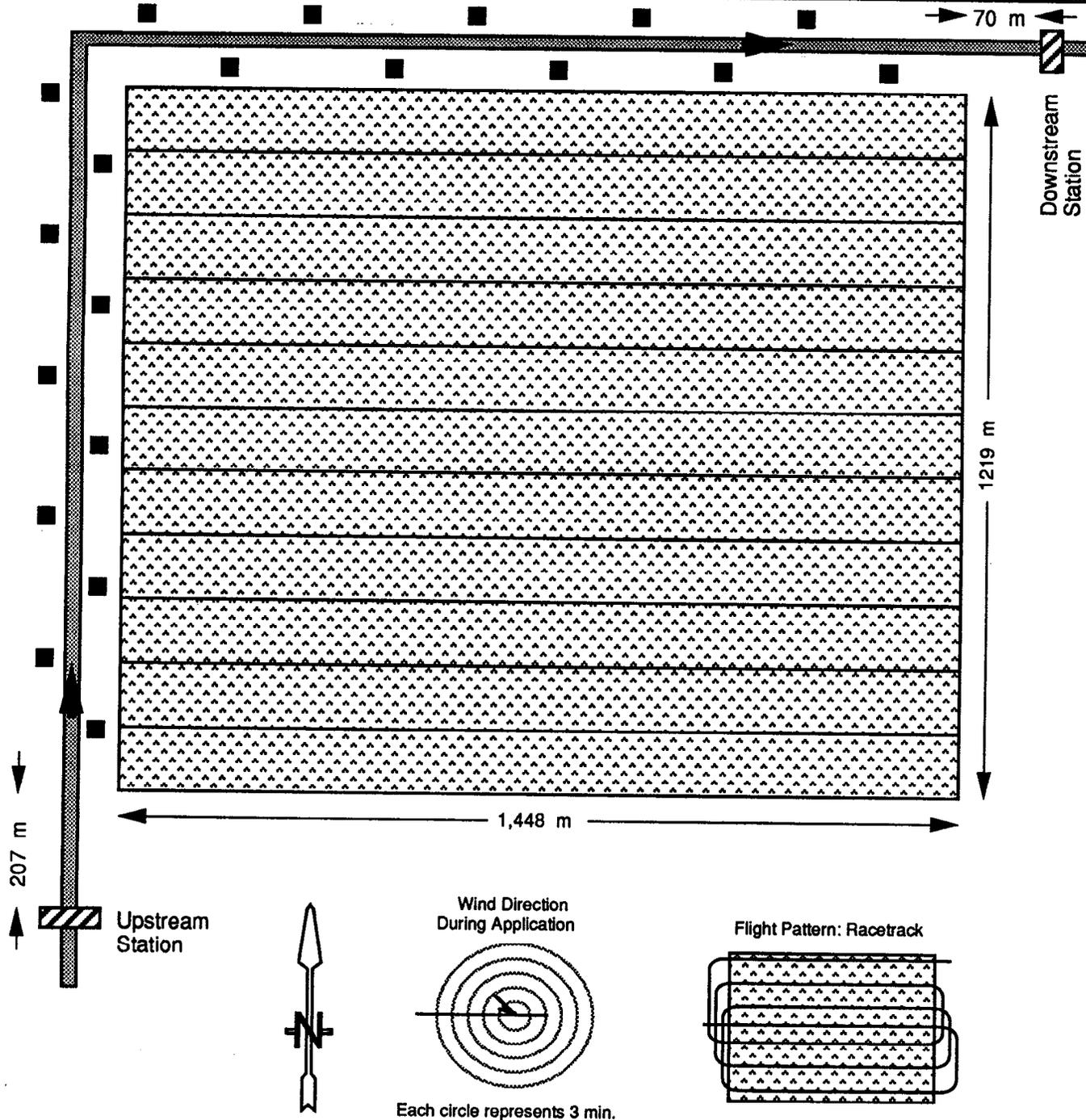


Figure 3. Physical layout of Site 2; location and sizes of field and agricultural drain; locations of aqueous mass deposition sampling stations; flight pattern and windrose for application period on 5/24/91. 30 Ha.

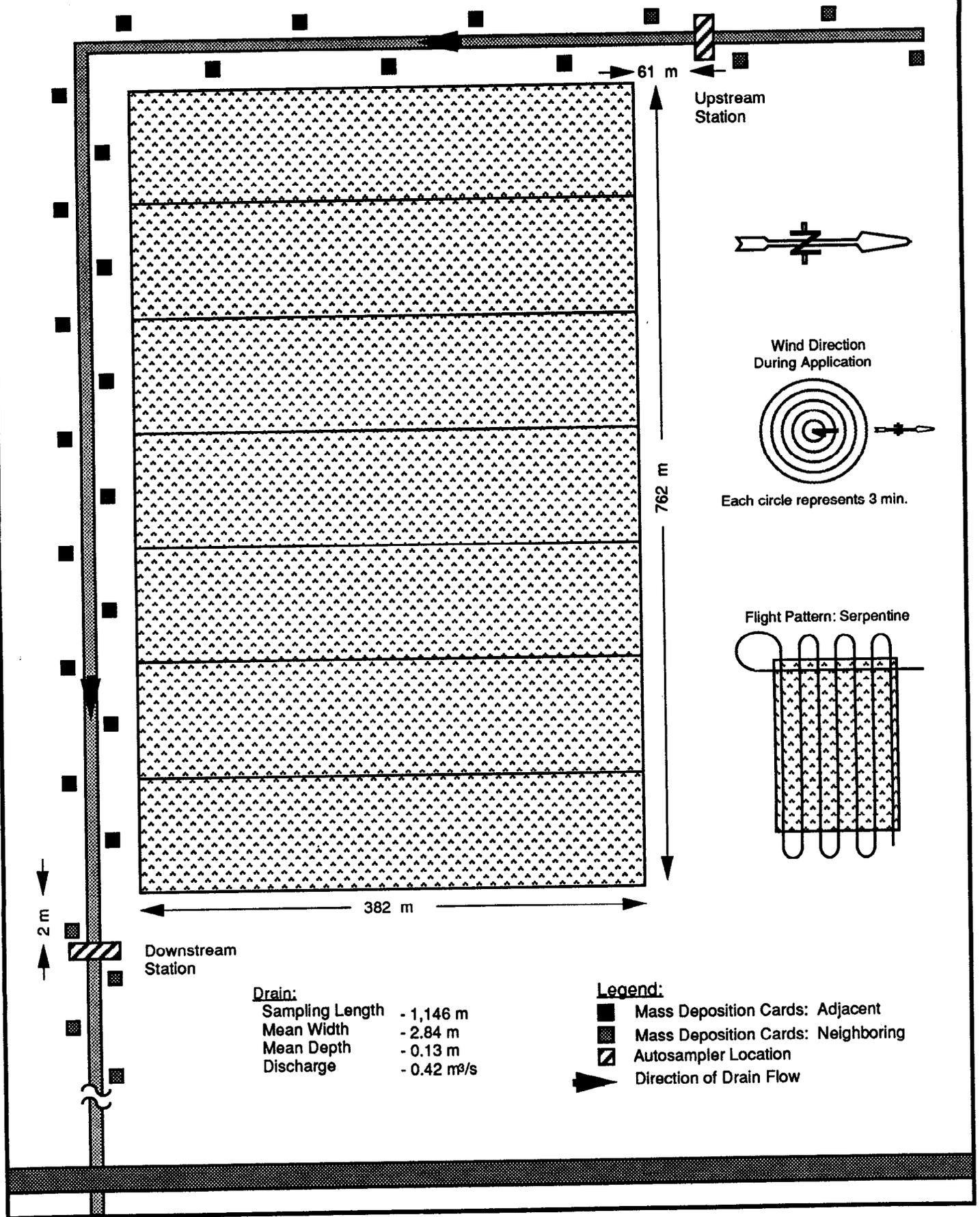


Figure 4. Physical layout of Site 3; location and sizes of field and agricultural drain; locations of aqueous mass deposition sampling stations; flight pattern and windrose for application period on 6/07/91. 38 Ha.

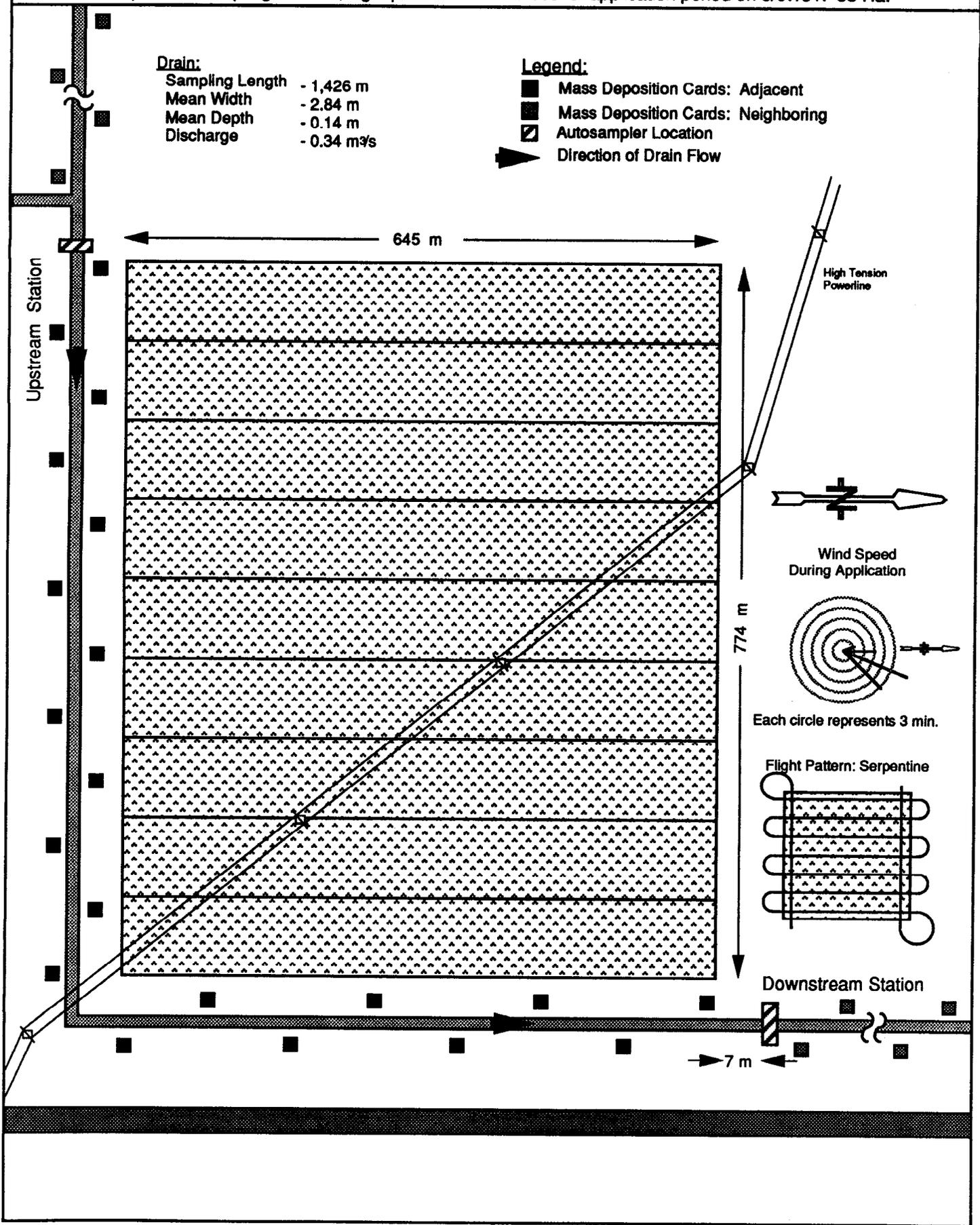
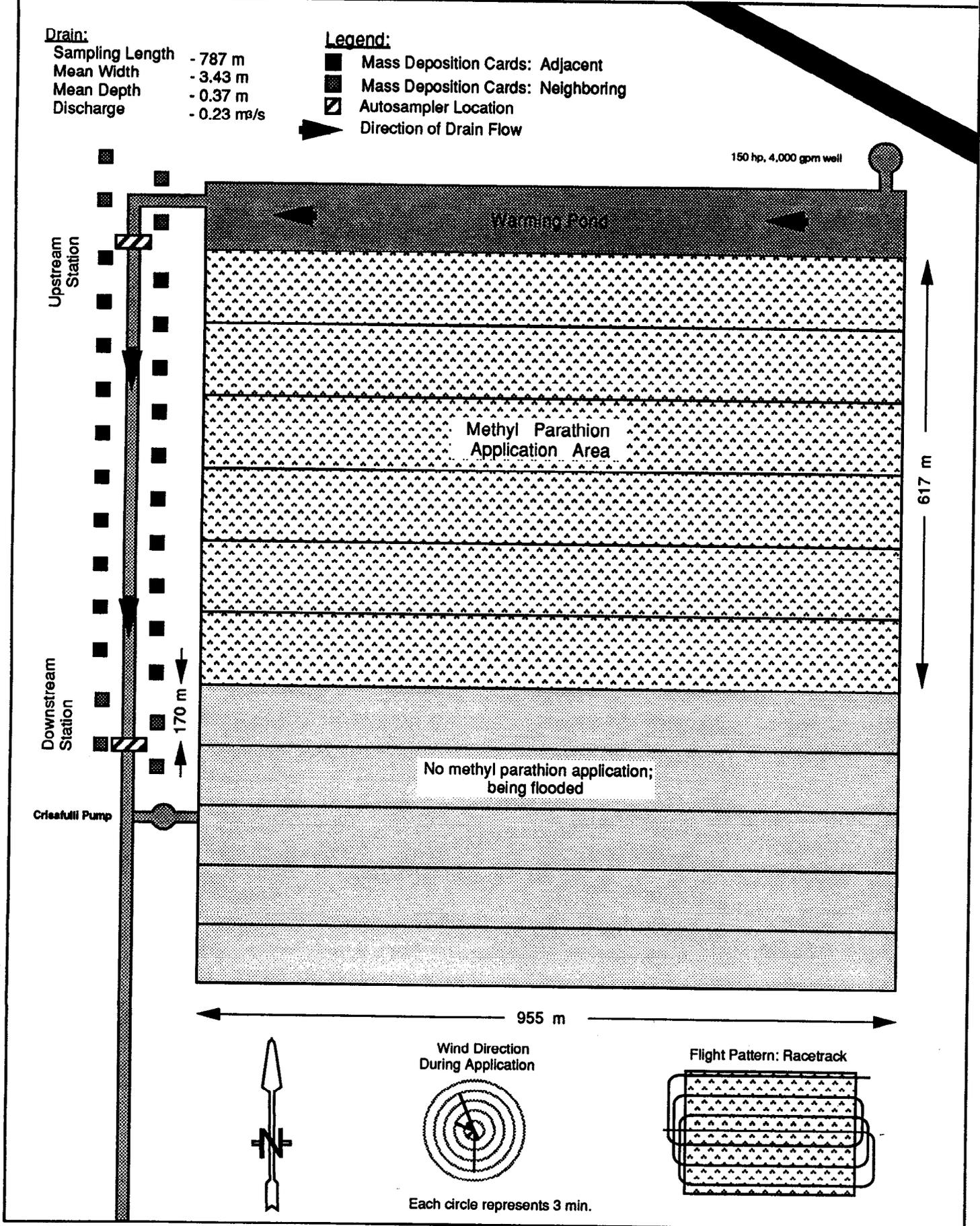


Figure 5. Physical layout of Site 4; location and sizes of field and agricultural drain; locations of aqueous mass deposition sampling stations; flight pattern and windrose for application period on 6/19/91. 55 Ha.



every 10 samples. Method development studies undertaken at the California Department of Food and Agriculture (CDFA) Chemistry Laboratory Services Branch lab indicated that aqueous MeP samples are more stable under acidic than neutral conditions (see Appendix A2: Tables A2-1 to A2-4, and Figs. A2-1 to A2-4). Samples were therefore adjusted to pH 3 with 3 N HCl after their collection. The bottles were capped with Teflon™-lined lids, placed on wet ice, and maintained at ~4 °C until their analysis. Samples were analyzed for MeP and its oxygen analog, methyl paraoxon (MePx).

Water Volume: On the day before MeP application, each drain was measured to determine a total sampling length; the drains were essentially rectangular so that cross-sectional area was estimated from mean drain width and depth. The flow velocity in the drain was measured at several locations using either a Swoffer Model 2100 Current Meter or a Mead Instruments Model HP-302 Current Meter. From these measurements an estimate was made of the time that it would take the contents of the sampling length to pass the downstream sampling station. This time was used to set the autosampler subsample time interval and volume parameters.

The discharge was also measured directly wherever the drain passed through a rectangular weir within the sampling length. There was at least one weir at each site, except Site 4 (the discharge there was initially calculated from the measured velocity profile). The discharge was used in deriving the MeP mass in the drain attributable to offsite deposition. Aqueous autosampling parameters and the site data on which they were based are summarized in Table 2.

Table 2. Parameters for aqueous autosampling in agricultural drains at four rice methyl parathion application sites.

Site	1	2	3	4
<u>Drain details</u>				
Length of drain sampled (m)	2,738	1,146	1,426	787
Water pH	7.9	8.0	7.5	7.8
Water density (g/L)	993.3	989.4	991.9	997.2
Water temperature (°C)	19.5	18.5	25.6	16.7 ^a
Velocity (m/sec)	0.20	0.27	0.41	0.37
<u>Sampling details</u>				
Application time (min)	30	7	50	45
Application fallout time (min)	90	90	90	90
Time required to sample slug (min)	234	72	56	43
Total sampling time allotted (min) ^b	400	288	360	296
Sample volume (mL)	1,800	1,800	1,800	1,800
<u>Upstream autosampler</u>				
Number of samples taken	7	8	8	8
Time interval/sample (min)	72	36	45	37
Number of subsamples/sample	24	18	22	18
Subsample interval (min)	3 ^c	2	2	2
Subsample volume (mL)	75	100	85	100
<u>Downstream autosampler</u>				
Number of samples taken	8	6 ^d	8	8
Time interval/sample (min)	50	51	45	37
Number of subsamples/sample	24	18	22	18
Subsample interval (min)	2	2	2	2
Subsample volume (mL)	75	100	85	100

a. Well was main source of drain water.

b. Total time includes extra time allotted to compensate for flow variations, etc.

c. Autosampler inadvertently programmed for 3-minute subsample intervals instead of 2-minute intervals.

d. Subsample time intervals inaccurate due to autosampler malfunction; final two samples were hand sampled.

Mass Deposition Samples: Direct collection of airborne MeP residue was achieved with MD cards attached to sampling platforms. Plastic-covered cardboard was mounted on stakes along each side of the drainage ditch. Just prior to spraying, 0.09-m² absorbent Kimbie™ paper sheets with plastic backing were affixed to the cardboard. Approximately ninety minutes after application, the MD cards were collected, folded plastic side out, and placed between aluminum foil sheets; the foil was folded airtight and placed in a manila envelope. These were transported on dry ice and stored at -10 °C until extraction. Samples were analyzed for MeP and MePx.

MeP offsite mass deposition was studied using MD cards at several locations at each site: A) on the drain bank adjacent to the field site (*adjacent* samples), and B) on the drain banks upstream and downstream from the field site (*neighboring* samples). In addition, a field blank was taken at each site.

A) Adjacent Samples: Twenty MD cards were set at equal intervals along the drain adjacent to the field, alternating from inner to outer bank. After application, the cards were collected and combined to yield four composite samples: inner bank, 1) **upstream** and 2) **downstream**; outer bank, 3) **upstream** and 4) **downstream** (where the inner bank was adjacent to the field and the downstream set spanned from the downstream edge of the field for half the distance to the upstream edge). Each of the four samples was analyzed for MeP and MePx.

B) Neighboring Samples: Two MD cards were placed along the inner bank of the drain, and two along the outer bank upstream and downstream from the test field. The same spacing was used as for the adjacent samples. Each set of four cards (an **upstream** set and a **downstream** set) was combined as a composite sample and analyzed for MeP and MePx. Due to time constraints in setting up for Site 1, no neighboring sample MD cards were placed.

Aerial Application

MeP was flown on early in the day at each of the four sites to avoid adverse wind conditions and higher temperatures (MeP labels caution against "application when weather conditions favor drift from areas treated" [Wilbur-Ellis, 1987]). Application rate was one pint/acre of the 5E formulation, which is equivalent to 0.70 kg active ingredient/hectare (70 mg/m²). Details are presented in Table 3 together with the prevailing meteorologic conditions.

Measurement of Offsite Deposition

Utilizing the autosamplers' time-delay option, aqueous autosampling was initiated simultaneously at the upstream and downstream stations just before the aerial application began. The intention was to subsample the entire MeP slug resulting from the application as it flowed past the downstream station. The autosampler was programmed to collect eight samples over the duration of the experiment. This spanned three time periods: application time, which was estimated in advance by the aerial applicator; an allowance for MeP airborne residue settling to the ground ("fallout period"), set constant at 90 minutes; and the time for the entire sampling length of the drain to pass the downstream station. This figure was calculated from the drain volume and its velocity measured on the morning of the application, and was extended to allow

Table 3. Parameters for pesticide application at four sites with accompanying meteorologic data.

Site	1	2	3	4
<u>Application details</u>				
Field size (ha)	174	30	38	55
Application date	5/12/91	5/24/91	6/7/91	6/19/91
Application time	0600-0630	1045-1052	0715-0805	0655-0740
Length of application (min)	30	7	50	45
Methyl parathion formulation	Wilbur-Ellis 5	Wilbur-Ellis 5	Wilbur-Ellis 5	Clean Crop 5E
Application rate (pints/acre)	1	1	1	1
(L/ha)	1.17	1.17	1.17	1.17
Number of loads	2	1	3	2
Application flight conformation	Racetrack	Serpentine	Serpentine	Racetrack
<u>Meteorologic conditions</u>				
Ambient temperature (°C)	7.6	26.3	16.4	13.0
Relative humidity (%)	96.1	34.1	78.5	82.4
Wind velocity (kph)	4.2	5.8	4.3	6.9
Wind direction	W & NW	NE & N	N & NNE	NNW & S

for flow variations. The volume and number of subsamples collected was adjusted to yield one 1800-mL sample in the appropriate time period. These parameters were programmed into the autosampler along with a time delay set to expire before the start of application; this allowed personnel time to retreat to the observation area. A safe period of 90 minutes after the end of application was observed before the field team re-entered the site. Personnel wore Tyvek™ protective suits and respirators for the sample collection phase.

Measurement of Sampling Variability

A sampling variability study was undertaken to determine whether placement of the autosampler intake tube at ~0.3 m deep mid-stream would give an adequate representation of MeP concentrations in the drain. These samples were collected following the application but while MeP was still expected to be present in the drain. Samples were hand collected at the downstream sampling station from a depth of ~0.3 m from four points evenly spaced across the drain transect. Four 120-mL samples were collected each minute over a 15-minute period yielding four 1.8-L composite samples. After this set of samples had been collected, a second set of four was collected in the same manner.

Meteorologic Measurements

A Met One weather station equipped with a CRI data logger was used to record prevailing weather conditions at a four-meter elevation during MeP application at each site. Meteorologic data included wind velocity and direction, ambient temperature, and relative humidity. At the conclusion of each experiment, the data were transferred to a data logger tape; the tape data were later transferred to a personal computer for analysis and plotting (see Appendix 3: Figs. A3-1 to A3-4).

Sample Extraction and Analysis

MeP and MePx were extracted from aqueous samples with methylene chloride. The organic phase was filtered, taken to dryness, and resuspended in acetone for gas chromatography analysis.

For MD-card samples, MeP and MePx were extracted with ethyl acetate. For MeP analysis, this extract was analyzed directly; for MePx analysis, the ethyl acetate extract was concentrated by taking it to dryness and redissolving the residue in a small amount of ethyl acetate.

All extracts were analyzed on an HP-17 (50% phenyl methyl silicone) column in a gas chromatograph using a ramped temperature program and an FPD detector. The complete CDFA Lab procedures are contained in Appendix 1.

III. RESULTS AND DISCUSSION

The results obtained from each of the four sites are presented in Tables 4-7 (a,b,c). The physical conditions are depicted in Figures 2-5, and the hourly data for MeP are plotted in Figures 6-9. An insignificant amount of MePx was detected ($< 0.12 \mu\text{g/L}$ in aqueous samples and $< 170 \mu\text{g/m}^2$ for MD cards), and all graphs and further analyses are presented for MeP alone. The analysis of aqueous and mass deposition data for all sites is summarized in Table 8; sample calculations for the Table are given in Appendix 5.

Maximum concentrations in the drains at the four sites were 5.3, 16.7, 2.8, and $4.7 \mu\text{g/L}$. The cumulative pesticide burdens (Table 8) in the drains, prorated for drain surface area, correspond to deposition rates of 7.0, 11.1, 1.2, and $2.5 \mu\text{g/m}^2$, or 9.9, 15.9, 1.7, and 3.5% of the label application rate

of 70 mg/m². This variability is probably typical for the relatively uncontrolled commercial applications analyzed. The mass of MeP observed in the drains (Table 8 and Appendix 5) may be compared to the total mass applied to the fields that they bordered (total mass applied = field area x 0.7 kg/ha). For the four fields studied, the ratios were 0.11%, 0.17%, 0.02%, and 0.02%. These ratios can be compared to the effect of discharge after the legal holding period using data for MeP degradation rates in rice fields reported in another DPR study (Kollman et al., 1992). This study shows that after the 24-day holding period, the MeP concentration is ~0.02% of the initial level (1,890 µg/L to 0.38 µg/L). Discharge of the field after the holding period would release a mass of MeP equivalent to ~0.02% of the mass originally applied.

Table 4a. Post-application concentrations of methyl parathion and methyl paraoxon residues in agricultural drain effluent at Site 1; collected by autosampler on 5/12/91.^a

Upstream Aqueous Samples (Background)^b		
Sampling Interval	Methyl Parathion	Methyl Paraoxon
	-----µg/L-----	
0600-0712	ND ^c	ND
0713-0824	ND	ND
0825-0936	ND	ND
0937-1048	0.05	ND
1049-1200	0.06	ND
1201-1312	0.11	ND
1313-1424	0.15	ND
	0.18 ^d	ND ^d
Downstream Aqueous Samples (Offsite Deposition)		
Sampling Interval	Methyl Parathion	Methyl Paraoxon
	-----µg/L-----	
0600-0649	0.58	ND
0650-0738	1.56	ND
0739-0827	3.78	ND
0828-0916	5.33	ND
0917-1005	4.16	ND
1006-1054	4.72	ND
	4.2 ^d	ND ^d
1055-1143	3.15	ND
1144-1232	1.22	ND

- a. Methyl parathion applied aerially 0600-0630.
Wilbur-Ellis 5 formulation applied at label rate of 70 mg/m².
- b. Autosampler inadvertently programmed for 3-min subsample intervals instead of 2-min intervals.
- c. ND = None detected.
Minimum detection limit for methyl parathion/paraoxon is 0.05 µg/L.
- d. This split sample also analyzed by the quality control lab, Enseco/Cal Lab, West Sacramento, CA. Results not part of analysis.

Table 4b. Sampling variability study for Site 1; two sets of aqueous samples collected by hand during post-application period on 5/12/91.^a

SET ONE		SET TWO	
Methyl Parathion	Methyl Paraoxon	Methyl Parathion	Methyl Paraoxon
-----µg/L-----		-----µg/L-----	
4.28	ND ^b	4.55	0.07
4.48	ND	4.82	0.06
4.95	0.05	4.69	ND
4.44	ND	4.10 ^c	0.10 ^c
		4.45	0.11
Mean = 4.54	Mean = N/A	Mean = 4.63	Mean = N/A
SD = 0.29	SD = N/A	SD = 0.16	SD = N/A
CV = 6.4%		CV = 3.4%	

- Four samples collected simultaneously across transverse section of drain at downstream station. Each sample was composed of fifteen 120-mL subsamples collected at 1-min intervals.
- Minimum detection limit is 0.05 µg/L for methyl parathion/paraoxon.
- This split sample also analyzed by quality control lab, Enseco/Cal Labs, West Sacramento, CA. Results not part of analysis.

Table 4c. Deposition rates for methyl parathion and methyl paraoxon residues on banks of agricultural drain at Site 1, collected on mass deposition cards during and after application.^a

Location	Methyl Paraoxon	Methyl Paraoxon
	-----µg/m ² -----	
Upstream bank:		
Outer	259.4	5.4
Inner	254.0	4.3
Downstream bank:		
Outer	1,860	28.0
Inner	2,706	54.9

- Minimum detection limit = 0.3 µg/0.09 m² for methyl parathion and methyl paraoxon.

Table 5a. Post-application concentrations of methyl parathion and methyl paraoxon residues in agricultural drain effluent at Site 2; collected by autosampler on 5/24/91.^a

Upstream Aqueous Samples (Background)		
Sampling Interval	Methyl Parathion	Methyl Paraoxon
	-----µg/L-----	
1000-1036	0.05	ND ^b
1037-1113	0.05	0.05
1114-1150	ND	ND
1151-1227	ND	ND
1228-1304	0.05	ND
1305-1341	ND	ND
1342-1418	ND	ND
	0.06 ^c	ND ^c
1419-1448	ND	ND
Downstream Aqueous Samples (Offsite Deposition)		
Sampling Interval	Methyl Parathion	Methyl Paraoxon
	-----µg/L-----	
1000-1051	0.09	ND
1052-1142	5.92	ND
1143-1233	16.72	ND
1234-1324	5.29	ND
1325-1415 ^d	0.31	ND
	0.38 ^c	ND ^c
1416-1506 ^d	0.21	ND

- a. Methyl parathion applied aerially 1045-1052. Wilbur-Ellis 5 formulation applied at label rate of 70 mg/m².
- b. ND = None detected. Minimum detection limit for methyl parathion/paraoxon is 0.05 µg/L.
- c. This split sample also analyzed by the quality control lab, Enseco/Cal Lab, West Sacramento, CA. Results not part of analysis.
- d. Time intervals inaccurate due to autosampler malfunction; final two samples were hand sampled.

Table 5b. Sampling variability study for Site 2; one set of aqueous samples collected by hand during post-application period on 5/24/91.^a

Methyl Parathion	Methyl Paraoxon
-----µg/L-----	
0.22	ND ^b
0.20	ND
0.23	ND
0.19	ND
0.29 ^c	ND ^c
Mean = 0.21	Mean = N/A
SD = 0.02	SD = N/A
CV = 9.5%	

- a. Four samples collected simultaneously across transverse section of drain at downstream station.
 b. ND = none detected. Minimum detection limit = 0.05 ug/L.
 c. This split sample also analyzed by quality control lab, Enseco/Cal Labs, West Sacramento, CA. Results not part of analysis.

Table 5c. Deposition rates for methyl parathion and methyl paraoxon residues on banks of agricultural drain at Site 2, collected on mass deposition cards during and after application.^a

Location	Methyl Parathion	Methyl Paraoxon
-----µg/m ² -----		
<u>Upstream Bank:</u>		
Outer	792.2	43.1
Inner	3,293.8	167.9
Neighboring	ND ^a	ND
<u>Downstream Bank:</u>		
Outer	1,418.7	72.1
Inner	2,501.5	121.6
Neighboring	58.1	3.2

- a. ND = None detected. Minimum detection limit = 0.3 µg/0.09 m² for methyl parathion and methyl paraoxon.

Table 6a. Post-application concentrations of methyl parathion and methyl paraoxon residues in agricultural drain effluent at Site 3; collected by autosampler on 6/07/91.^a

Upstream Aqueous Samples (Background)

Sampling Interval	Methyl Parathion	Methyl Paraoxon
	-----µg/L-----	
0630-0715	ND ^b	ND
0716-0800	0.06	ND
0801-0845	ND	ND
0846-0930	ND	ND
0931-1015	ND	ND
	ND ^c	ND ^c
1016-1100	ND	ND
1101-1145	ND	ND
1146-1230	ND	ND

Downstream Aqueous Samples (Offsite Deposition)

Sampling Interval	Methyl Parathion	Methyl Paraoxon
	-----µg/L-----	
0630-0715	ND	ND
0716-0800	0.05	ND
0801-0845	0.41	ND
0846-0930	1.67	ND
	1.8 ^c	ND ^c
0931-1015	2.76	ND
1016-1100	0.22	ND
1101-1145	0.05	ND
1146-1230	ND	ND

- a. Methyl parathion applied aerially 0715-0805.
Clean Crop 5E formulation applied at label rate of 70 mg/m².
- b. ND = None detected.
Minimum detection limit for methyl parathion/paraoxon is 0.05 µg/L.
- c. This split sample also analyzed by the quality control lab, Enseco/Cal Lab, West Sacramento, CA. Results not part of analysis.

Table 6b. Sampling variability study for Site 3; two sets of aqueous samples collected by hand during post-application period on 6/07/91.^a

SET ONE		SET TWO	
Methyl Parathion	Methyl Paraoxon	Methyl Parathion	Methyl Paraoxon
-----µg/L-----		-----µg/L-----	
0.09	ND ^b	ND	ND
0.08	ND	ND	ND
0.09	ND	0.05	ND
0.05	ND	0.05	ND
0.10 ^c	ND ^c		
Mean = 0.08	Mean = N/A	Mean = N/A	Mean = N D
SD = 0.02	SD = N/A	SD = N/A	SD = N/A
CV = 25%			

- a. Four samples collected simultaneously across transverse section of drain at downstream station. Each sample was composed of fifteen 120-mL subsamples collected at one-minute intervals.
- b. ND = none detected. Minimum detection limit for methyl parathion/paraoxon is 0.05 µg/L.
- c. This split sample also analyzed by quality control lab, Enseco/Cal Labs, West Sacramento, CA. Results not part of analysis.

Table 6c. Deposition rates for methyl parathion and methyl paraoxon residues on banks of agricultural drain at Site 3, collected on mass deposition cards during and after application.^a

Location	Methyl Parathion	Methyl Paraoxon
	-----µg/m ² -----	
Upstream Bank:		
Outer	36.6	2.2
Inner	16.2	1.1
Neighboring	58.1	3.2
Downstream Bank:		
Outer	279.9	18.3
Inner	670.6	28.0
Neighboring	ND ^a	ND

- a. ND = None detected. Minimum detection limit = 0.3 µg/0.09 m² for methyl parathion and methyl paraoxon.

Table 7a. Post-application concentrations of methyl parathion and methyl paraoxon residues in agricultural drain effluent at Site 4; collected by autosampler on 6/19/91.^a

Upstream Aqueous Samples (Background)

Sampling Interval	Methyl Parathion	Methyl Paraoxon
	-----µg/L-----	
0645-0722	ND ^b	ND
0723-0759	1.41	ND
0800-0836	4.44	ND
0837-0913	7.62	ND
	9.64 ^c	ND ^c
0914-0950	12.63	ND
0951-1027	8.95	ND
1028-1104	9.36	ND
1105-1141	8.91	ND

Downstream Aqueous Samples (Offsite Deposition)

Sampling Interval	Methyl Parathion	Methyl Paraoxon
	-----µg/L-----	
0645-0722	ND	ND
0723-0759	0.24	ND
0800-0836	4.15	ND
0837-0913	4.73	ND
	5.0 ^c	ND ^c
0914-0950	2.25	ND
0951-1027	1.08	ND
1028-1104	2.21	ND
1105-1141	4.35	ND

- a. Methyl parathion applied aerially 0655-0740.
Wilbur-Ellis 5 formulation applied at label rate of 70 mg/m².
- b. ND = None detected.
Minimum detection limit for methyl parathion/paraoxon is 0.05 µg/L.
- c. This split sample also analyzed by the quality control lab, Enseco/Cal Lab, West Sacramento, CA. Results not part of analysis.

Table 7b. Sampling variability study for Site 4; two sets of aqueous samples collected by hand during post-application period on 6/19/91.^a

SET ONE		SET TWO	
Methyl Parathion	Methyl Paraoxon	Methyl Parathion	Methyl Paraoxon
-----µg/L-----		-----µg/L-----	
2.22	ND	4.52	ND
2.37	ND	4.38	ND
2.77	ND	4.01	ND
2.72	ND	4.9 ^c	ND ^c
		4.8	ND
Mean = 2.52	Mean = ND	Mean = 4.43	Mean = ND
SD = 0.27	SD = N/A	SD = 0.33	SD = N/A
CV = 25%		CV = 7.4%	

- Four samples collected simultaneously across transverse section of drain at downstream station. Each sample was composed of fifteen 120-mL subsamples collected at 1-min intervals.
- ND = none detected. Minimum detection limit for methyl parathion/paraoxon is 0.05 µg/L.
- This split sample also analyzed by quality control lab, Enseco/Cal Labs, West Sacramento, CA. Results not part of analysis.

Table 7c. Deposition rates for methyl parathion and methyl paraoxon residues on banks of agricultural drain at Site 4, collected on mass deposition cards during and after application.^a

Location	Methyl Parathion	Methyl Paraoxon
	-----µg/m ² -----	
<u>Upstream bank:</u>		
Outer	141.0	5.4
Inner	201.3	10.8
Neighboring	160.4	5.4
<u>Downstream bank:</u>		
Outer	381.0	14.0
Inner	1,197.0	37.7
Neighboring	2.2	ND ^a

- ND = None detected. Minimum detection limit = 0.3 µg/0.09 m² for methyl parathion and methyl paraoxon.

Comments on Site-Specific Conditions

Site 1 was a large field, with a correspondingly large drain, in a closed irrigation system; the drain dimensions are presented in Table 2. At this Site the drain discharge was measured directly at the downstream station at a rectangular weir, and the elution time was estimated from the corresponding flow rate. The upstream (background) autosampler was inadvertently programmed for a three-minute rather than a two-minute cycle, and sampled the drain for a longer time than the downstream autosampler. Low background levels of MeP were found at the upstream station (maximum of 0.15 $\mu\text{g/L}$), and the observed concentration of MeP at the downstream station peaked at 5.33 $\mu\text{g/L}$. The downstream set of MD cards (on the north side of the field) showed significant deposition of MeP (2,706 $\mu\text{g/m}^2$ on the inner bank, and 1,860 $\mu\text{g/m}^2$ on the outer bank), while those on the upstream, westerly, side showed little (254 $\mu\text{g/m}^2$ inner bank and 259 $\mu\text{g/m}^2$ outer bank; see Table 4c and Figure 2). The flight pattern here was a "racetrack" or "round-robin" conformation (Figure 2), with the application leg parallel to the downstream edge of the field. The prevailing wind was from slightly north of west and would tend to blow MeP away from the upstream edge and, to a lesser extent, away from the downstream edge. A similar amount of MeP was deposited on MD cards on inner and outer upstream banks; however, the downstream outer bank level was ~30% lower than the inner bank set. Due to time constraints, the neighboring field MD samples were not taken. The aqueous concentrations at the downstream station were still slightly elevated at the end of measurement (see Figure 6). This indicates that the MeP slug did not clear the drain in the period of a single traversal at the measured velocity; this is not unexpected for so large a drain where diffusion and mixing would be significant factors.

Figure 6. Concentrations of methyl parathion at downstream autosampler during post-application period at Site 1 on 5/12/91.

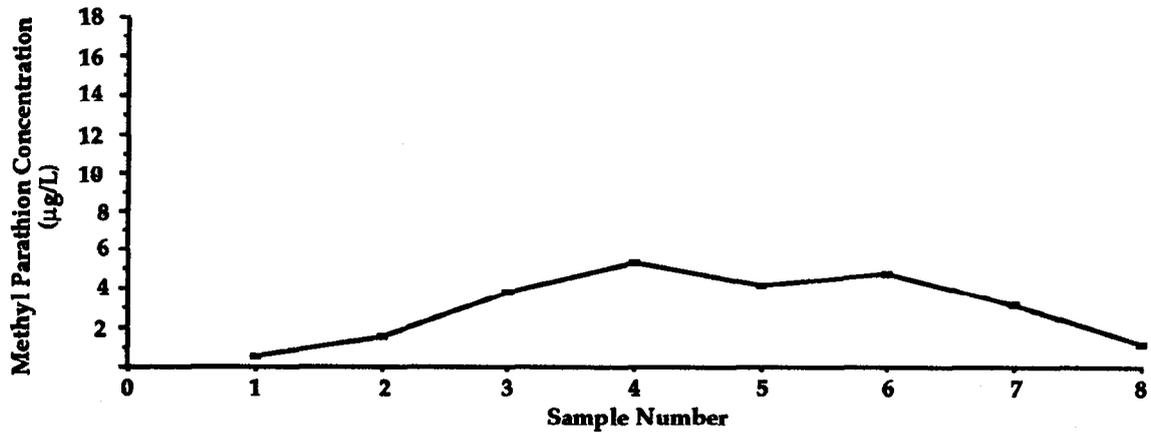


Figure 7. Concentrations of methyl parathion at downstream autosampler during post-application period at Site 2 on 5/24/91.

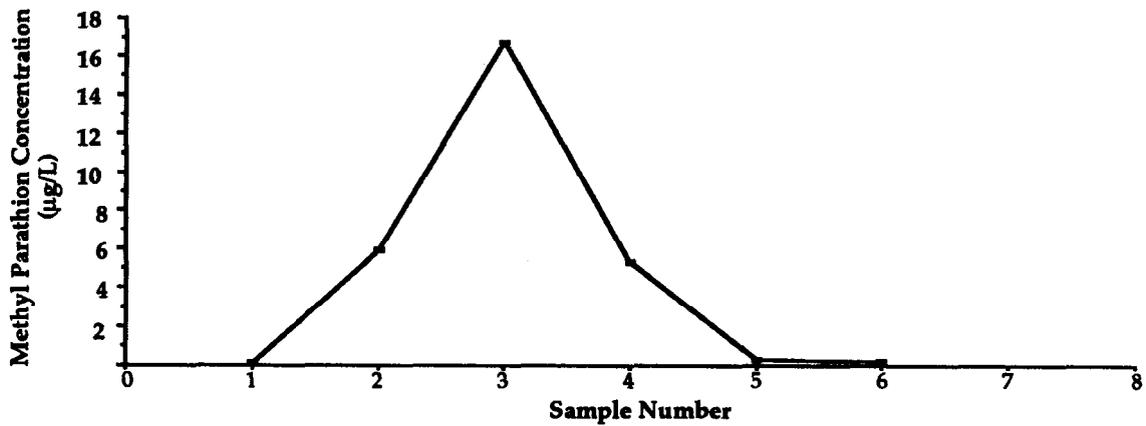


Figure 8. Concentrations of methyl parathion at downstream autosampler during post-application period at Site 3 on 6/7/91.

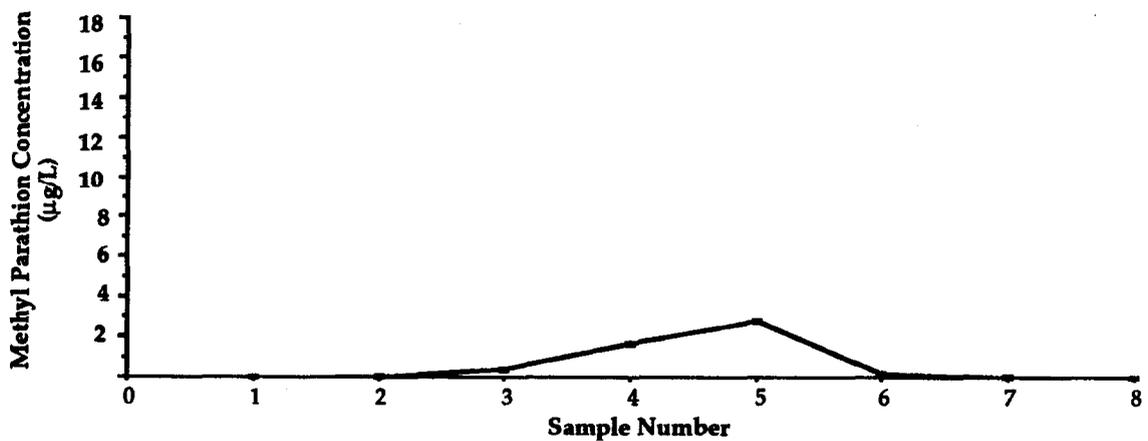


Figure 9a. Concentrations of methyl parathion at upstream autosampler during post-application period at Site 1 on 6/19/91.

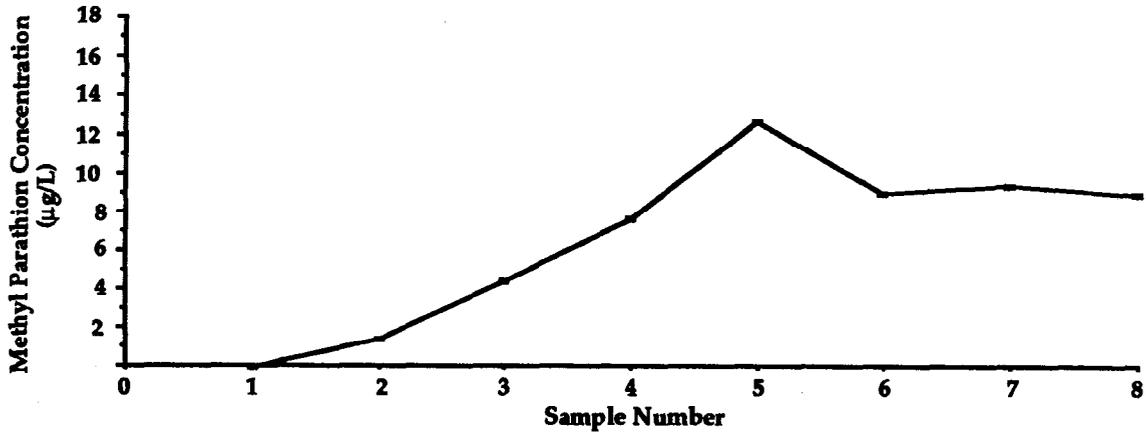
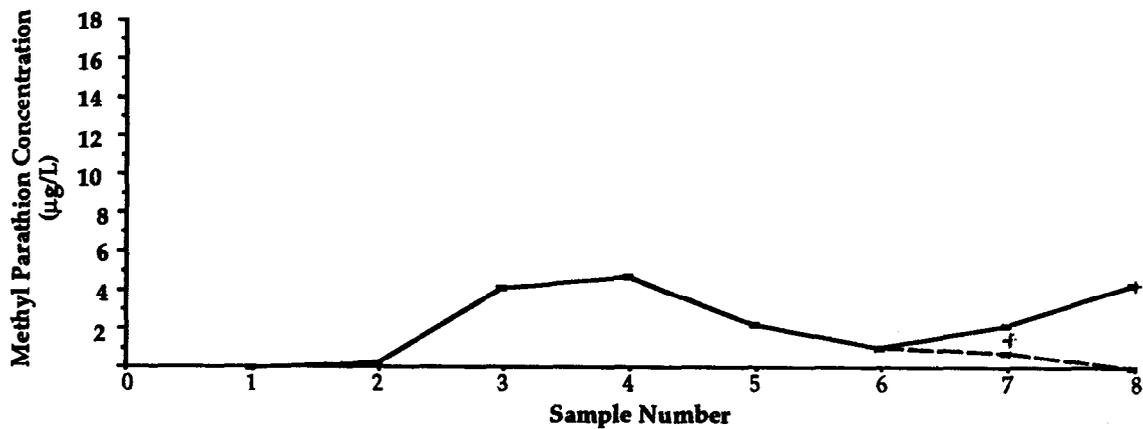


Figure 9b. Concentrations of methyl parathion at downstream autosampler during post-application period at Site 4 on 6/19/91.



- Legend:**
- Observations measured at downstream autosampler.
 - + Concentrations at upstream autosampler, offset by six periods (so that upstream 3 coincides with downstream 8- see table 7a).
 - Estimated contribution from sampling length of ditch after correction for upstream level.

At *Site 2*, the downstream autosampler malfunctioned during sample collection and the last two samples were hand collected. Due to the resulting time constraints, only one set of sampling variability data were collected. Both upstream and downstream MD cards showed elevated deposition (792 to 3,294 $\mu\text{g}/\text{m}^2$; see Table 5c and Figure 3). The outer bank had much lower levels than the inner bank (downstream: 1,419 $\mu\text{g}/\text{m}^2$ outer bank and 2,501 $\mu\text{g}/\text{m}^2$ inner bank; upstream: 792 $\mu\text{g}/\text{m}^2$ outer bank and 3,294 $\mu\text{g}/\text{m}^2$ inner bank). The prevailing wind was very light from the north, which would tend to blow MeP toward the downstream edge. The flight pattern was serpentine (see Figure 3), with the application leg aligned on the southerly (downstream) edge; the pesticide was applied in a single load. Although only trace amounts of MeP (up to 0.05 $\mu\text{g}/\text{L}$) were present in the background samples, a maximum of 16.7 $\mu\text{g}/\text{L}$ was found at the downstream station. The MeP concentrations at the downstream station returned to baseline well within the term of the experiment (see Figure 7).

At *Site 3*, a high tension power line angled across the field and interfered slightly with the application. Mass deposition cards showed low levels of deposition (16-671 $\mu\text{g}/\text{m}^2$), concentrated mainly on the inner bank along the downstream edge of the field (671 $\mu\text{g}/\text{m}^2$; see Table 6c and Figure 4). The prevailing wind was from slightly east of north which would tend to blow MeP away from the downstream edge towards the upstream edge. The flight pattern was serpentine with the application leg aligned along the field's downstream edge. Only one background sample was above the MeP detection limit (0.06 $\mu\text{g}/\text{L}$). A peak of 1.67 $\mu\text{g}/\text{L}$ was found at the downstream station, and concentrations returned to baseline within the duration of measurement (see Figure 8).

Site 4 had a topology that complicated the experiment. The drain beside the field was fed with water from a warming pond at the top of the field, which was supplied by a pumped well (see Figure 5). Samples from the upstream autosampler showed large and increasing amounts of MeP flowing into the drain from the warming pond (from "none detected" just after the application to 12.6 $\mu\text{g/L}$ approximately two hours post application; see Table 7a). This suggests that either substantial drift or swath displacement occurred. As the warming pond was shallow (estimated depth ~ 8 cm), any offsite deposition to the pond itself could have resulted in significant concentrations (a full application of 70 mg/m^2 in a 10-cm deep pond is equivalent to $\sim 700 \mu\text{g/L}$). The prevailing wind was highly variable with one main component from slightly west of north; this would tend to blow MeP from the warming pond back into the field and to similarly affect the entire sampling drain. However, there was also a southerly component that may have had the opposite effect.

At the downstream autosampler, observed MeP concentrations peaked at 4.73 $\mu\text{g/L}$, declined, but then began to rise again during the last two sampling periods (from 1.1 to 4.35 $\mu\text{g/L}$), probably due to the passage of the warming pond MeP residue (see Figure 9). These concentrations were corrected for by skewing the upstream readings along the time axis until they matched the upswing at the downstream station. This skewed data and the corrected readings are also shown in Figure 9, and the results in Table 8. These corrections are approximate, but only affect the final two samples, and follow the observed trend.

A further complication was the malfunction of the Crisafulli Pump downstream from the Site, which pumped water from the drain into the lower half of the

Table 8. Comparative summary of results for four rice methyl parathion application sites; observed aqueous concentrations of methyl parathion in agricultural drains and observed mass deposition rates on banks of drains.

Site	1	2	3	4
Application rate (mg/m ²)	70	70	70	70
Drain data				
Mean width (m)	7.01	2.84	2.84	3.44
Mean depth (m)	1.34	0.13	0.14	0.37
Sampling length (m)	2,738	1,146	1,426	787
Cross section (m ²)	9.39	0.37	0.40	1.27
Surface area (m ²)	19,193.4	3,254.6	4,049.8	2,707.3
Ditch volume (m ³)	25,719.1	423.1	567.0	1,001.7
Discharge (m ³ /s)	1.851	0.419	0.341	0.23 ^a
Mean velocity (m/s)	0.197	0.265	0.406	0.183 ^a
Density (g/cm ³)	0.993	0.989	0.992	0.997
Downstream sampling data (per bottle)				
Interval (s)	2,962	3,060	2,700	2,213
Discharge water volume (m ³)	5,482.7	1,282.1	920.7	509.0
Discharge water mass (mg)	5.44E+12	1.27E+12	9.13E+11	5.07E+11
Mass of MeP in aqueous samples (concentration x discharge mass)				
Sample 1 (mg)	3,157.7	114.1	0.0	0.0
Sample 2 (mg)	8,493.1	7,506.8	46.1	121.8
Sample 3 (mg)	20,579.4	21,201.6	374.5	2,106.0
Sample 4 (mg)	9,023.5	6,707.9	1,522.5	2,400.3
Sample 5 (mg)	22,648.2	393.1	2,520.8	1,142.3
Sample 6 (mg)	25,702.5	266.3	200.9	548.1
Sample 7 (mg)	17,149.5	n/a	46.1	406.0 ^b
Sample 8 (mg)	6,647.5	n/a	22.8	0.0 ^b
Total MeP (mg)	133,401.4	36,189.8	4,733.7	6,724.5
MeP/ditch area (mg/m ²)	6.95	11.12	1.17	2.48
Percent of 100% application	9.9%	15.9%	1.7%	3.5%
Mass deposition cards				
Upper inner bank (mg/m ²)	0.25	3.30	0.02	0.20
Upper outer bank (mg/m ²)	0.26	0.79	0.04	0.14
Downstream inner bank (mg/m ²)	2.71	2.50	0.67	1.20
Downstream outer bank (mg/m ²)	1.86	1.42	0.28	0.38
Mean MeP/area (mg/m ²)	1.27	2.00	0.25	0.48
Percentage of aqueous	18.3%	18.0%	21.5%	19.3%
Percentage of applied	1.8%	2.9%	0.4%	0.7%

a. These values estimated from the profile of the concentrations measured at the downstream station.

b. These values estimated from upstream background methyl parathion concentrations to predict effect of offsite deposition to warming pond.

field. The pump stopped at some indeterminate point during the safe period. The result was a change in the drain flow rate, which appeared to be about half of that measured before the application. An estimation of the flow rate for this drain was made from the observed concentration profile as follows. Each concentration profile can be considered as a signal processing event, the response of the drain to a stimulus, with a period or duration related to the flow rate of the drain. The idealized response would be rectangular, but the effects of mixing, diffusion, application, and settling time, etc. distort this to the general forms in Figures 1, 2, and 3. A convenient measure related to the period of such signals is the time duration between the two points where the concentration is half the maximum, the half-height width. For each of the first three sites the half-height width was determined and compared to the period for passage of the MeP slug predicted from the flow rate. The mean ratio was 1.3, and this was used to convert the duration between half-height points at Site 4 to a flow rate; this flow rate was used in Table 8.

The drain was situated along a single side of this field and all MD cards showed some deposition (see Table 7c), but this was most pronounced at the downstream inner bank. The flight conformation was a "racetrack" or "round-robin" (see Figure 5) with the application leg perpendicular to the drain. The wind direction was highly variable, but predominantly parallel to the drain. The MD cards in the upstream neighboring group also showed some deposition, consistent with the proposition that MeP entered the warming pond area.

Site 4 was located within a recirculating water district and the drain water was being pumped into the lower half of the field below the downstream sampling location; however, this warming pond configuration could occur in sites with more direct egress to public waterways.

Aqueous Samples

The aqueous sampling results for each site were accumulated to yield a total pesticide burden for the volume of water that passed the downstream station during the sampling period. This period had been calculated to allow the entire contents of the drain adjacent to the field to pass the downstream station. The pesticide burden for the drain was transformed to an equivalent deposition rate from the known surface area of the drain (see Appendix 5 and Table 8). The assumptions are that the MeP is well mixed in the water, and that the flow patterns of the drain did not leave behind pockets of significantly pesticide-laden water.

The efficiency of aqueous mixing is demonstrated by the sampling variability results (Tables 4b-7b). Between-sample variability was low at each of the sites ($SD = 0.02-0.33 \mu\text{g/L}$) indicating that placement of the autosampler intake tubing yielded a representative sample. The general trend toward low terminal values for the autosampler samples (Figures 6-9) indicates that mixing is adequate; there is certainly some mixing inefficiency at Site 4 due to the flow conditions described above, and a smaller effect at Site 1 where the drain was very large. If pesticide residue still remained in the drain adjacent to the field after the sampling period, the results would underestimate the magnitude of offsite deposition.

None of the sites had significant MeP levels at either the upstream or downstream stations at the beginning of the sample collection. Thus the MeP concentrations detected downstream may be attributed to effects of this application. Since there was negligible movement of water from the fields into the test drains, it is reasonable to attribute the levels found to deposition of MeP into the drain during the application either from wind-driven drift or from swath displacement.

After the peak MeP level had passed the downstream station, concentrations did not taper off as rapidly as anticipated from flow-rate calculations. This may be due to either flow rate, drift rate, or elution problems. The drain velocity generally changed between site preparation and application (by a factor of 10 at Site 1), and estimates for autosampler settings were made as close to the application time as possible, usually at ~4 am. Flow rates remained relatively constant during sampling. The assumption that most of the airborne residue would have settled to the ground in 90 minutes may be incorrect. However, the most likely factor is elution of MeP-contaminated water. Clean water flowing in at the upstream end may mix with and dilute the sampling water rather than pushing it out as a slug.

Mass Deposition Samples

The MD samples demonstrated that offsite deposition was variable at each site, and that little MeP fell on the cards monitoring neighboring fields. In general, less MeP was detected on the outer bank than on the inner bank. More MeP was found on MD cards that paralleled the application leg of flight patterns at sites where drain location allowed this comparison.

The mean MeP values for MD cards are significantly lower than the depositions calculated from the aqueous burden of the drain; MD card levels range from 18.3% to 21.5% of the aqueous values. Recoveries for MD cards spiked at the lab were close to 100% so the discrepancy is most likely due to experimental factors. One possibility is that cards may not collect a representative sample of aerial deposition. Evaporation and photolysis of MeP were other uncontrolled factors (Woodrow, et al. 1978). MeP application took place in late spring with ambient temperatures of 7.6 to 26.3 °C. The MD cards were left exposed for up to two hours after the end of the application (90 minutes before re-entry and ~30 minutes collection time). The actual MeP recovery rate for MD cards under field conditions needs to be established to distinguish between these factors. An experiment to determine MeP recoveries after exposure of spiked MD cards to photolytic conditions and elevated temperatures for up to two hours is planned.

IV. CONCLUSIONS

Significant concentrations of MeP were observed in agricultural drains at the sites of aerial pesticide application. Peak levels in all drains exceeded the 1991 target levels. The study shows that this is probably the result of off-site deposition at the time of application. MeP is detected in locations where the prevailing wind blows back toward the field, and appears to be related to the application process rather than wind-induced drift. Higher residues were observed where the flight path paralleled sets of MD cards, suggesting that swath misalignment may be a factor. If further studies confirm that this is the case, some mitigation could result from conservative flight path practices around agricultural drains.

The pesticide burden in the drain moves as a slug into the effluent reticulation of the drainage system, presumably merging, diluting, and dissipating as it goes. The rate at which concentrations diminish to acceptable levels depends upon flow rates and irrigation management practices downstream. A broader study correlating MeP concentrations in downstream waterways with rice cultivation events involving MeP would be required to ascertain the potential impact of these releases on sensitive aquatic species.

Sources of Error. The MeP concentrations measured at the autosampler are fairly accurate (2-4% CV for the concentration maxima); drain water with these reported concentrations did move on downstream. However, the calculated deposition rates are only approximate: The drain surface area has a likely error of $\pm 10\%$; discharge varied during each experiment and has a possible error of $\pm 20\%$. The deposition therefore has a possible error of $\pm 30\%$. The accuracy for the MD card MeP analyses was 3-6% under lab conditions for the MeP deposition range observed at the field sites. However, the actual experimental values were consistently $\sim 20\%$ of the calculated deposition (regression equation is: expected MeP mass deposition = $-0.25 \text{ mg/m}^2 + 5.68$ (observed mass deposition), $r = 1.0$). This discrepancy may be due to exposure of the MD cards to sunlight during safe time, and this is currently under investigation. There are no reports showing that MD cards are an accurate means of detecting application levels in the field where ambient conditions are inherently variable.

The poor correlation of the MD card MeP levels with the calculated deposition from aqueous concentrations and the possible errors in the latter require that care be used in applying these results operationally.

V. REFERENCES

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A P P E N D I C E S

Appendix 1: Sample Extraction and Analysis Methods

CALIFORNIA DEPT. OF FOOD & AGRIC.
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ENVIRONMENTAL MONITORING SECTION
3292 Meadowview Road
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(916) 427-4649/4999

Original Date: 06/09/89
Supercedes: New
Current Date: 07/02/91
Method #:

METHYL PARATHION AND METHYL PARAOXON IN RICE DRAIN WATER

SCOPE:

This method is for the determination of Methyl Parathion and Methyl Paraoxon in rice drain water.

PRINCIPLE:

The samples of water were extracted by shaking in a separatory funnel with methylene chloride. The extract was filtered and evaporated to dryness. It was then transferred and brought up to final volume with acetone. The extract was analyzed by gas chromatography using a flame photometric detector (FPD).

REAGENTS AND EQUIPMENT:

Methylene chloride and acetone (pesticide residue grade)
Sodium sulfate (anhydrous)
Steam bath (Precision Scientific Inc.)
Nitrogen evaporator (Organomation Model # 12)
Vortex mixer for test tubes
Balance (Mettler PC 4400)

ANALYSIS:

- 1) Remove samples from refrigerated storage and allow them to come to room temperature. Samples consist of approximately 1 L and are stored in 1 L amber glass bottles to prevent any photodegradation from occurring.
- 2) Record weight of the sample by weighing sample bottle before and after transfer.
- 3) Extract sample by shaking with 100 mL of methylene chloride for 2 min. Pressure builds up during extraction so venting is necessary.
- 4) Allow layers to separate and filter the organic layer through 25 g anhydrous sodium sulfate and filter paper. Collect extract in a 500 mL boiling flask.
- 5) Repeat steps 3 & 4 two more times using 80 mL of methylene chloride each time.
- 6) Rinse sodium sulfate with 20 mL additional methylene chloride and collect in the same 500 mL boiling flask.

- 7) Take extract just to dryness on a steam bath. Add 1-2 mL acetone to the flask to rinse down the sides.
- 8) Transfer extract to a graduated test tube. Rinse flask 3 times each with 2 mL of acetone. Transfer each wash to the same graduated test tube.
- 9) Place extract in a nitrogen evaporator with waterbath set at 35°C and evaporate to a final volume of 1 mL under a gentle stream of nitrogen.
- 10) Stopper the graduated test tube and mix contents by placing on a vibrating mixer for about 15 seconds. Submit sample for gas chromatographic analysis.

EQUIPMENT CONDITIONS:

Shimadzu: GC-14 A with FPD "P mode"
 Column: HP-17 (50% phenol methyl silicone) 10 m x 0.53 mm
 x 2.0 um
 Carrier gas: Helium, Flow rate: 20 mL/min
 Injector: 230°C
 Detector: 260°C
 Temperature Program: Initial temp: 170°C held for 1 minute
 Rate: 10°C/minute
 Final temp: 220°C held for 4 minutes
 Injection volume: 2 uL
 Retention times: Methyl Parathion 3.53 ± 0.1 min. Methyl Paraoxon 3.12 ± 0.1 min.

Varian: 3700 GC WITH FPD "P mode"
 Column: DB-210 (50% tri-fluoropropyl methyl polysiloxane) 15 m x 0.537 mm
 x 1.0 um
 Carrier gas: Helium, Flow rate: 17 mL/min
 Injector: 220°C
 Detector: 250°C
 Temperature: 190°C isothermal
 Injection volume: 2 uL
 Retention times: Methyl Parathion 1.38 ± 0.1 min. Methyl Paraoxon 1.80 ± 0.1 min.

CALCULATIONS:

PPB Methyl Parathion and Methyl Paraoxon

$$\text{ppb in sample} = \frac{(\text{peak height sample})(\text{ng/uL std})(\text{uL injected std})(\text{final volume mLs})(1000)}{(\text{peak height std})(\text{uL injected sample})(\text{weight of sample g})}$$

RECOVERIES:

*** Recoveries of Methyl Parathion and Methyl Paraoxon**

Levels	Methyl Parathion		Methyl Paraoxon	
	(Mean)	(SD)	(Mean)	(SD)
0.1 ppb (n=3)	103	15.4	113	5.77
1.0 ppb (n=3)	97	1.7	101	5.57
10.0 ppb (n=3)	96	3.1	99	1.0
100 ppb (n=3)	99	1.5	102	4.36
500 ppb (n=3)	97	5.5	---	---
1000 ppb (n=3)	102	5.03	---	---

Recovery validation was done prior to samples.

MINIMUM DETECTABLE LEVEL:

The minimum detectable level was 0.05 ppb with the S/N=3.

DISCUSSION:

Since levels varied widely, contamination was a real concern. One source of contamination was the rotary evaporator so a steam bath was used. The nitrogen blow down apparatus used disposable pipet tips which were changed after every sample to reduce the chance of cross contamination.

REFERENCE:

- 1) White, Jane, *Malation and Malaoxon in Water*, 1990, Environmental Monitoring Methods, California Department of Food and Agriculture.

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Original Date: 06/09/89
Supercedes: New
Current Date: 07/02/91
Method #:

METHYL PARATHION AND METHYL PARAOXON ON MASS DEPOSITION SAMPLES

SCOPE:

This method is for the determination of Methyl Parathion and Methyl Paraoxon on Kimbies[®].

PRINCIPLE:

Residues of Methyl Parathion and Methyl Paraoxon were extracted from Kimbies[®] absorbant towels (with a plastic backing) by shaking them with ethyl acetate. The extract was then concentrated for Methyl Paraoxon and analyzed by gas chromatograph using a flame photometric detector (FPD). Since the levels of Methyl Parathion were in milligram amounts an aliquot was taken and analyzed by gas chromatography using a flame photometric detector (FPD).

REAGENTS AND EQUIPMENT:

Ethyl acetate (pesticide residue grade)
Wide-mouth gallon jars / lids lined with tin foil
Mechanical shaker (G10 Gyrotory Shaker)
Rotary evaporator (Buchi/Brinkmann, R110)
Nitrogen evaporator (Organomation Model # 12)
Vibrating mixer for test tubes
Kimbie[®] (Kimberly-Clark Corp.)

ANALYSIS:

Place the folded Kimbies[®] in a gallon jar. Add 1000 mL of ethyl acetate and shake on a mechanical shaker for 30 min. at a setting of ~ 170 RPM.

Methyl Paraoxon

- 1) Take 350 mL of extract to be analyzed for methyl parathion and concentrate down just to dryness on a rotary evaporator with water bath set at 65°C. Rinse sides of flask with a few milliliters of ethyl acetate.
- 2) Transfer extract to a graduated test tube. Rinse flask 3 times each with 2 mL of ethyl acetate. Transfer each wash to the same graduated test tube.
- 3) Place extract on a nitrogen evaporator with water bath set at 35°C and evaporate to a final volume of 1 mL under a gentle stream of nitrogen.
- 4) Stopper the graduated test tube and mix contents by placing on a vibrating mixer for about 15 seconds. Submit sample for gas

chromatographic analysis.

Methyl Parathion

- 1) Take the initial ethyl acetate extract and submit sample for gas chromatographic analysis.

EQUIPMENT CONDITIONS:

METHYL PARAOXON

Shimadzu: GC-14 A with FPD "P mode"

Column: HP-17 (50% phenol methyl silicone) 10 m x 0.53 mm x 2.0 um

Carrier gas: Helium, flow rate: 15 psi

Injector: 230°C

Detector: 260°C

Temperature Program: Initial Temp: 170°C held 1 minute

Rate: 10°C/minute

Final Temp: 220° held for 4 minutes

Injection volume: 2 uL

Retention times: Methyl Parathion 3.53 ± 0.1 min. Methyl Paraoxon 3.12 ± 0.1 min.

METHYL PARATHION

VARIAN 3700 GC WITH FPD "P mode"

Column: DB-210 (50% tri-fluoropropyl methyl polysiloxane) 15 m x 0.537 mm x 1.0 um

Carrier gas: Helium, flow rate: 20 psi

Injector: 220°C

Detector: 250°C

Temperature: 190°C isothermal

Injection volume: 2 uL

Retention times: Methyl Parathion 1.39 ± 0.05 Methyl parathion 1.80 ± 0.05

CALCULATIONS:

Micrograms (UG) METHYL PARAOXON

$$\text{ug in sample} = \frac{(\text{peak height sample})(\text{ng/uL std})(\text{uL injected std})(1000 \text{ mL})(\text{final volume mL})}{(\text{peak height std})(\text{uL injected sample})(350 \text{ mL})}$$

Micrograms (UG) METHYL PARATHION

$$\text{ug in sample} = \frac{(\text{peak height sample})(\text{ng/uL std})(\text{uL injected std})(\text{final volume mLs})}{(\text{peak height std})(\text{uL injected sample})}$$

FORTIFICATION:

Methyl Parathion and Methyl Paraoxon were spiked onto separate Kimbie[®] sheets at the levels listed below. The Kimbies[®] were allowed to dry before extracting them.

RECOVERIES:

*** Recoveries of Methyl Parathion and Methyl Paraaxon**

Levels	Methyl Parathion		Methyl Paraaxon	
	(Mean)	(SD)	(Mean)	(SD)
0.6 ug (n=3)	92	4.0	93	7.02
5.0 ug (n=3)	95	2.5	90	4.16
50 ug (n=3)	101	3.5	95	6.9
250 ug (n=3)	98	6.0	96	3.6
1000 ug (n=3)	98	1.2	97	2.9
5000 ug (n=3)	99	2.3	--	--
20,000 ug (n=3)	96	4.9	--	--

Recovery validation was done prior to the samples.

MINIMUM DETECTABLE LEVEL:

The minimum detectable level was 0.3 ug (5 kimble per sample) S/N-3

DISCUSSION:

Since levels varied widely, contamination was a real concern. The steam bath was considered, but the solvent in this case was ethyl acetate and would take a long time to evaporate. The rotary evaporator was used with a 50 mL acetone wash placed in between each sample.

REFERENCE:

- 1) White, Jane., *Malathion and Malaoxon on Mass Deposition Samples*, 1990, Environmental Monitoring Methods, California Department of Food and Agriculture.

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APPROVED BY: S. Mark Lee

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TITLE: Research Agricultural Chemist

Appendix 2: Laboratory Quality Control Methods and Results

Table A2-1. Storage dissipation data for the methyl parathion field studies (refrigerated at pH 3).

Study: 107/108							Sample Type: Surface Water			
Analyte: Methyl parathion							Lab: CDFA			
Detection Limit: 0.05 ppb							Chemist: Jane White			
Date: 4/23/91										
Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV %	
1638	0	3/25/91	3/26/91	19.1	20	95				
1639	0	3/25/91	3/26/91	17.6	20	88	92	4.9	5.4	
1695	2	3/27/91	4/1/91	18.38	20	92				
1696	2	3/27/91	4/1/91	18.46	20	92	92	0.0	0.0	
1709	4	3/29/91	3/29/91	19.69	20	98				
1710	4	3/29/91	3/29/91	19.56	20	98	98	0.0	0.0	
1728	8	4/2/91	4/2/91	18.63	20	93				
1729	8	4/2/91	4/2/91	19.69	20	98	96	3.5	3.7	
1800	10	4/4/91	4/9/91	19.94	20	99				
1801	10	4/4/91	4/9/91	20.04	20	100	100	0.7	0.7	
1844	14	4/8/91	4/9/91	19.81	20	99				
1845	14	4/8/91	4/9/91	19.86	20	99	99	0.0	0.0	

Table A2-2. Storage dissipation data for the methyl parathion field studies (refrigerated at pH 8.5).

Study: 107/108							Sample Type: Surface Water			
Analyte: Methyl parathion							Lab: CDFA			
Detection Limit: 0.05 ppb							Chemist: Jane White			
Date: 4/23/91										
Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV %	
1640	0	3/25/91	3/26/91	17.03	20	85				
1641	0	3/25/91	3/26/91	19.04	20	95	90	7.1	7.9	
1697	2	3/27/91	4/1/91	17.85	20	89				
1698	2	3/27/91	4/1/91	19.27	20	96	93	4.9	5.4	
1712	4	3/29/91	3/29/91	18.39	20	92				
1711	4	3/29/91	3/29/91	19.45	20	97	95	3.5	3.7	
1730	8	4/2/91	4/2/91	17.63	20	88				
1731	8	4/2/91	4/2/91	18.86	20	94	91	4.2	4.7	
1802	10	4/4/91	4/9/91	18.94	20	95				
1803	10	4/4/91	4/9/91	18.53	20	93	94	1.4	1.5	
1846	14	4/8/91	4/9/91	19.51	20	98				
1847	14	4/8/91	4/9/91	18.01	20	90	94	5.7	6.0	

Table A2-3. Storage dissipation data for the methyl parathion field studies (refrigerated at pH 3).

Study: 107/108				Sample Type: Surface Water					
Analyte: Methyl paraoxon				Lab: CDFA					
Detection Limit: 0.05 ppb				Chemist: Jane White					
Date: 4/23/91									
Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV %
1634	0	3/25/91	3/26/91	19.30	20	97			
1635	0	3/25/91	3/26/91	18.75	20	94	96	2.1	2.2
1699	2	3/27/91	4/1/91	19.69	20	98			
1700	2	3/27/91	4/1/91	20.00	20	100	99	1.4	1.4
1713	4	3/29/91	4/1/91	20.43	20	102			
1714	4	3/29/91	4/1/91	20.00	20	100	101	1.4	1.4
1732	8	4/2/91	4/2/91	19.43	20	97			
1733	8	4/2/91	4/2/91	19.15	20	96	97	0.7	0.7
1804	10	4/4/91	4/9/91	19.86	20	99			
1805	10	4/4/91	4/9/91	21.00	20	110	105	7.8	7.4
1848	14	4/8/91	4/9/91	20.34	20	102			
1849	14	4/8/91	4/9/91	19.82	20	99	101	2.1	2.1

Table A2-4. Storage dissipation data for the methyl parathion field studies (refrigerated at pH 8.5).

Study: 107/108				Sample Type: Surface Water					
Analyte: Methyl paraoxon				Lab: CDFA					
Detection Limit: 0.05 ppb				Chemist: Jane White					
Date: 4/23/91									
Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV %
1636	0	3/25/91	3/26/91	20.74	20	104			
1637	0	3/25/91	3/26/91	18.02	20	90	97	9.9	10.2
1701	2	3/27/91	4/1/91	14.54	20	72			
1702	2	3/27/91	4/1/91	13.33	20	67	70	3.5	5.1
1715	4	3/29/91	4/1/91	11.29	20	56			
1716	4	3/29/91	4/1/91	10.64	20	53	55	2.1	3.9
1734	8	4/2/91	4/2/91	5.9	20	30			
1735	8	4/2/91	4/2/91	5.94	20	30	30	0.0	0.0
1806	10	4/4/91	4/9/91	4.52	20	23			
1807	10	4/4/91	4/9/91	4.31	20	22	23	0.7	3.1
1850	14	4/8/91	4/9/91	1.21	20	6			
1851	14	4/8/91	4/9/91	1.25	20	6	6	0.0	0.0

Table A2-5. Storage dissipation data for the methyl parathion field studies.

Study: 107/108							Sample Type: Kimbie			
Analyte: Methyl parathion							Lab: CDFA			
Detection Limit: 0.3 ug/sample							Chemist: Jane White			
Date: 4/23/91										
Lab	Date	Date	Results	Spike Level	Recovery	\bar{X}	SD	CV		
Sample #	Day	Extracted	Analyzed (ug/sample)	(ug/sample)	%			%		
1643	0	3/25/91	3/25/91	96.83	100	97				
1644	0	3/25/91	3/25/91	94.94	100	95	96	1.4	1.5	
1704	2	3/27/91	3/27/91	96.08	100	96				
1705	2	3/27/91	3/27/91	91.47	100	91	94	3.5	3.8	
1718	4	3/29/91	4/1/91	89.00	100	89				
1719	4	3/29/91	4/1/91	89.98	100	90	90	0.7	0.8	
1723	8	4/2/91	4/2/91	89.16	100	89				
1724	8	4/2/91	4/2/91	89.77	100	90	90	0.7	0.8	
1810	10	4/4/91	4/9/91	95.63	100	96				
1811	10	4/4/91	4/9/91	100.14	100	100	98	2.8	2.9	
1839	14	4/8/91	4/9/91	97.34	100	97				
1840	14	4/8/91	4/9/91	93.72	100	94	96	2.1	2.2	

Table A2-6. Storage dissipation data for the methyl parathion field studies.

Study: 107/108							Sample Type: Kimbie			
Analyte: Methyl paraoxon							Lab: CDFA			
Detection Limit: 0.3 ug/sample							Chemist: Jane White			
Date: 4/23/91										
Lab	Date	Date	Results	Spike Level	Recovery	\bar{X}	SD	CV		
Sample #	Day	Extracted	Analyzed (ug/sample)	(ug/sample)	%			%		
1645	0	3/25/91	3/25/91	82.97	100	83				
1646	0	3/25/91	3/25/91	91.38	100	91	87	5.7	6.5	
1706	2	3/27/91	3/27/91	83.86	100	84				
1707	2	3/27/91	3/27/91	89.66	100	90	87	4.2	4.9	
1720	4	3/29/91	4/1/91	99.23	100	99				
1721	4	3/29/91	4/1/91	90.19	100	90	95	6.4	6.7	
1725	8	4/2/91	4/2/91	89.81	100	90				
1726	8	4/2/91	4/2/91	93.86	100	94	92	2.8	3.1	
1812	10	4/4/91	4/9/91	91.47	100	91				
1813	10	4/4/91	4/9/91	107.05	100	107	99	11.3	11.4	
1841	14	4/8/91	4/9/91	92.07	100	92				
1842	14	4/8/91	4/9/91	92.68	100	93	93	0.7	0.8	

Table A2-7. Method validation data (% recoveries) for the methyl parathion field studies.

Study: 107/108
 Analyte: Methyl parathion
 MDL: 0.05 ppb
 Date of Report: 4/13/91

Sample Type: Surface Water
 Lab: CDFA
 Chemist: Jane White

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
1821	0.13	0.1	130			
1837	0.09	0.1	89			
1856	0.09	0.1	93	104	22.6	21.7
1822	0.96	1.0	96			
1836	0.99	1.0	99			
1857	0.96	1.0	96	97	1.7	1.8
1823	9.96	10	99			
1836	9.28	10	93			
1858	9.73	10	97	96	3.1	3.2
1824	100.80	100	101			
1834	99.48	100	99			
1859	98.39	100	98	99	1.5	1.5
1825	486.00	500	97			
1833	513.00	500	103			
1860	459.00	500	92	97	5.5	5.7
1826	1448.00	1500	97			
1832	1544.00	1500	103			
1861	1608.00	1500	107	102	5.03	4.92
OVERALL:				99	8.8	8.8
\bar{X}	SD	LWL	UWL	LCL	UCL	
99	8.8	90	108	81	117	

Table A2-8. Method validation data (% recoveries) for the methyl parathion field studies.

Study: 107/108
 Analyte: Methyl paraoxon
 MDL: 0.05 ppb
 Date of Report: 4/13/91

Sample Type: Surface Water
 Lab: CDFA
 Chemist: Jane White

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
1817	0.11	0.1	110			
1831	0.12	0.1	120			
1862	0.11	0.1	110	113	5.77	5.09
1818	1.00	1.0	100			
1830	0.96	1.0	96			
1863	1.07	1.0	107	101	5.57	5.51
1819	9.81	10	98			
1829	10.01	10	100			
1864	9.88	10	99	99	1.0	1.0
1820	96.72	100	97			
1828	104.85	100	105			
1865	103.63	100	104	102	4.36	4.27
OVERALL:				104	7.03	6.77
\bar{X}	SD	LWL	UWL	LCL	UCL	
102	7.03	95	109	88	116	

LWL/UWL (lower warning limit/ upper warning limit) = mean +/- SD
 LCL/UCL (lower control limit/ upper control limit) = mean +/- 2 SD

Table A2-9. Method validation data (% recoveries) for the methyl parathion field studies.

Study: 107/108				Sample Type: Kimbie		
Analyte: Methyl parathion				Lab: CDFA		
MDL: 0.3 ug/sample				Chemist: Jane White		
Date of Report: 4/23/91						
Lab Sample #	Results (ug/sample)	Spike Level (ug/sample)	Recovery %	\bar{X}	SD	CV (%)
1930	0.55	0.6	92			
1968	0.54	0.6	89			
1976	0.58	0.6	97	93	4.0	4.4
1931	4.90	5.0	98			
1969	4.73	5.0	95			
1977	4.64	5.0	93	95	2.5	2.6
1932	52.60	50	105			
1970	49.75	50	99			
1978	49.86	50	99	101	3.5	3.4
1933	229	250	92			
1971	242	250	97			
1979	260	250	104	98	6.0	6.2
1934	994	1000	99			
1972	972	1000	97			
1980	998	1000	99	98	1.2	1.2
1935	5122	5000	102			
1973	4883	5000	98			
1981	4933	5000	98	99	2.3	2.3
1936	18605	20000	93			
1974	18706	20000	94			
1982	20355	20000	102	96	4.9	5.1
OVERALL:				97	4.1	4.2
\bar{X}	SD	LWL	UWL	LCL	UCL	
97	4.1	93	101	89	105	

Table A2-10. Method validation data (% recoveries) for the methyl parathion field studies.

Study: 107/108				Sample Type: Kimbie		
Analyte: Methyl paraoxon				Lab: CDFA		
MDL: 0.3 ug/sample				Chemist: Jane White		
Date of Report: 4/23/91						
Lab Sample #	Results (ug/sample)	Spike Level (ug/sample)	Recovery %	\bar{X}	SD	CV (%)
1925	0.55	0.6	92			
1963	0.51	0.6	86			
1983	0.60	0.6	100	93	7.02	7.58
1926	4.46	5.0	89			
1964	4.74	5.0	95			
1984	4.43	5.0	87	90	4.16	4.61
1927	49.54	50	99			
1965	49.76	50	99			
1985	43.33	50	87	95	6.9	7.3
1928	243	250	97			
1966	230	250	92			
1986	247	250	99	96	3.6	3.8
1929	1000	1000	100			
1967	955	1000	95			
1987	946	1000	95	97	2.9	3.0
OVERALL:				94	5.0	5.3
\bar{X}	SD	LWL	UWL	LCL	UCL	
94	5.0	89	99	84	104	

LWL/UWL (lower warning limit/ upper warning limit) = mean +/- SD

LCL/UCL (lower control limit/ upper control limit) = mean +/- 2 SD

Table A2-11. Continuing quality control data for the methyl parathion field study.

Study: 108
 Analyte: Methyl parathion
 MDL: 0.05 ppb
 Date of Report: 7/10/91

Sample Type: Surface Water
 Lab: CDFA
 Chemist: Jane White

Extraction Set Sample No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
1009-20	2396	0.098	0.10	98			
1001-5, 1021-25, 1031	2399	0.48	0.5	96			
4001-11	2922	0.46	0.5	92	94	3.5	3.7
1049, 1051, 1053, 2001	2436	0.99	1.0	99			
3006, 3019-26	2778	0.95	1.0	95			
4073-74	2958	0.92	1.0	92	95	3.5	3.7
2001-4, 2015-20	2655	4.65	5.0	93			
2005-14	2669	4.99	5.0	99			
3001-12	2776	4.86	5.0	98			
4026-30	2925	4.78	5.0	96			
4012-21, 4025	2925	4.78	5.0	98	97	2.4	2.5

OVERALL: 96 2.7 2.8

Table A2-12. Continuing quality control data for the methyl parathion field study.

Study: 108
 Analyte: Methyl paraoxon
 MDL: 0.05 ppb
 Date of Report: 7/10/91

Sample Type: Surface Water
 Lab: CDFA
 Chemist: Jane White

Extraction Set Sample No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
1049, 1051, 1053	2439	1.08	1.0	108			
2005-14	2668	0.90	1.0	90			

OVERALL: 99 13 13

Table A2-13. Duplicate quality control results for aqueous methyl parathion/paraoxon analyses. Field samples split and analyzed by CDFA Lab (detection limit = MDL = 0.05 µg/L for methyl parathion/paraoxon) and by Enseco/Cal Lab (MDL = 0.05 µg/L for methyl parathion, and 0.10 µg/L for methyl paraoxon).

Site	Methyl Parathion		µg/L	Methyl Paraoxon	
	CDFA Lab	Enseco Lab		CDFA Lab	Enseco Lab
1	0.15	0.18		ND ^a	ND
	4.72	4.2		ND	ND
	4.69	4.1		ND	0.1
2	ND	0.06		ND	ND
	0.31	0.38		ND	ND
	0.19	0.29		ND	ND
3	ND	ND		ND	ND
	1.67	1.8		ND	ND
	0.05	0.1		ND	ND
4	7.62	9.64		ND	ND
	4.73	5.0		ND	ND
	4.01	4.9		ND	ND

a. ND = none detected.

Table A2-14. Continuing quality control data for the methyl parathion field study.

Study: 108
 Analyte: Methyl parathion
 MDL: 0.3 ug/sample
 Date of Report: 7/10/91

Sample Type: Kimbie
 Lab: CDFA
 Chemist: Jane White

Extraction Set Sample No.'s	Lab #	Results (ug/sample)	Spike Level (ug/sample)	Recovery %	\bar{X}	SD	CV (%)
1034-39	2403	0.58	0.6	96			
2034-40	2774	984.5	1000	98			
3034-40	2847	1015	1000	102			
4034-40	2956	962.0	1000	96			

OVERALL: 98 2.8 2.9

Table A2-15. Continuing quality control data (blind spikes) for the methyl parathion field study.

Study: 107/108
 Analyte: Methyl parathion
 MDL: 0.05 ppb
 Date of Report: 7/10/91

Sample Type: Surface Water
 Lab: Enseco-Cal, CDFA
 Chemist: Calvin Tanaka (Enseco-Cal)
 Chemist: Jane White(CDFA)

Lab	Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
Enseco-Cal	2050	1.0	1.0	95			
Enseco-Cal	2038	1.1	1.0	110			
Enseco-Cal	1038	1.1	1.0	110			
Enseco-Cal	3089	1.0	1.0	100	104	7.5	7.2
CDFA	1037	0.76	1.0	76			
CDFA	4021	0.88	1.0	88	82	8.5	10.3

Table A2-16. Continuing quality control data (duplicate matrix spikes) for the methyl parathion field study.

Study: 108
 Analyte: Methyl parathion
 MDL: 0.05 ppb
 Date of Report: 7/10/91

Sample Type: Surface Water
 Lab: Enseco-Cal Analytical
 Chemist: Calvin Tanaka

Extraction Set Sample No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
2061, 2067, 2074, 3032	58577	0.48	0.50	96			
		0.46	0.50	92	94	2.8	3.0
3059, 3066, 3074, 3089, 5027	58788	0.44	0.50	89			
		0.54	0.50	109	99	14.1	14.3
OVERALL:					97	8.8	9.1

Table A2-17. Continuing quality control data (duplicate matrix spikes) for the methyl parathion field study.

Study: 108
 Analyte: Methyl paraoxon
 MDL: 0.10 ppb
 Date of Report: 7/10/91

Sample Type: Surface Water
 Lab: Enseco-Cal Analytical
 Chemist: Calvin Tanaka

Extraction Set Sample No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
2061, 2067, 2074, 3032	58577	0.47	0.50	94			
		0.46	0.50	91	93	2.1	2.3
3059, 3066, 3074, 3089, 5027	58788	0.48	0.50	97			
		0.53	0.50	106	102	6.4	6.3
OVERALL:					97	6.5	6.7

Figure A2-1: Storage dissipation results for methyl parathion recovered from water. Samples were spiked at 20.0 $\mu\text{g/L}$ at pH 3.0 and stored at 4 $^{\circ}\text{C}$ prior to extraction. (MDL = 0.05 $\mu\text{g/L}$).

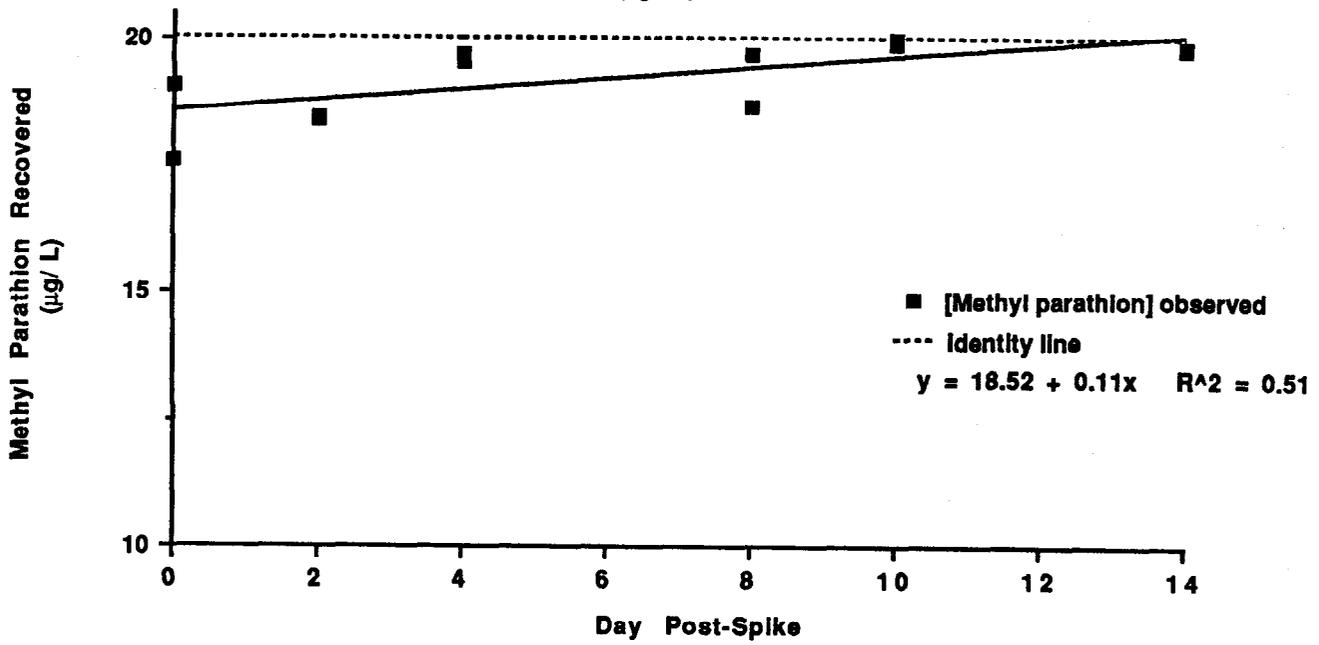


Figure A2-2: Storage dissipation results for methyl parathion recovered from water. Samples were spiked at 20.0 $\mu\text{g/L}$ at pH 8.5 and stored at 4 $^{\circ}\text{C}$ prior to extraction. (MDL = 0.05 $\mu\text{g/L}$).

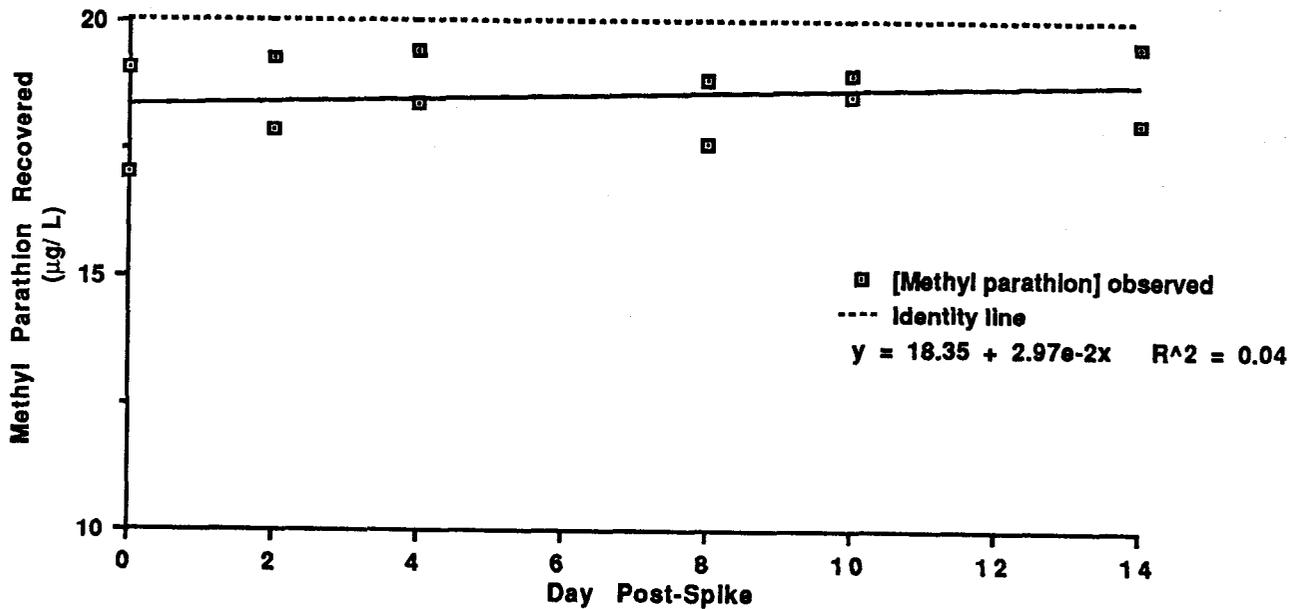


Figure A2-3: Storage dissipation results for methyl paraoxon recovered from water. Samples were spiked at 20.0 µg/ L at pH 3.0 and stored at 4 °C prior to extraction. (MDL = 0.05 µg/ L).

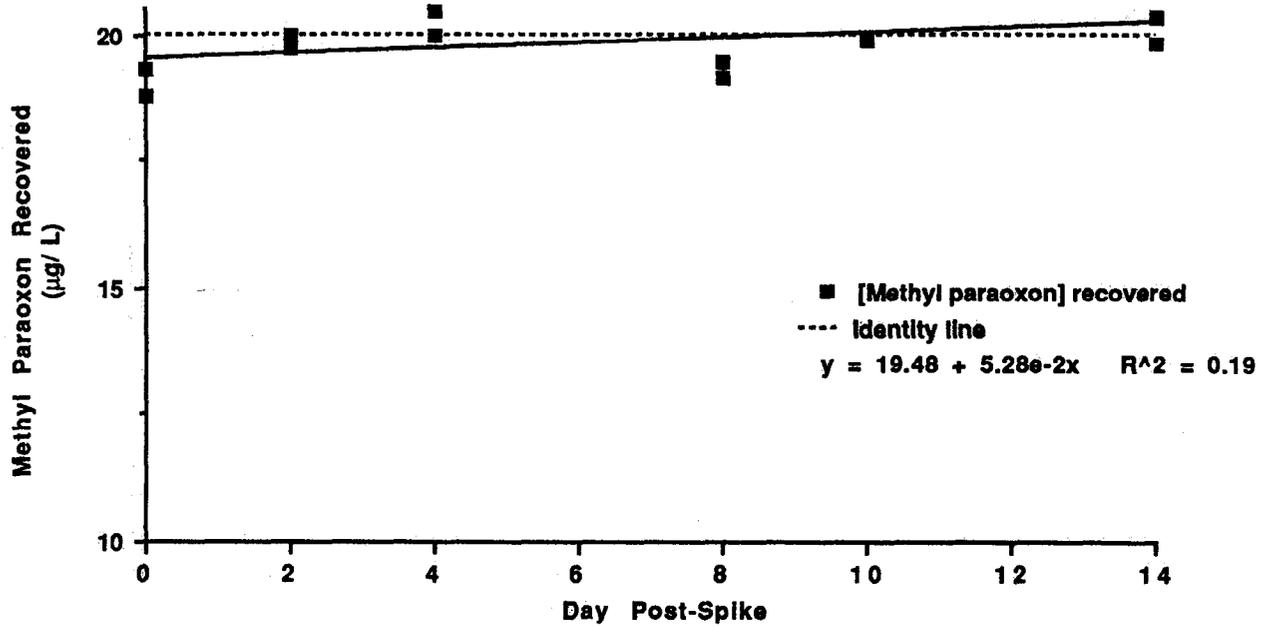


Figure A2-4: Storage dissipation results for methyl paraoxon recovered from water. Samples were spiked at 20.0 µg/ L at pH 8.5 and stored at 4 °C prior to extraction. (MDL = 0.05 µg/L).

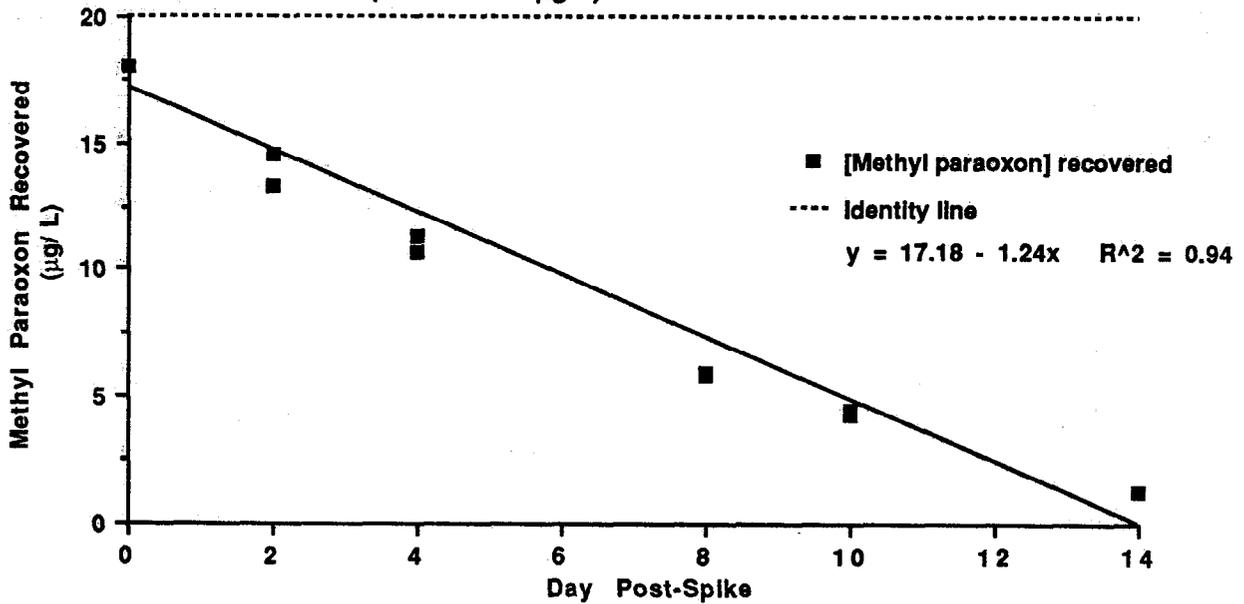


Figure A2-5: Storage dissipation results for methyl parathion recovered from mass deposition cards. Samples were spiked at 100 $\mu\text{g}/0.09\text{ m}^2$ and stored frozen prior to extraction. (MDL = 0.30 $\mu\text{g}/0.09\text{ m}^2$).

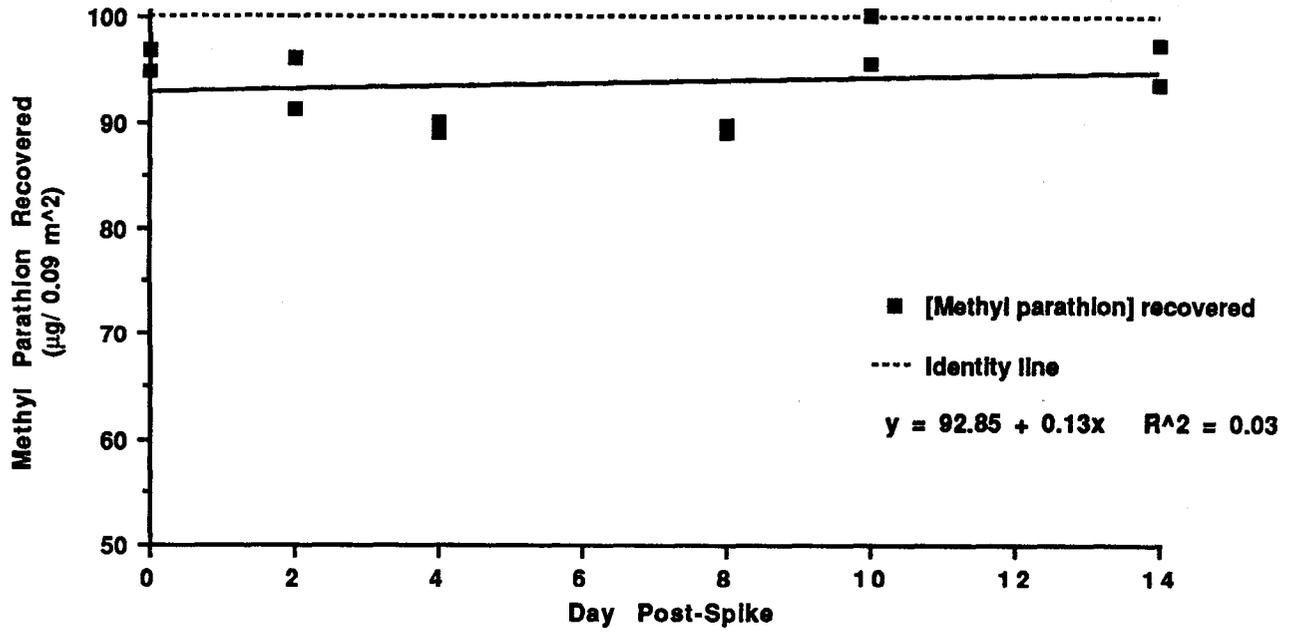


Figure A2-6: Storage dissipation results for methyl paraoxon recovered from mass deposition cards. Samples were spiked at 100 $\mu\text{g}/0.09\text{ m}^2$ and stored frozen prior to extraction. (MDL = 0.30 $\mu\text{g}/0.09\text{ m}^2$).

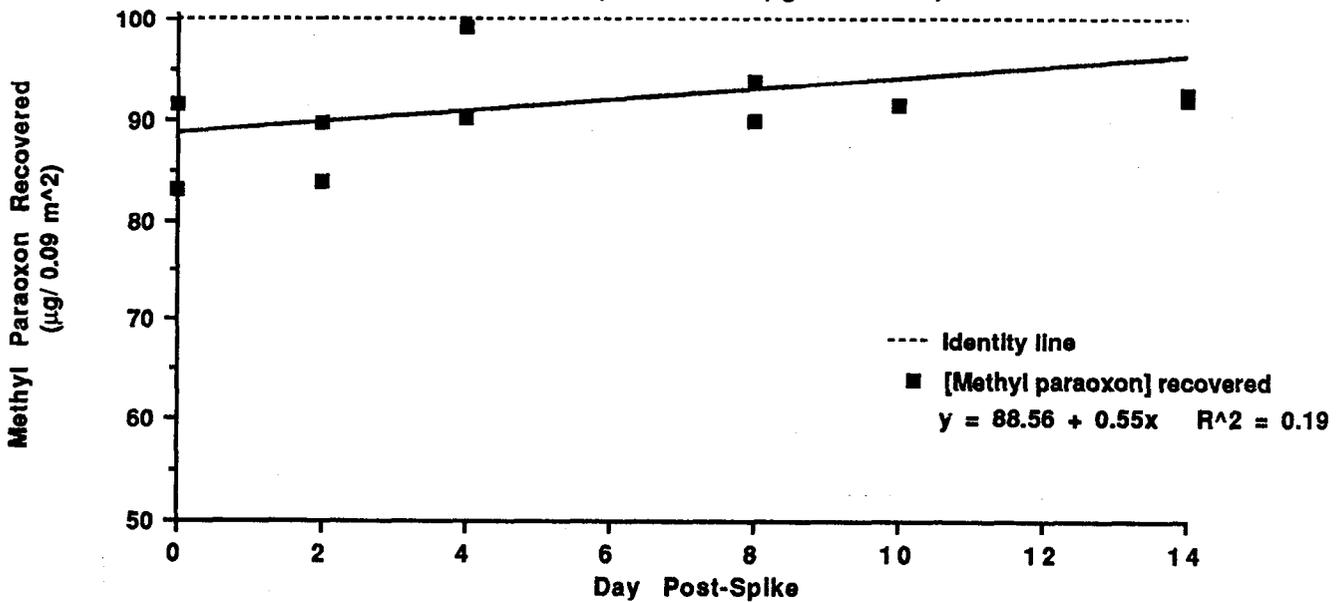


Figure A2-7. Methyl parathion aqueous concentrations (detection limit 0.05 µg/L) recovered from spiked linearity samples.

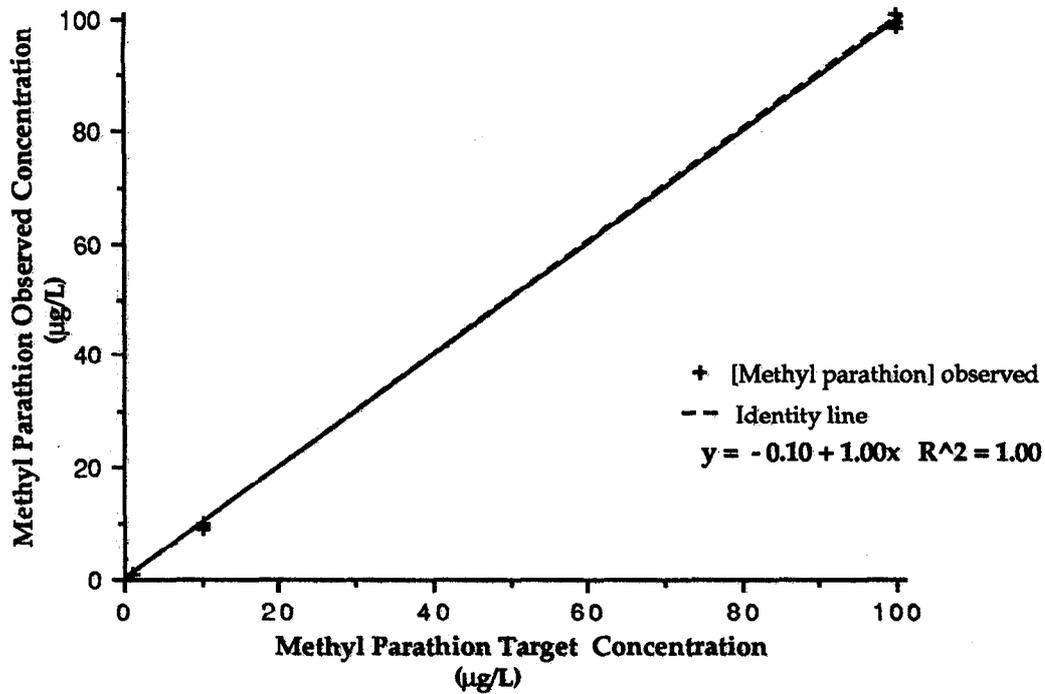


Figure A2-8. Methyl paraoxon aqueous concentrations (detection limit 0.05 µg/L) recovered from spiked linearity samples.

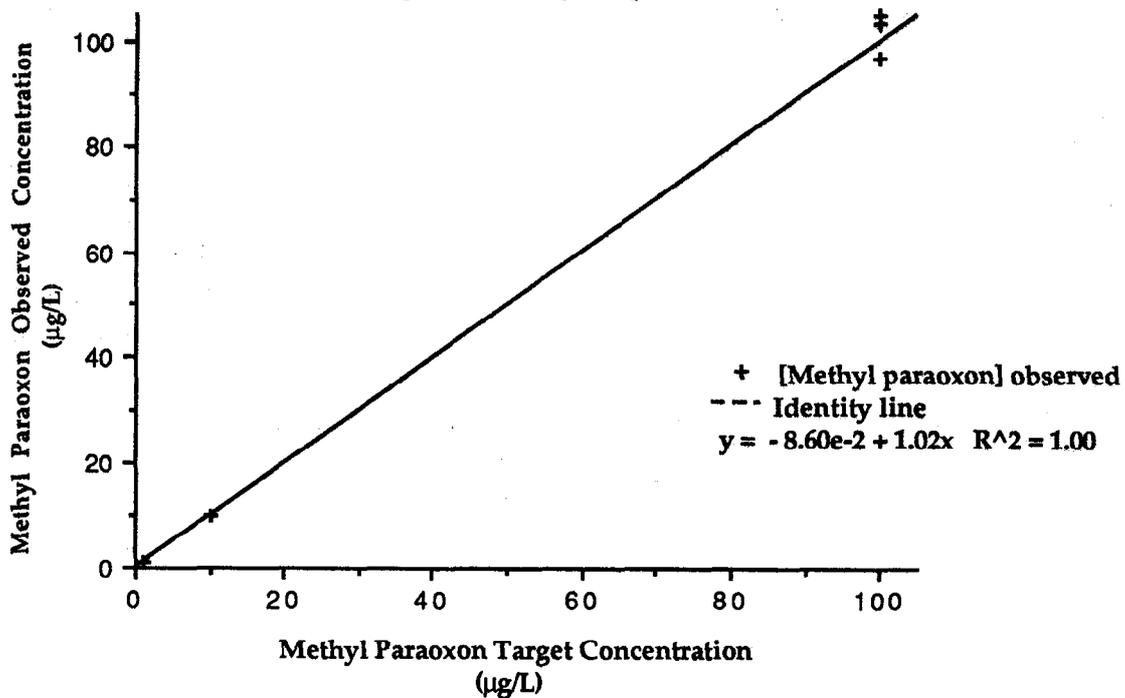


Figure A2-9. Methyl parathion mass deposition card recoveries (detection limit = $0.3\mu\text{g}/0.09\text{ m}^2$) from spiked linearity samples.

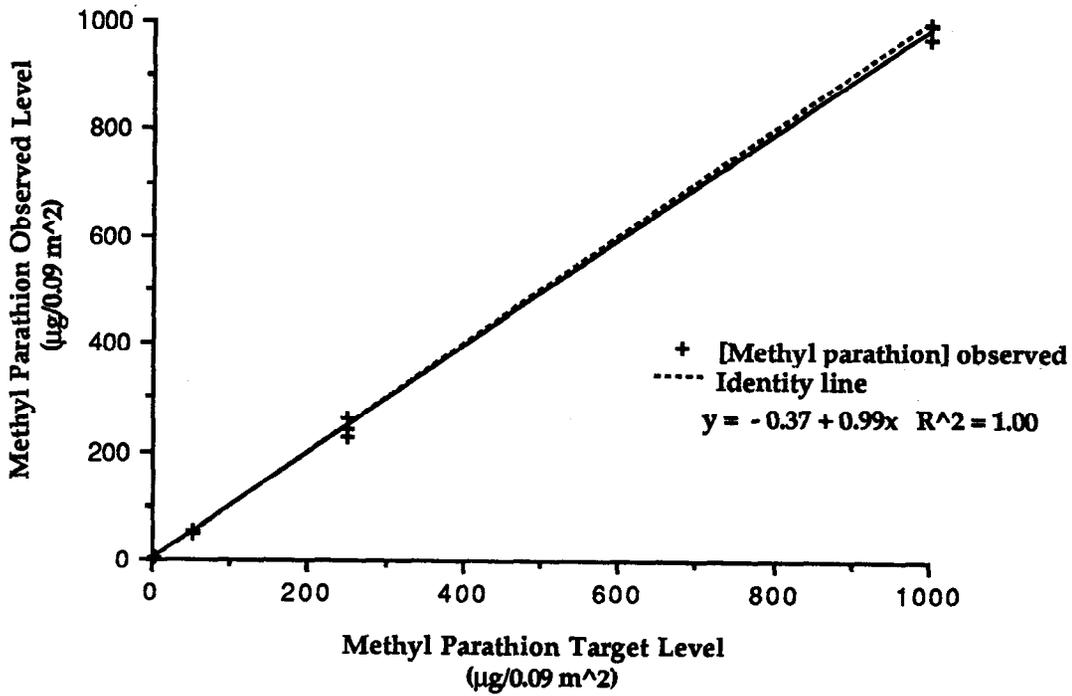


Figure A2-10. Methyl paraoxon mass deposition card recoveries (detection limit = $0.3\mu\text{g}/0.09\text{ m}^2$) from spiked linearity samples.

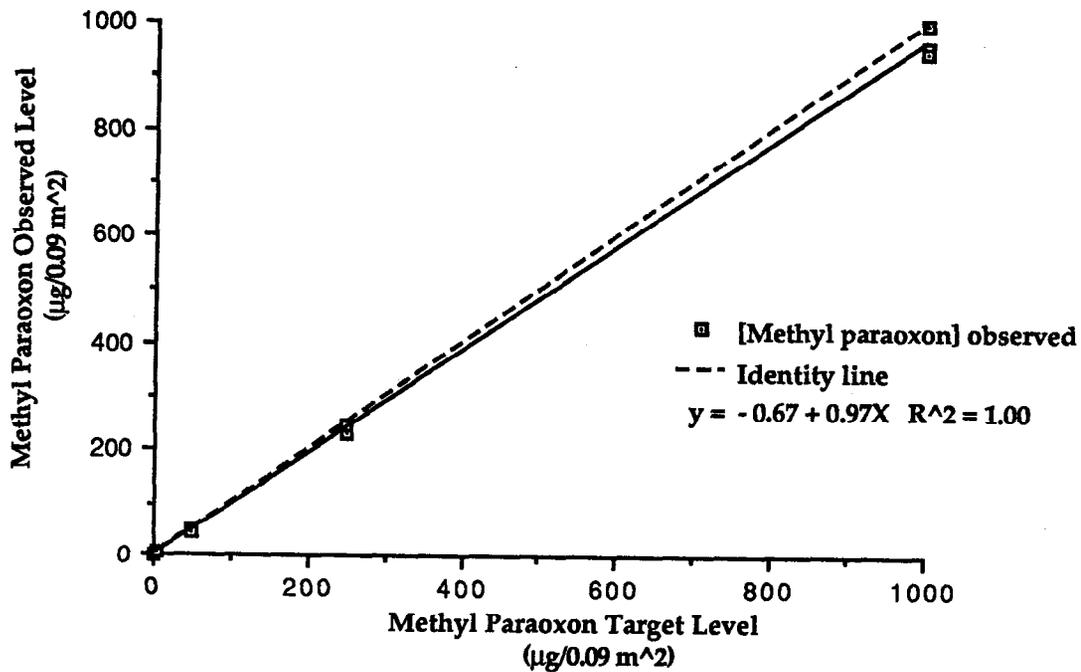


Figure A2-11: Methyl parathion aqueous continuing quality control results from matrix spike recoveries (CDFA Lab; detection limit = 0.05 µg/L).

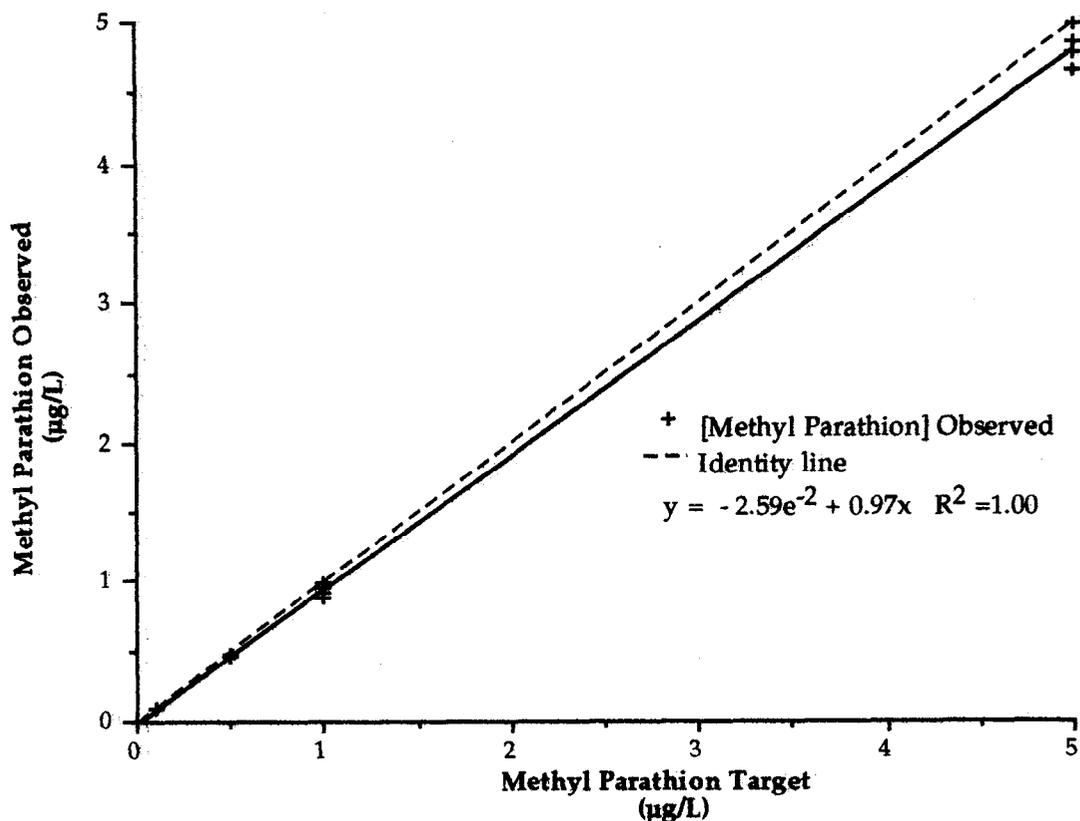


Figure A2-12. Duplicate quality control results for aqueous methyl parathion analyses. Field samples were split and analyzed by CDFA Lab (detection limit = MDL = 0.05µg/L) and Enseco/Cal Lab (MDL = 0.05 µg/L). "Trace" is plotted as (0.5)(MDL).

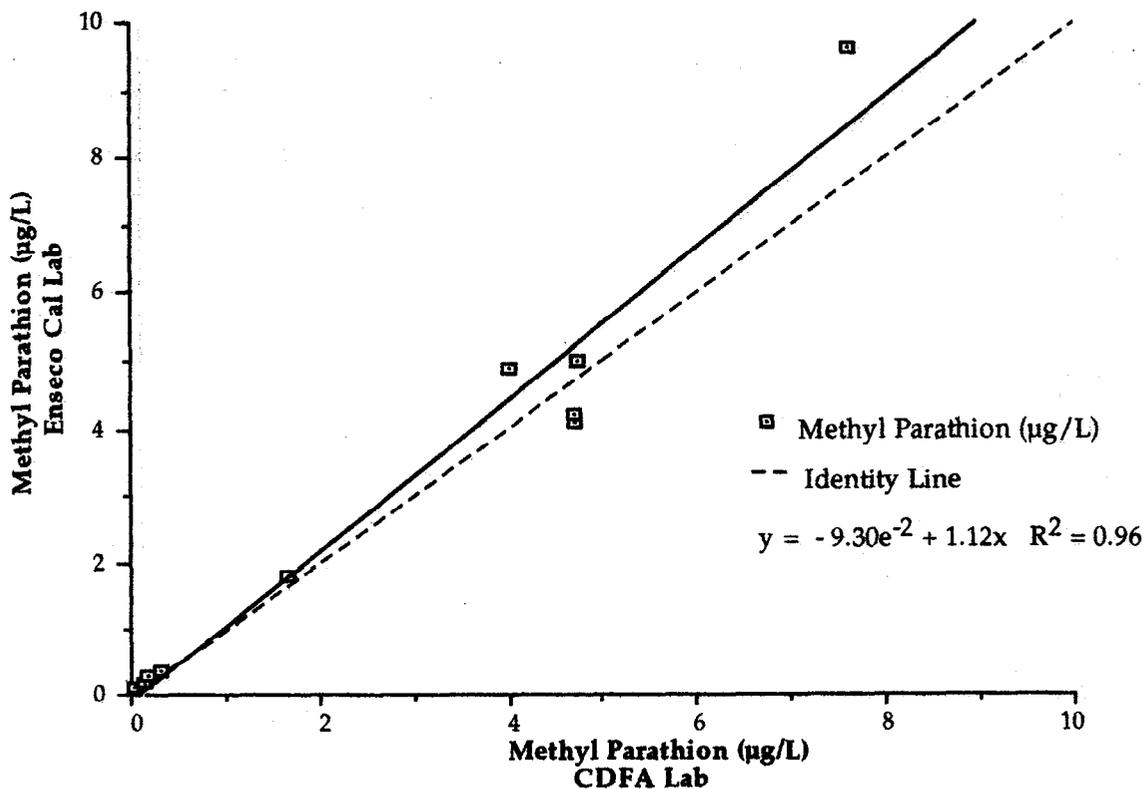
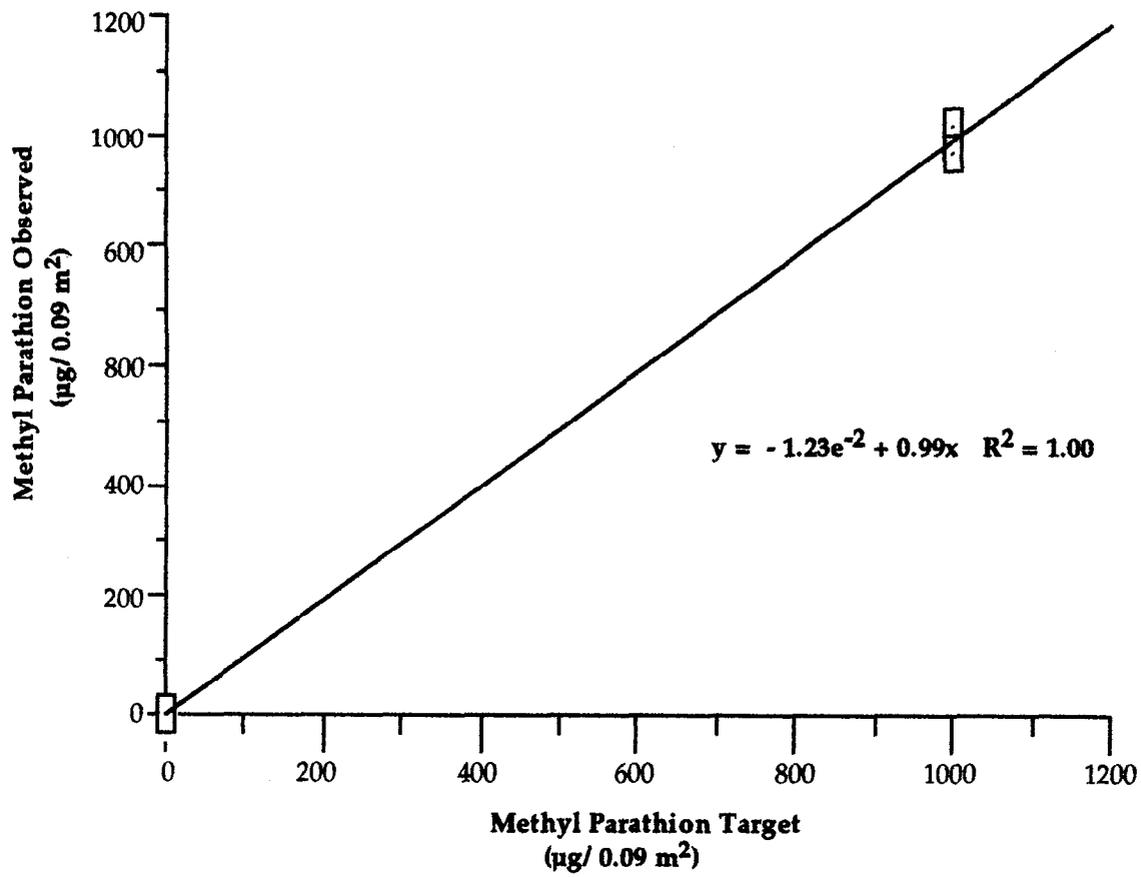
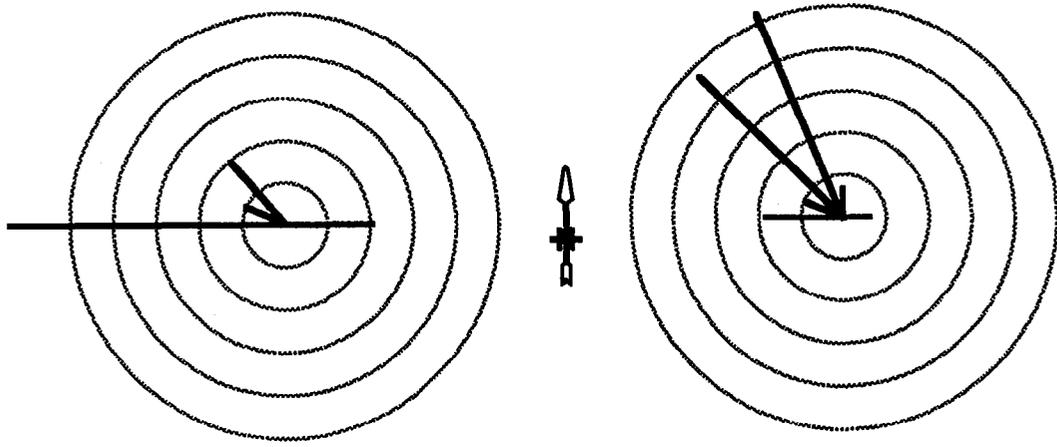


Figure A2-13: Methyl parathion mass deposition card continuing quality control results from matrix spike recoveries (CDEA Lab; detection limit = 0.3 $\mu\text{g}/0.09\text{ m}^2$).



Appendix 3: Meteorologic Data

Figure A3-1 **Site 1: Meterological Data**



Application Period.
Each circle represents 3 min.

Application and fallout periods.
Each circle represents 10 min.

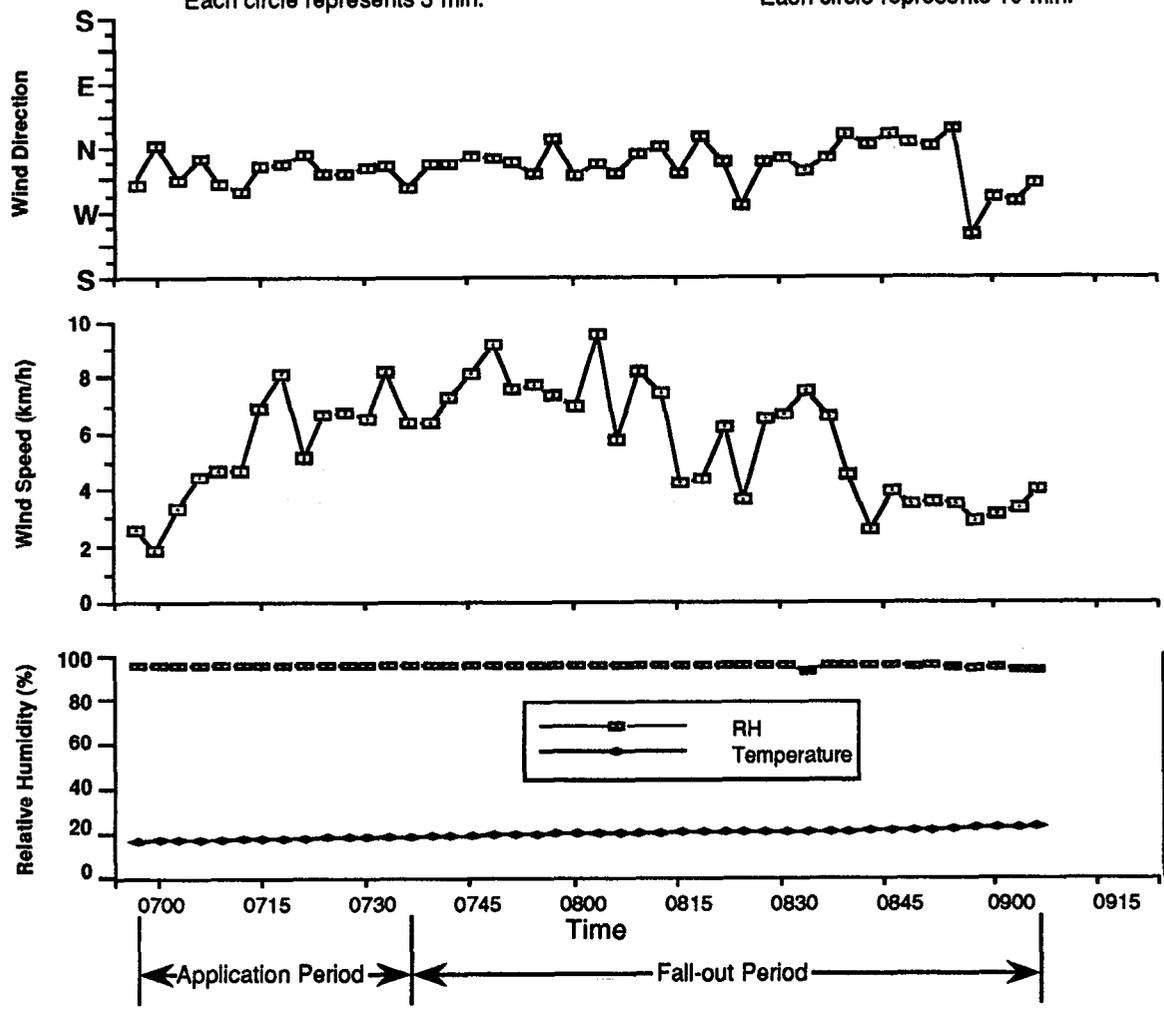
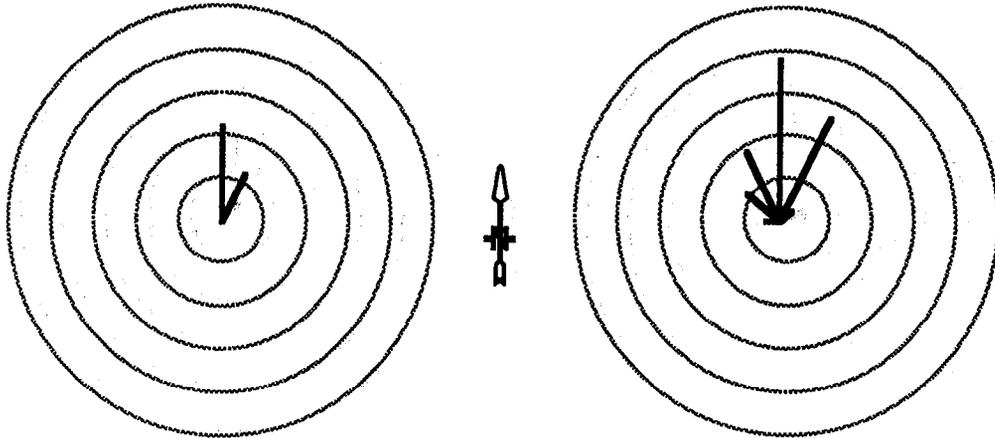


Figure A3-2

Site 2: Meterological Data



Application Period.
Each circle represents 3 min.

Application and fallout periods.
Each circle represents 10 min.

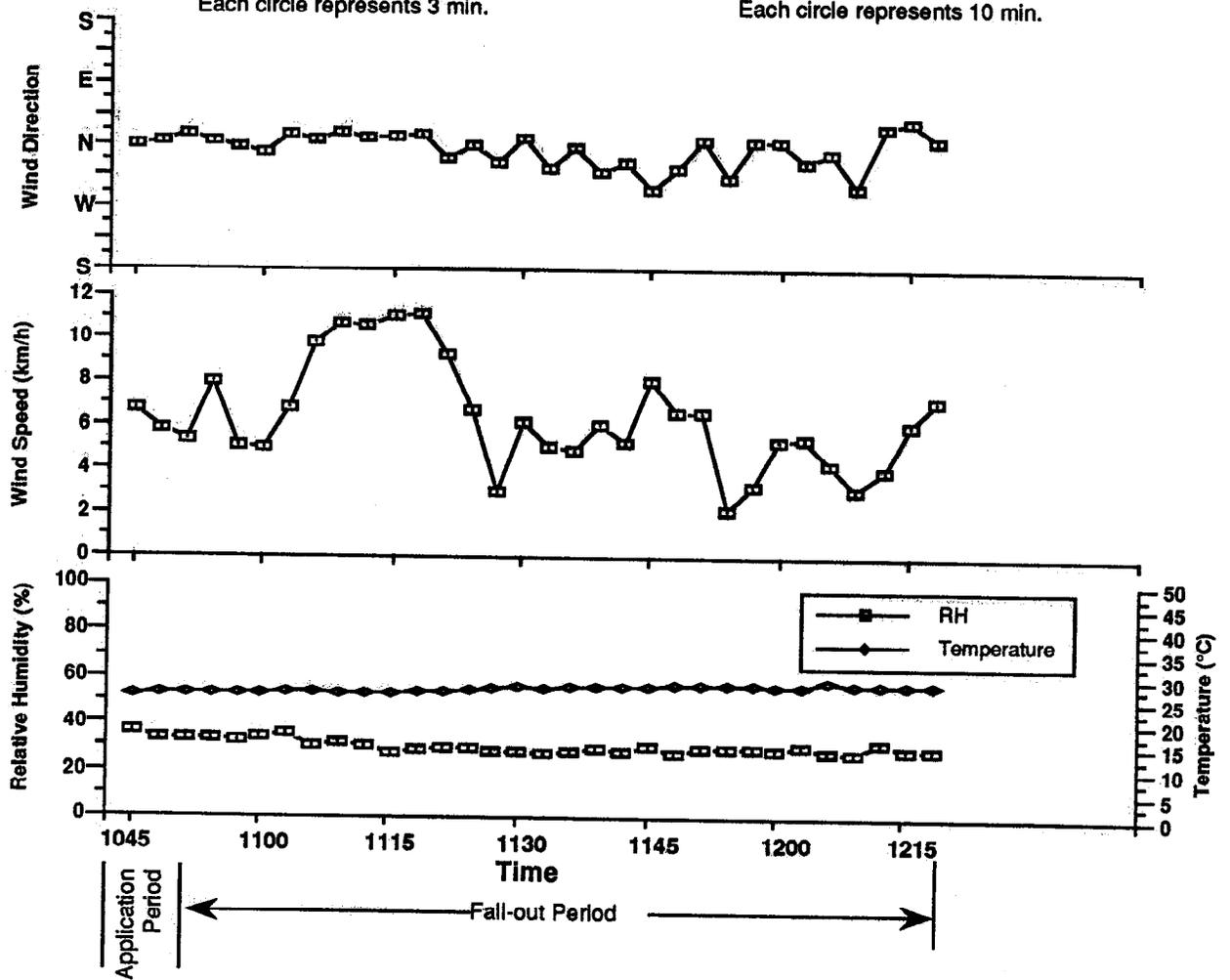
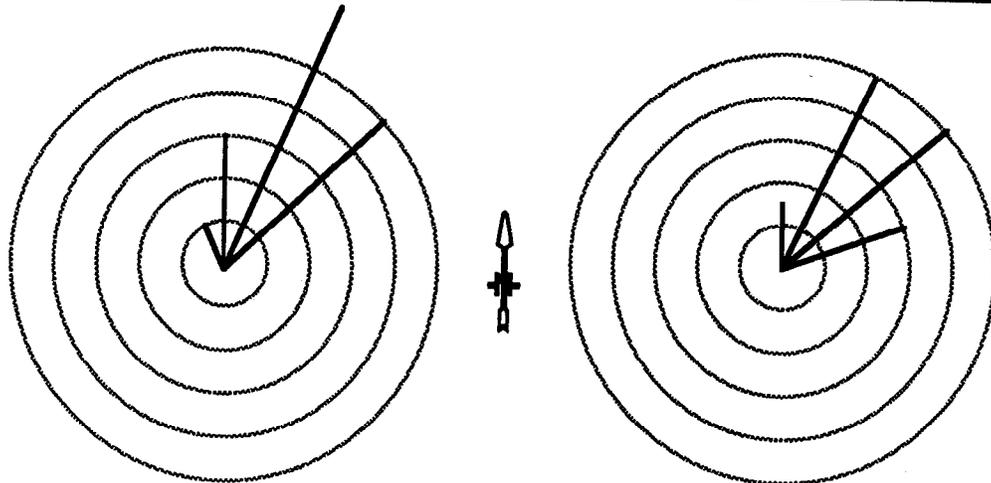


Figure A3-3 **Site 3: Meterological Data**



Application Period.
Each circle represents 3 min.

Application and fallout periods.
Each circle represents 10 min.

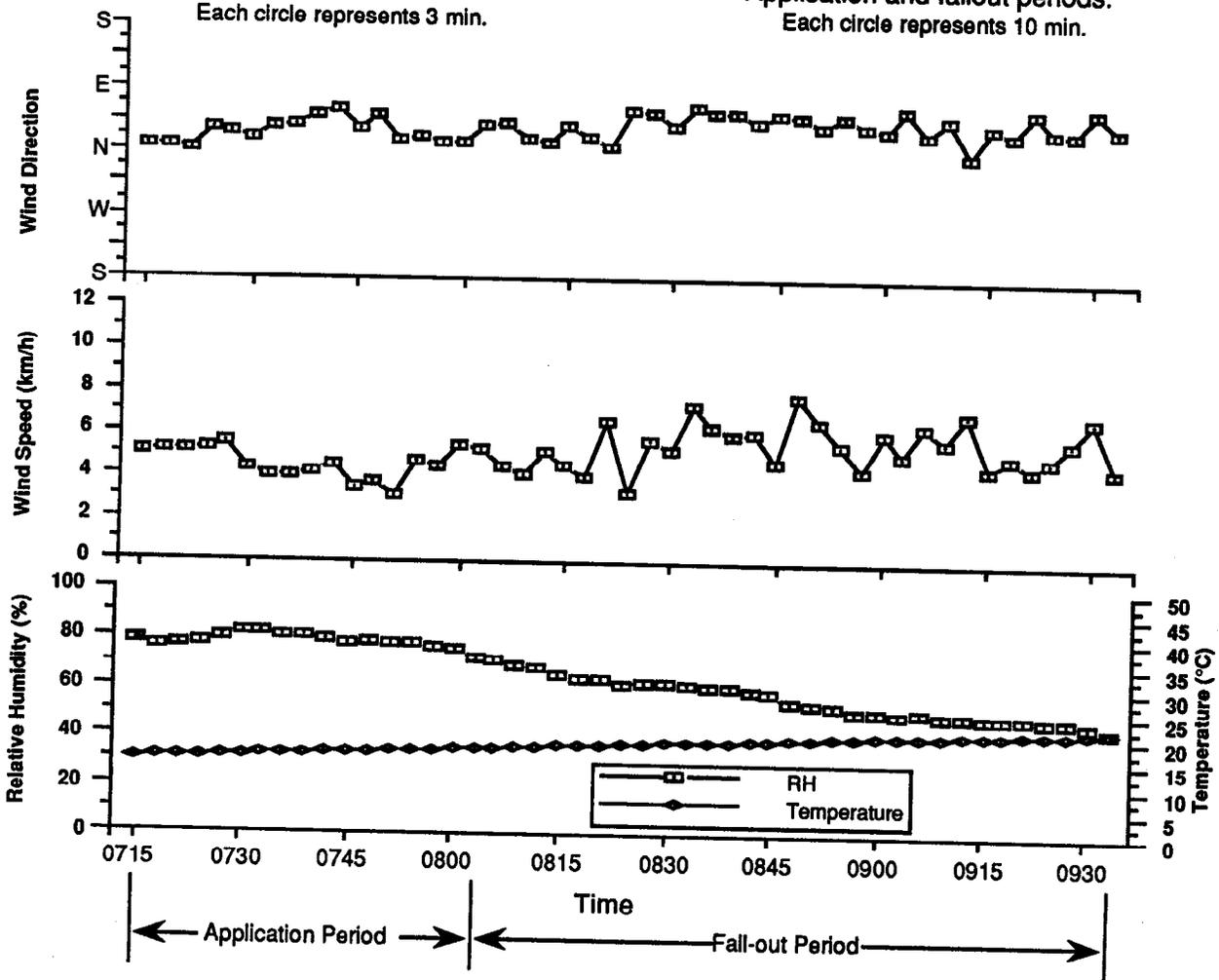
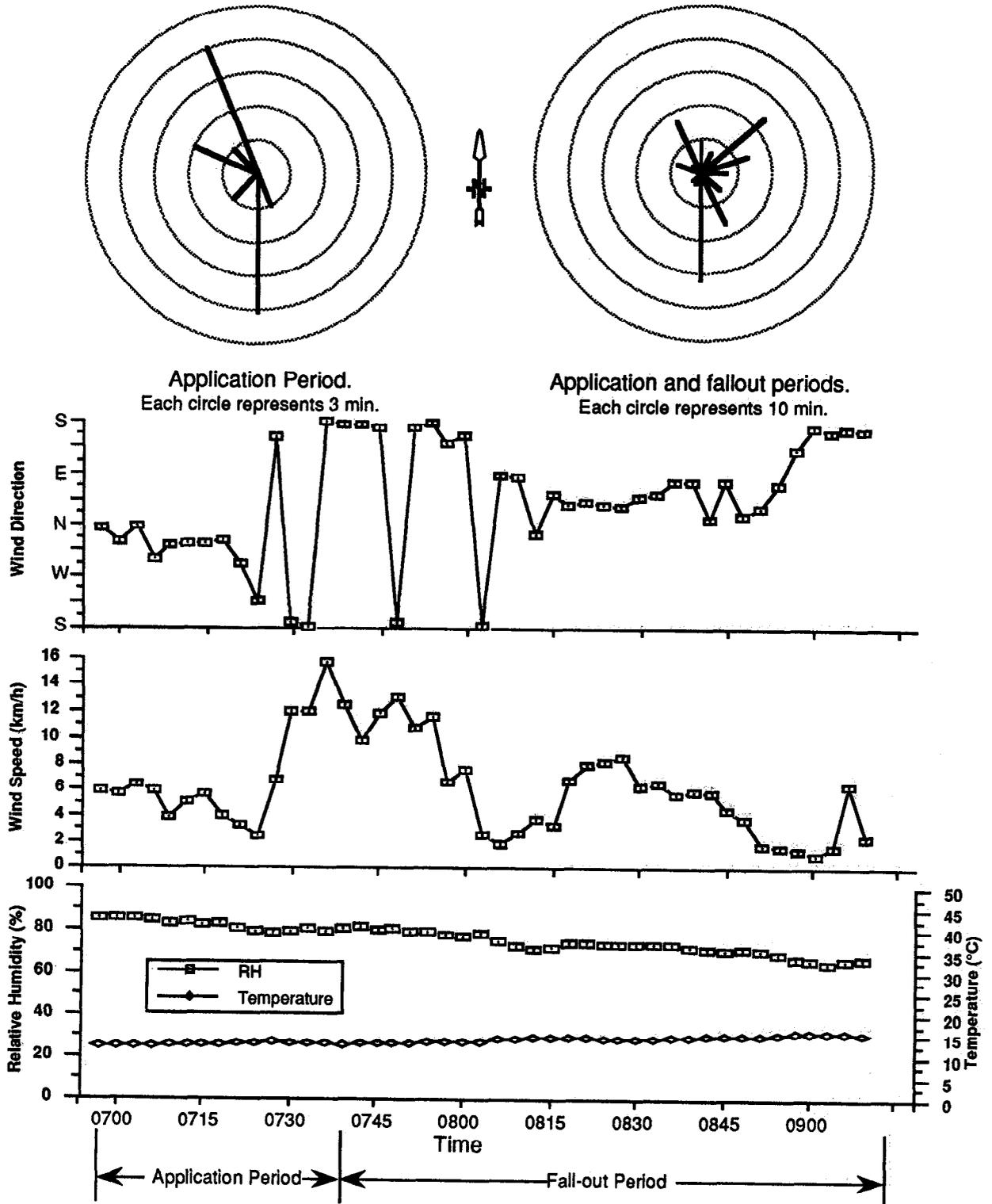


Figure A3-4

Site 4: Meterological Data



Appendix 4 Sample Chain-of-Custody Form

CHAIN OF CUSTODY DETAILS

<u>Column</u>	<u>Explanation</u>
2	* = Split (see also columns 46-49)
3-5	Study number (#108)
6-9	Sample number
10-15	Today's date
16-17	Your initials
18	Site number: 1-4
19	Type of site: P = Primary and B = Backup
20-22	Type of sample: WAT = Water and KIM = Kimbie(s)
23-24	Sample location: UP = Upstream (Water and Kimbie samples) DO = Downstream (Water and Kimbie samples) IB = Inner bank of ditch (Kimbie samples only) OB = Outer bank of ditch (Kimbie samples only) FI = Field (Kimbie samples only)
25-26	Sample purpose: BG = Background (upstream sampling station only) OD = Offsite deposition (upstream, downstream, inner bank and outer bank) SV = Sampling variability (downstream only) AE = Application efficacy (field only)
27	Replicate number: 1-4 for sampling variability 1-8 for application efficacy
28	Sampling method: A = Autosampling (upstream and downstream sites) H = Handsampling (sampling variability study only)
29-32	Sampling start time (Handsampling and autosampling)
33-36	Sampling stop time (Handsampling and autosampling)
37-40	Collection time (min) = sampling stop time - sampling start time
41-43	Subsample volume (mL) for autosampling and handsampling
44-45	Subsample interval (min) = time between subsamples (autosampler)
46-49	If this sample is a split, enter companion sample number here
50	Sampling variability period: 1 (first 15-min period) 2 (second 15-min period)
51	ISCO autosampler ID number
52	Has pH of water sample been adjusted to pH 3? Y = yes and N = no
53	Number of Kimbies in composite sample
77-80	Lab identification code: CDFA = 4323 and Enseco (Cal Lab) = 9527

Don't forget to sign off CoC before sending to West Sac.
Remove pinks from sample CoC's before storing in refrigerator or freezer.
Fill out check-in sheet and attach pinks to it.
Leave on Debbie's desk in warehouse.

Appendix 5: Sample Calculations for Table 8

TABLE 8 CALCULATIONS

1. Application Rate:

$$(5 \text{ lbs a.i. MeP/gallon (from label)}) / (8 \text{ pints/gallon}) = 0.625 \text{ lb/pint}$$

$$(0.625 \text{ lb/pint})(1 \text{ pint/acre}) = 0.625 \text{ lb/acre}$$

$$(0.625 \text{ lb/acre})(0.454 \text{ kg/lb}) = 0.284 \text{ kg/acre}$$

$$(0.284 \text{ kg/acre})(2.471 \text{ acres/ha}) = 0.700 \text{ kg/ha}$$

$$(0.700 \text{ kg/ha})(\text{ha}/1 \times 10^4 \text{ m}^2)(1 \times 10^6 \text{ mg/kg}) = 70 \text{ mg/m}^2$$

Drain Data

2. Mean Width: measured on site

3. Mean Depth: measured on site

4. Sampling Length: measured on site

5. Cross Section: (mean width)(mean depth)

6. Surface Area: (mean width)(sampling length)

7. Ditch Volume: (mean width)(mean depth)(sampling length)

8. Discharge: measured on site

9. Mean Velocity: measured on site

10. Density (of water samples): measured at lab

Downstream Sampling Data (per bottle)

11. Interval: [(total sampling time allotted(min))/(8 samples)][60 sec/min]

12. Discharge Volume of Water: (Discharge)(Interval)

13. Discharge Mass of Water:

$$= (\text{Density})(\text{Discharge Volume})(1 \times 10^3 \text{ mg/g})(1 \times 10^6 \text{ cm}^3/\text{m}^3)$$

14. Mass of MeP in Aqueous Samples:

$$= (\text{Concentration MeP}^a \text{ in } \mu\text{g MeP}/\mu\text{g Water}^b)(\text{Discharge Mass of Water})$$

^a aqueous concentration from Tables 5a, 6a, 7a, 8a

^b by definition of ppb

15. **Total MeP:** \sum mass of MeP from 8 samples
16. **MeP/Ditch Area:** (Total MeP)/(Surface Area of Ditch)
17. **Percent of 100% Application:** [(MeP/Ditch Area)/(Application Rate)] x 100
18. **Mass Deposition Cards:**
= Deposition Rate (from Tables 4c,5c,6c,7c) x (1 mg/l x 10³ μ g)
19. **Mean MeP/Area:** Average of MeP mass from mass deposition cards
20. **Percentage of Aqueous:** [(Mean MeP/Area)/(MeP/Ditch Area)] x 100
21. **Percentage of Applied:** [(Mean MeP/Area)/(Application Rate)] x 100