RESULTS OF MONITORING FOR THE HERBICIDE MCPA IN SURFACE WATER OF THE SACRAMENTO RIVER BASIN

By

P.L. Wofford[1] and P. Lee[2]

[1]Cal/EPA, Department of Pesticide Regulation,
Environmental Hazards Assessment Program

[2]California Department of Food and Agriculture,
Chemistry Laboratory Services

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Environmental Hazards Assessment Program
Department of Pesticide Regulation
California Environmental Protection Agency
Sacramento, CA 95814-5624

ABSTRACT

The study described in this report was undertaken as a preliminary investigation to quantify the extent and magnitude of MCPA contamination in the Sacramento River Basin, and address concerns over concentrations of MCPA previously detected in the Sacramento River Basin. Because of high use on winter wheat and barley and decreased use of MCPA on rice during the summer, the study was directed toward the winter season.

The Environmental Hazards Assessment Program of the Department of Pesticide Regulation (DPR) monitored seven sites on waterways draining the Sacramento River Basin: including the Colusa Basin Drain, the Sacramento Slough, the Feather River, the Sacramento River. Sampling continued twice a week for eight weeks during the late winter through early spring of 1992. Samples were analyzed for MCPA, 2,4-D, and dicamba. Pesticide use reports and rainfall data were reviewed to formulate a possible explanation for contamination.

MCPA was detected in measurable amounts at only three sampling sites: the Colusa Basin Drain, the Sacramento Slough, and the Feather River with the highest level (0.52 ppb) in the Sacramento Slough. Eleven percent of all samples collected contained measurable amounts of MCPA. 2,4-D was detected on each sampling date from March 3 to April 7 and April 14, 1992. 2,4-D was detected at all sites, except the northern most Sacramento River site and the Feather River site. The highest number of positive detections and concentration (2.8 ppb) came from the Colusa Basin Drain sampling site. 2,4-D was detected in 20 percent of all samples collected for the duration of the study. Only two water samples, both collected from the Colusa Basin Drain site, contained detectable amounts of dicamba. Concentrations of 1.8 and 0.1 ppb were detected on March 6 and March 10, 1992, respectively.

Although MCPA, 2,4-D, and dicamba were present at various times and levels in waterways of the Sacramento River Basin, all of the detections were below any reported health concern levels. The contamination from the herbicides appears to coincide with rainfall events causing runoff from the fields to the waterways draining the Sacramento River Basin.

ACKNOWLEDGMENTS

This study was conducted by the California Department of Pesticide Regulation. We would like to thank: Wendy Wyels and Rudy Schnagel from the RWQCB for information and assistance; Colusa, Glenn, Tehama, Yolo, Yuba and Sutter Counties for their assistance in obtaining the pesticide use reports; Jane Stewart from DWR for her assistance in obtaining flow for the Sacramento Slough and Colusa Basin Drain. I would also like to thank all the people at the Department of Pesticide Regulation, Environmental Monitoring and Pest Management Branch, who helped in the formulation of the project and field monitoring.

DISCLAIMER

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INTRODUCTION

The phenoxy herbicides, MCPA (2-methyl-4-chlorophenoxyacetic acid), 2,4-D (2,4-Dichlorophenoxyacetic acid), and related products, are chemicals widely used in crop, forest, range and aquatic weed management. These herbicides are functionally similar to naturally occurring plant growth regulators and cause malfunctions in growth processes. MCPA, a restricted, post-emergent broadleaf herbicide, is used predominantly on small-grain crops, rice, and in home-use mixtures for lawns. In 1992, 221,530 pounds of MCPA was applied in California, 94% of that to small-grain crops and rice (CDPR, 1992). Summer use of MCPA on rice had dropped due to an increase in the use of a more effective herbicide (Londax®), but resistance problems with Londax have resulted in an increase in MCPA use (Table 1). The United States Environmental Protection Agency (U.S. EPA) has determined that MCPA acid is moderately toxic to avian species, slightly toxic to freshwater fish, practically nontoxic to freshwater invertebrates and estuarine and marine organisms (U.S. EPA, 1989). When used properly it should not occur in water at levels that are considered toxic to fish and wildlife.

Table 1. Historical use of MCPA on rice from CDFA and DPR Pesticide Use Reports.

YEAR	ACRES	POUNDS (active ingredient)
1984	208,755	235,536
1985	181,420	190,554
1986	169,626	175,607
1987	251,001	279,203
1988	N/A	N/A
1989	N/A	N/A
1990	21,670	18,198
1991	24,454	19,865
1992	29,794	29,696

N/A = data not available

Many chemicals applied to crops are eventually transported to surface waters by various means, such as nonpoint source runoff and atmospheric drift. Measuring the loss of applied chlorophenoxy and chlorobenzoic acid herbicides to a large watershed in Canada, Frank and Sirons (1980) estimated that losses to surface water represented 0.03% of agricultural applications and 0.5% of non-agricultural applications, such as rights-of-way and ditch bank applications. Wauchope (1978) estimated that pesticide losses are generally around 0.5% or less of the amounts applied, unless intense rainfall events occur within 1-2 weeks following application. He described a critical runoff event as one which occurs within 2 weeks of pesticide application, has at least a centimeter (cm) of rain, and has a runoff volume which is 50% or more of the precipitation. A critical event will most often produce the majority of the runoff losses observed for an entire season. Since the high-use period for MCPA, 2,4-D, and dicamba on winter grown grains, February-April, coincides with the rainy season there is a high potential for runoff contamination into the Sacramento River.

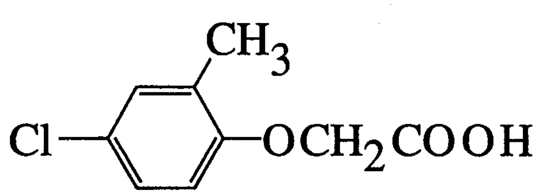
On March 5, 1991, during a storm runoff study by the Central Valley Regional Water Quality Control Board (CVRWQCB), a water sample taken from the Sacramento River just upstream of the confluence of the American River contained 23 ppb MCPA (Schnagl and Wyels, 1991). The concentration found was greater than twice the U.S. EPA health advisory level of 11.0 ppb and also exceeded the National Academy of Science's suggested No-Adverse-Response Level (SNARL) of 8.75 ppb (Marshack, 1991). Additional samples taken on March 26, 1991, were found to contain concentrations of 6 ppb in the Colusa Basin Drain, 7 ppb in the Sacramento Slough and Sacramento River at Village Marina, and 10 ppb in the Feather River. However, there is some concern over the validity of the concentrations due to discrepancies in the laboratory analysis (Wyels, 1991).

This report was undertaken as a preliminary investigation to quantify the extent and magnitude of MCPA contamination in the Sacramento River Basin. MCPA applications to rice in the spring has decreased from a historically higher use prior to the introduction of Londax®. In addition, MCPA has not been detected in various rice herbicide studies (SWRCB and CVRWQCB, 1990). For these reasons the study was conducted only during the winter months when MCPA is applied to oats, barley and wheat. The purpose of sampling was to determine whether MCPA occurs in the Sacramento River Basin waterways draining the agricultural areas where it is used and if so, at what concentration. Pesticide use reports submitted during the study period were obtained from the six counties (Butte, Colusa, Glenn, Sutter, Yolo, and Yuba) that comprise most of the Sacramento River Basin and where most of the MCPA use historically occurred. The reports were used to determine general use areas and proximity of applications to waterways.

MATERIAL AND METHODS

Technical MCPA is white to light brown and can be a solid, flakes, crystal powder or liquid. It has no odor or can have a slight phenolic smell. The melting point is 114 to 119° C and has a solubility of 0.03 g/ 100 g water at 20° C. The log K_{ow} and log K_{oc} for the dimethylamine formulation is 2.82 and 2.87, respectively, and 0.33 and 1.56 for the sodium salt formulation, respectively. MCPA is a plant growth regulator that stimulates nucleic acid and protein synthesis, and affects enzyme activity, respiration and cell division. It is absorbed through the leaves and roots and translocated readily throughout the plant (U.S. EPA, 1989). MCPA is registered in California as a formulation of dimethylamine salt or sodium salt. Either formulation is mixed with water and applied as a solution. Application is usually aerial.

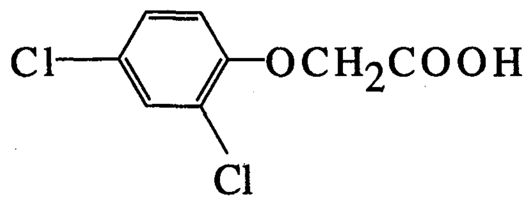
Structural formula:



MCPA (2-methyl-4-chlorophenoxyacetic acid)

Because an analytical screen was available that would also detect the presence of 2,4-D and dicamba during the analysis for MCPA, their concentrations were also monitored as a secondary part of the study. 2,4-D is a post-emergence, systemic, broadleaf chlorinated phenoxy growth regulator. It is widely applied, either by air or ground, for control of broadleaf weeds in grain crops, orchards, turf, pastures and non-crop land. 2,4-D is most often formulated as an inorganic salt, amine or ester. The amine formulation is available as a water soluble dimethylamine salt and as an oil amine salt formulation that is essentially insoluble in water. Most of the formulations of 2,4-D are considered to be non-hazardous, but environmental toxicity has been associated with the ester formulation which has only occasional use in California.

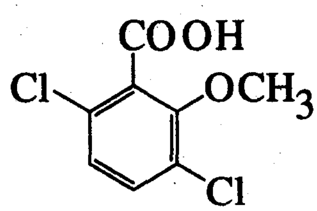
Structural formula:



2,4-D (2,4-Dichlorophenoxyacetic acid)

Dicamba (3,6-dichloro-o-anisic acid) is a pre-emergence and post-emergence benzoic acid-type herbicide that is foliar and soil applied to control phenoxy-tolerant broadleaf weeds. The majority of dicamba use is on wheat and small grains crops, and landscape maintenance. It is available as a granule or soluble concentrate that is often used in combination with other herbicides. Dicamba is resistant to oxidation and hydrolysis under normal conditions and has a solubility in water of 0.45 g/100 ml (Weed Science Society of America, 1983). Application may be either aerial or ground.

Structural formula:



Dicamba (3,6-dicloro-o-anisic acid)

Study Sites

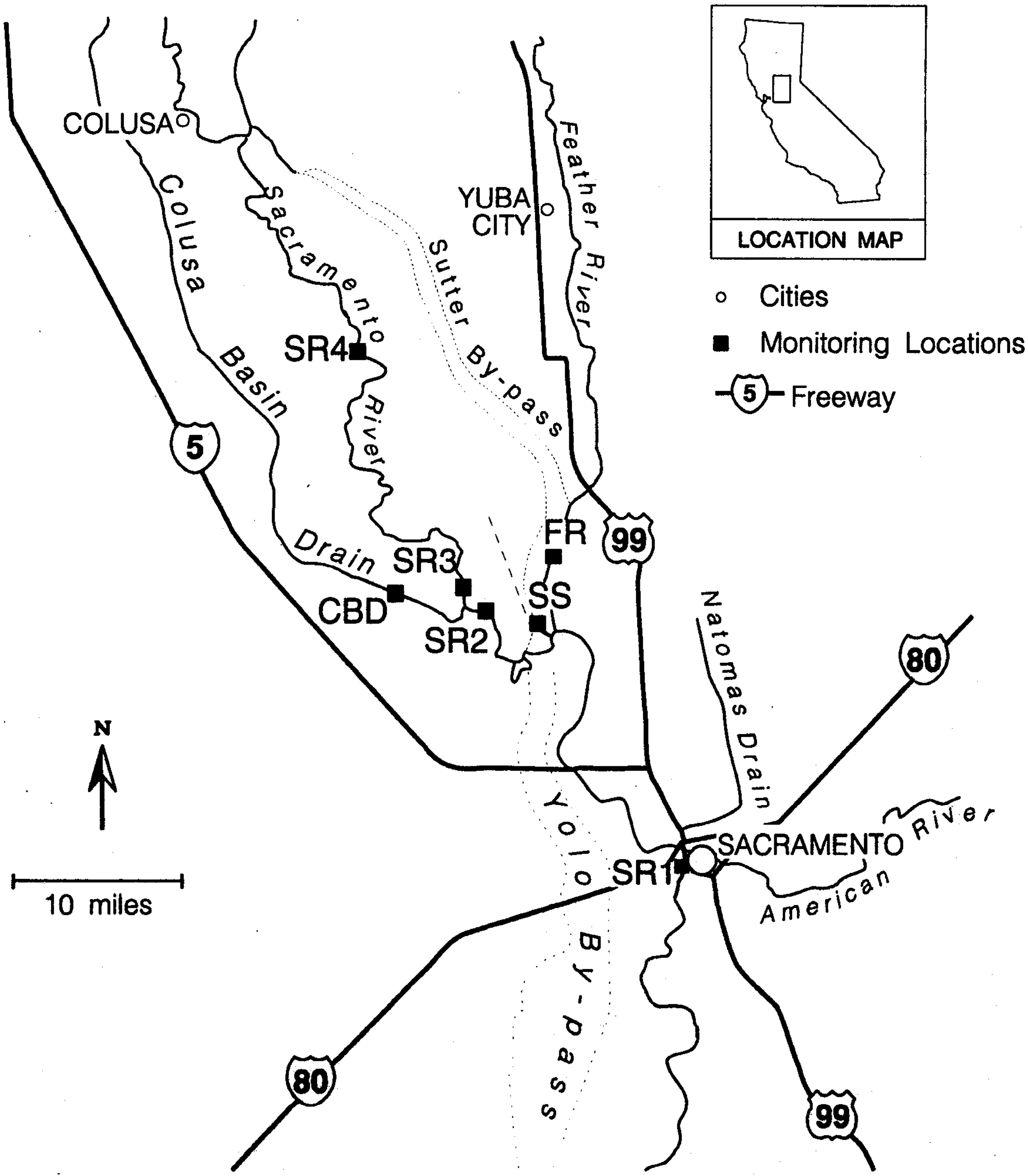
The following seven sites along the Sacramento River, Feather River, and main drains flowing into the Sacramento River north of the city of Sacramento were selected as sampling sites for monitoring the Sacramento River Basin (Fig. 1):

Location ID:	Description:
SR1	Sacramento River at the I Street Bridge in Sacramento County,
SR2	Sacramento River at the Knights Landing Bridge on Highway 113 between Sutter and Yolo Counties,
SR3	Sacramento River approximately 0.4 km upstream from confluence of the Colusa Basin Drain in Yolo County,
SR4	Sacramento River approximately 2.8 km downstream from Wilkens Slough in Sutter County,
CBD	Colusa Basin Drain at intersection of Roads 99E and 108 in Yolo County,
SS	Sacramento Slough near Karnak, approximately 0.25 km downstream from confluence of Reclamation Slough and Sutter By-Pass in Sutter County,
FR	Feather River approximately 6 km upstream from confluence of Sacramento River in Sutter County.

The sites were selected for their location on or downstream of agricultural drains which transport irrigation and rain runoff water from high-use areas into the main waterways of the Sacramento River Basin.

Samples were collected at each site twice a week from February 21 to April 14, 1992. Sampling was started upon notification from county agriculture commissioners that submittance of Notice of Intents for MCPA applications had begun. Once initiated, sampling continued for the following eight weeks.

Figure 1. Surface water monitoring sites.



Sampling

At sites where the water was determined to be well mixed, grab samples were taken from the side of the waterway or from structures in and over the water. Grab samples were taken using a clean 0.95 ℓ glass jar attached to a 4.5 m aluminum extension pole by emersing the jar upside down to a depth of approximately 1 m and then turning it to allow it to fill with water. Approximately 3 ℓ were collected and poured into a stainless steel bucket for mixing. The sample mixture was then poured through a ten-port splitter (Geotech® Dekaport) into 1-liter amber glass bottles to produce equal sample splits and sealed with Teflon®-lined caps.

On the drains and small waterways where adequate mixing does not occur, samples were collected by equal increment, depth-integration sampling across the flow of the waterway using the method of Guy and Norman (1970) to obtain a representative cross-sectional sample. Sampling was done from bridges using a USGS D-77 sampler equipped with a Teflon® bottle. The sample was split into two discrete samples using the same method described earlier. Two 1-liter water samples were collected at each sampling site, one as the primary sample and the second to serve as a backup. Samples were maintained at 4° C through storage and transportation to the laboratory for analysis.

Chemical Analysis

The samples were analyzed by the California Department of Food and Agriculture (CDFA) Laboratory Services located in Meadowview, California, for the presence of MCPA, dicamba and 2,4-D. The water samples were acidified at the laboratory to a pH below 1. The protonated MCPA, dicamba and 2,4-D were extracted with diethyl ether. The residues were derivatized with diazomethane, and the extracts analyzed on a Hewlett-Packard Model 5890 Gas Chromatograph equipped with a series 5970 Mass Selective Detector, Model 9000-340 Computer System, Model 7673A Autosampler and an HP-1 (cross-linked methyl silicon), 25 m x 0.2 mm x 0.33 μm column. The carrier gas (helium) flow rate was set at 0.9 ml/min. Column temperature was set at 60° C for 0.5 min and was increased at a rate of 20° C/min to 250° C. Injector and detector temperatures were both 250° C. Retention time was 9.3 min for dicamba, 9.4 min for MCPA and 10.0 min for 2,4-D. The Minimum Detection Limit (MDL) for this method is 0.1 ppb for all three chemicals.

Continuing quality control (QC) consisted of spiked samples analyzed with each extraction set. Equipment cleanup at each sampling site consisted of a triple rinse of all sampling equipment with deionized water. To test equipment cleansing techniques and transport contamination, a field "rinse blank" was collected every other sampling date at a randomly selected site. The "rinse blank" consisted of a sample of deionized water which was rinsed through the sampling system following cleanup and collected and handled similar to a field sample. Field rinse samples were transported and stored with field samples, and analyzed for all three chemicals.

Method Validation

Analysis was originally contracted to the Agriculture and Priority Pollutants Laboratories, Inc. (APPL, INC) in Fresno, Ca. Seven weeks into the study it was determined that the standards used to set up the analysis were incorrect, producing inaccurate results. Backup samples for sampling dates February 21 - April 3 were sent to CDFA Laboratory Services for immediate analysis, consequently some of the backup samples had been in storage for up to 46 days before extraction. Unfortunately, storage dissipation studies performed by the CDFA Laboratory Services were carried out for only 14 days. The studies determined that MCPA, 2,4-D, and dicamba are stable for up to 14 days if kept refrigerated at 4°C and adjusted to pH 3 or pH 8.5. All following samples were sent to CDFA for immediate analysis. Results of the CDFA's method validation study are presented in Appendix A. Continuing QC matrix spike recoveries for MCPA ranged from 82 to 120%, and dicamba and 2,4-D ranged from 72 to 131% and 78 to 123%, respectively (Appendix A). None of the data received from APPL, INC was used in the data analysis.

RESULTS AND DISCUSSION

MCPA

The results of chemical analysis for MCPA are presented in Table 2. MCPA was detected in measurable amounts at only three sampling sites: the Colusa Basin Drain (CBD), the Sacramento Slough (SS) and the Feather River (FR). The highest level (0.52 ppb) was measured on February 21 in the Sacramento Slough. Over the 8-week sampling period, 11% of all samples collected contained measurable amounts of MCPA.

Table 2. MCPA concentration levels (ppb) for the seven sampling sites.

DATE	SR1	SR2	SR3	SR4	CBD	SS	FR
Feb 21	ND	ND	ND	ND	ND	**0.52**	ND
Feb 25	ND	ND	ND	ND	ND	ND	**0.10**
Feb 28	ND	ND	ND	ND	ND	ND	ND
Mar 3	ND	ND	ND	ND	**0.10**	ND	ND
Mar 6	ND	ND	ND	ND	**0.37**	ND	ND
Mar 10	ND	ND	ND	ND	**0.10**	**0.10**	ND
Mar 13	ND	ND	ND	ND	**0.20**	**0.10**	ND
Mar 17	ND	ND	ND	ND	**0.20**	**0.25**	ND
Mar 20	ND	ND	ND	ND	**0.10**	ND	ND
Mar 24	ND	ND	ND	ND	**0.10**	ND	ND
Mar 27	ND	ND	ND	ND	ND	ND	ND
Mar 31	ND	ND	ND	ND	ND	ND	ND
Apr 3	ND	ND	ND	ND	ND	ND	ND
Apr 7	ND	ND	ND	ND	ND	ND	ND
Apr 10	ND	ND	ND	ND	ND	ND	ND
Apr 14	ND	ND	ND	ND	ND	ND	ND

ND = no detectable amount (MDL for MCPA is 0.1 ppb)

2,4-D

Analytical results for 2,4-D are presented in Table 3. 2,4-D was detected on each sampling date from March 3 to April 7 and April 14. 2,4-D was detected at all sites, except the northern most Sacramento River site (SR1), and the Feather River site (FR). The highest number of positive detections came from the Colusa Basin Drain (CBD) sampling site, with the highest concentration (2.8 ppb) on March 6. 2,4-D was detected in 20% of all samples collected for the duration of the study.

Table 3. 2,4-D concentration levels (ppb) for the seven sampling sites.

DATE	SR1	SR2	SR3	SR4	CBD	SS	FR
Feb 21	ND	ND	ND	ND	ND	ND	ND
Feb 25	ND	ND	ND	ND	ND	ND	ND
Feb 28	ND	ND	ND	ND	ND	ND	ND
Mar 3	ND	ND	ND	ND	**0.10**	ND	ND
Mar 6	**0.10**	**0.10**	ND	ND	**2.78**	ND	ND
Mar 10	ND	ND	ND	ND	**0.10**	ND	ND
Mar 13	ND	ND	**0.10**	ND	**0.67**	**0.10**	ND
Mar 17	**0.10**	**0.10**	**0.20**	ND	**2.10**	**0.30**	ND
Mar 20	ND	ND	ND	ND	**0.40**	**0.20**	ND
Mar 24	ND	ND	ND	ND	**0.26**	**0.10**	ND
Mar 27	ND	ND	ND	ND	**0.26**	ND	ND
Mar 31	ND	ND	ND	ND	**0.46**	ND	ND
Apr 3	ND	ND	ND	ND	**0.10**	ND	ND
Apr 7	ND	ND	ND	ND	**0.63**	ND	ND
Apr 10	ND	ND	ND	ND	ND	ND	ND
Apr 14	**0.10**	ND	ND	ND	ND	ND	ND

ND = no detectable amount (MDL for 2,4-D is 0.1 ppb)

Dicamba

Only two water samples, both collected from the Colusa Basin Drain site, contained detectable amounts of dicamba. Concentrations of 1.8 and 0.1 ppb were detected on March 6 and March 10, respectively. The raw data is presented in Appendix B.

Pesticide Use Report Data

Table 4 is a summary of the Pesticide Use Reports submitted for MCPA applications made February 20 - April 14, 1992. A total of 54,630 pounds of active ingredient (lbs ai) of MCPA was applied to the 6 counties that constitute most of the Sacramento River Basin. Of the total amount of MCPA applied to the basin, 70% was applied by air and over 98% of the applications were made to wheat, oats and barley crops. Of the total 87,836 lbs ai of 2,4-D applied to the basin, 61% was applied by air (Table 5). While 2,4-D was applied to a more diverse list of crops, wheat, oats and barley accounted for 74% of the herbicide applications. A total of 4,710 lbs ai of dicamba was applied to 42,561 acres during the study period, with 92% of the total applied to the same three small grain crops (Table 6). The daily application data for the three chemicals are located in Appendix C-E.

Table 4. Summary of MCPA applications in study area February 20 - April 14, 1992

		Pounds of Active Ingredient	Total Acres Treated
Total Use:		54,630	72,608
Application Method:			
	Aerial	38,020	51,459
	Ground	16,609	21,149
Crop:			
	Wheat	47,292	60,579
	Oats	4,229	6,656
	Barley	2,110	3,229
	Peas	776	1,916
	Rangeland	189	191
	Misc. crops	34	36

Table 5. Summary of 2,4-D applications in study area February-April 1992.

		Pounds of Active Ingredient	Total Acres Treated
Total Use:		87,836	119,115
Application Method:			
	Aerial	53,975	62,825
	Ground	33,861	56,289
Crop:			
	Wheat	58,389	82,520
	Orchards	12,403	29,104
	Rangeland	6,671	6,387
	Oats	4,196	5,837
	Barley	2,138	2,774
	Fallow	1,826	1,330
	Corn	964	1,305
	Rice	929	903
	Clover	321	412

Table 6. Summary of dicamba applications in study area February 20 -April 14, 1992

		Pounds of Active Ingredient	Total Acres Treated
Total Use:		4,710	42,561
Application Method:			
	Aerial	4,241	37,408
	Ground	470	5,153
Crop:			
	Wheat	3,596	34,078
	Oats	556	4,012
	Pasture	355	1,876
	Barley	170	2,352
	Turf	33	243

Rainfall Event Data

Rain runoff from treated fields flows into nearby drains and waterways of the Sacramento River watershed which drain into the Sacramento River. Rainfall data from three weather stations located across the study area for February through mid-April is presented in Appendix F. Rainfall was intermittent but occurred consistently throughout the sampling period. During the study period a total of nine days with critical rainfall events, ≥ 1 cm, were measured at one or more of the three weather stations in the study area.

Most of the detections for both MCPA and 2,4-D occurred in the Colusa Basin Drain and Sacramento Slough samples. Chemical application in lbs ai, detections, and the average amount of rainfall in the two areas are presented in Figures 2-5. A rainfall event on March 5 produced an average of 2.9 cm of rainfall in the Colusa Basin Drain. In the two weeks previous to March 5, 34,500 lbs ai or 63% of the total use of MCPA and 33,842 lbs ai or 39% of the total use of 2,4-D for the season, were applied to the Sacramento River Basin. A rainfall of that magnitude should produce ample runoff from the fields, which coincides with the highest concentrations of MCPA and 2,4-D being found in the samples collected on March 6. The flow through the gates of the Colusa Basin Drain at Knights Landing was 843 cubic feet per second, the highest daily flow for the season (Appendix G). Both the Colusa Basin Drain and the Sacramento Slough receive direct drainage waters from surrounding fields. Measurable amounts of 2,4-D were detected in all water samples taken from March 3 to April 7, 1992, coinciding with nearly daily rainfall until March 18, 1992. The detections between March 24 - April 7 do not follow significant rainfall.

In the Sacramento Slough, the highest measured MCPA concentration (0.52 ppb) was detected in the sample collected on February 21. Persistent rainfall flooded the Sacramento Slough from February 15 to February 26. During the first two weeks of February, 750 lbs ai of MCPA were applied to fields in the Sacramento Slough drainage area. Rainfall prohibited applications until February 18 when a single aerial application of 98 lbs ai of MCPA was made to a site near the Sutter Bypass, which runs directly into the Sacramento Slough. Rainfall runoff previous to the onset of sampling may be responsible for the concentration detected on February 21. The amount of 2,4-D applied in the area from the beginning of February through the monitoring period (4,600 lbs ai) was 57% less that the amount of MCPA applied (10,600 lbs ai).

Figure 2. Amount of MCPA applied, concentrations detected, and rainfall in the Colusa Basin Drainage area.

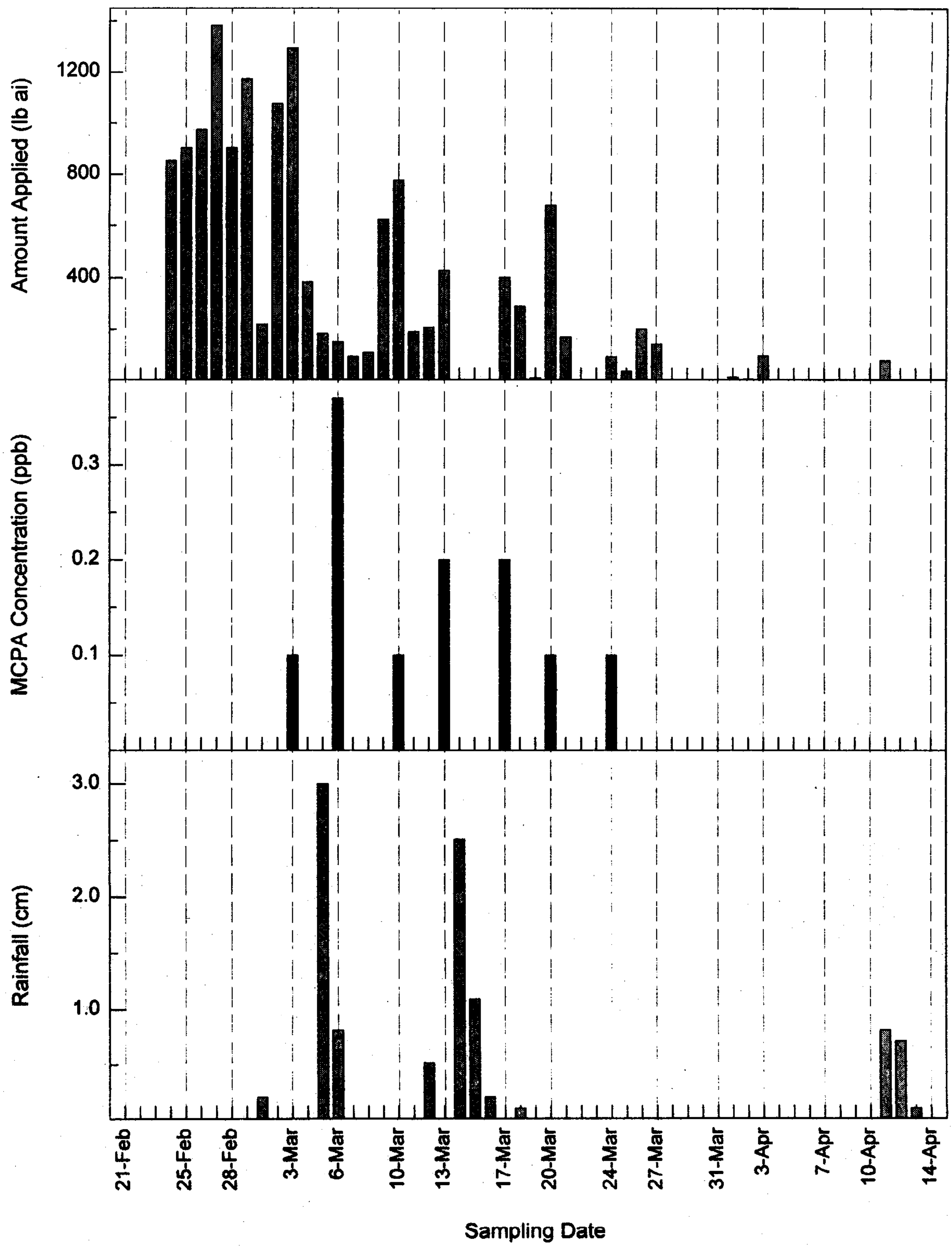


Figure 3. Amount of 2,4-D applied, concentrations detected, and rainfall in the Colusa Basin Drainage area.

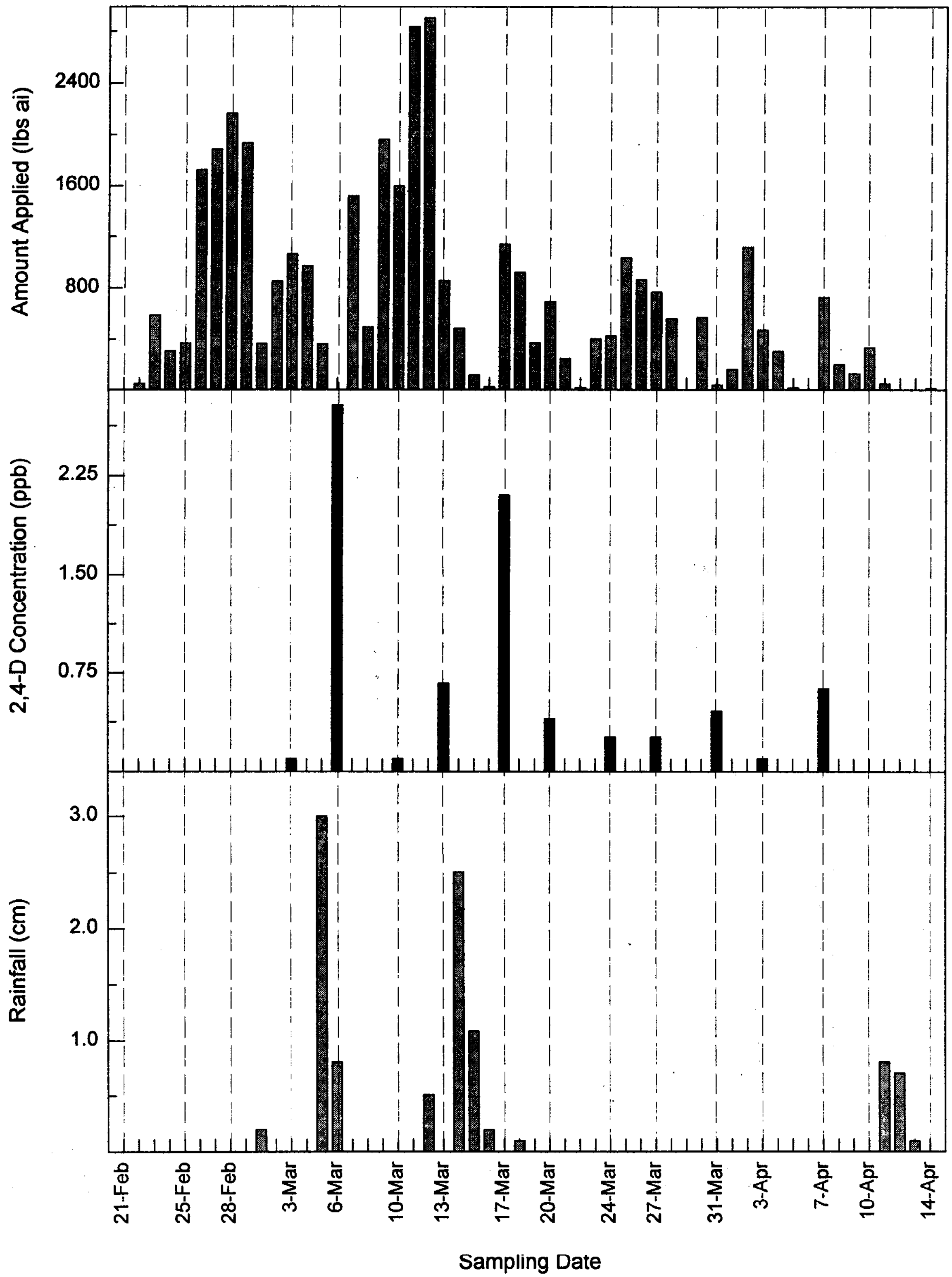


Figure 4. Amount of MCPA applied, concentrations detected, and rainfall in the Sacramento Slough Drainage area.

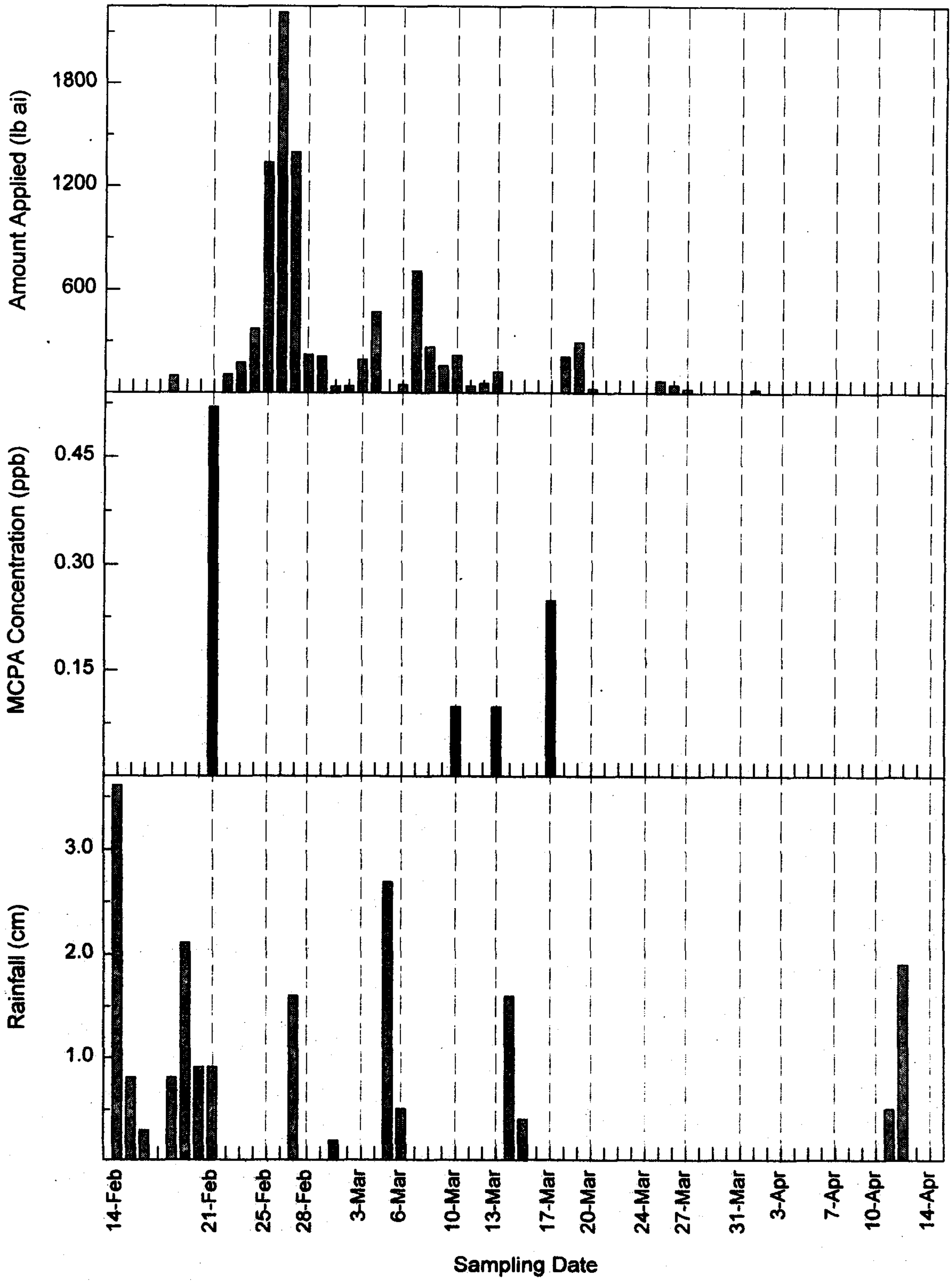
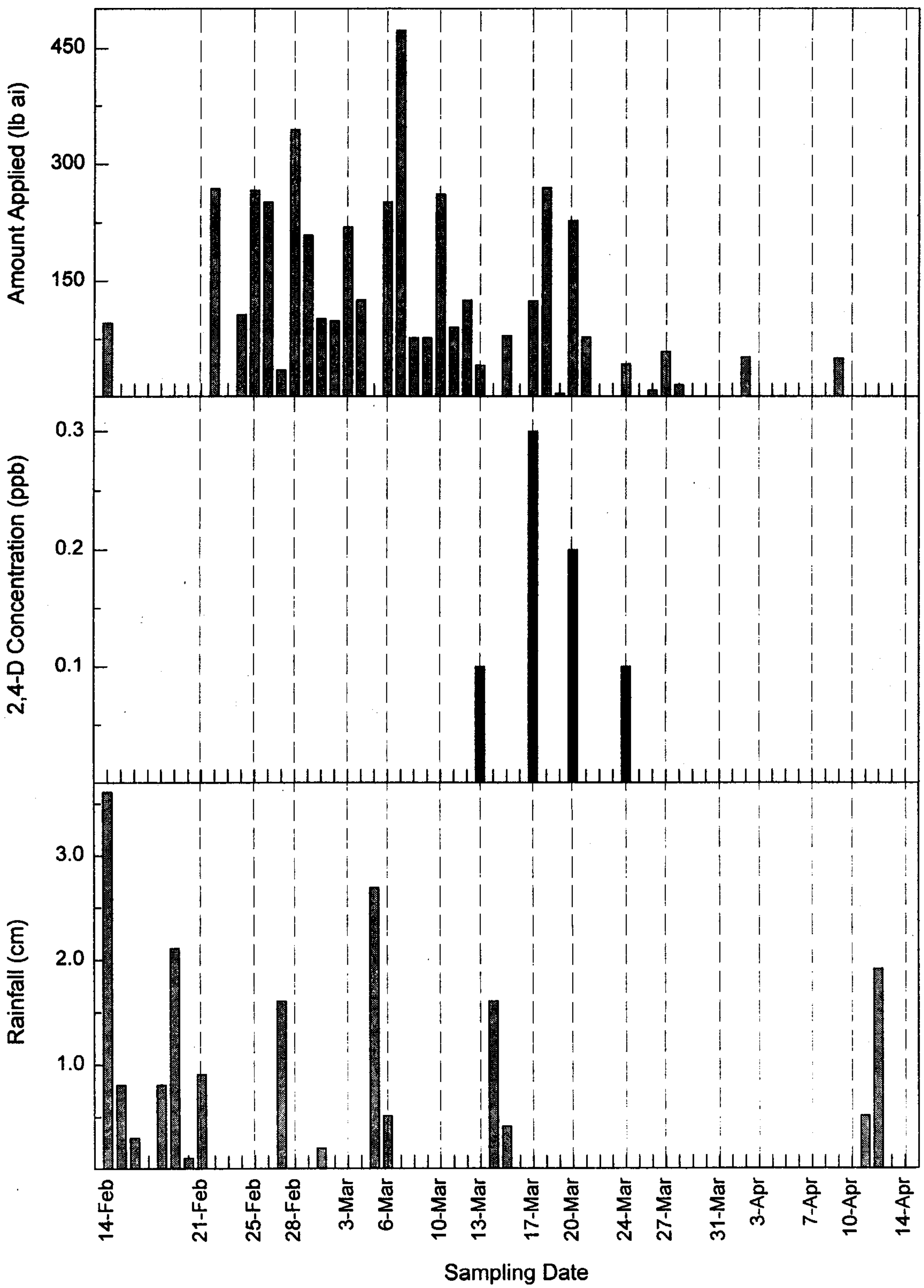


Figure 5. Amount of 2,4-D applied, concentrations detected, and rainfall in the Sacramento Slough Drainage area.



Drift

Contamination of waterways can also occur during chemical applications due to drift of small droplets from their intended application sites. Sampling by Soderquist and Crosby (1975) indicated that, when applied to orchards, about 52% of aerially applied MCPA did not reach the target crop. In another study (Crosby and Bowers, 1985), researchers monitoring two rice fields treated aerially with MCPA could only account for 43 and 24% of the applied herbicide. Other studies (Crosby et al., 1981 and Cheney et al., 1978) detected measurable amounts of aerially applied MCPA 400 and 800 m downwind from application sites. Since 70% of the MCPA applications in the region were aerial, the potential exists for drift over the many creeks, sloughs, canals and other types of waterways which flow eventually into the Sacramento River.

CONCLUSION

Although MCPA, 2,4-D and dicamba were present at various times and levels in waterways of the Sacramento River Basin, all of the detections were below any reported health concern levels. The contamination from the herbicides appears to coincide with rainfall events causing runoff from the fields to the waterways draining the Sacramento River Basin. The water solubility and timing of application of these herbicides on crops grown during the winter season means the possibility of runoff due to storm events will always be present. Future studies into the control of off-site movement from applications during heavy rainfall seasons may decrease the potential contamination of the herbicides in the waterways draining the fields.

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APPENDICES

Appendix A. Method validation and QA/QC for CDFA Chemistry Laboratory Services samples.

Table 1. Method Validation Data (% recoveries) for the 1992 Sacramento River Study

Study: 117
Analyte: MCPA
MDL: 0.1 ppb
Date of Report: 2/24/92

Sample Type: Surface Water
Labs: CDFA
Chemist: Paul Lee

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{x}$	SD	CV (%)	LCL	UCL
2874	0.12	0.1	120					
	0.11	0.1	110					
	0.12	0.1	120					
	0.14	0.1	140					
	0.12	0.1	120	122	11.0	9.02		
2875	0.50	0.5	100					
	0.54	0.5	108					
	0.66	0.5	132					
	0.50	0.5	100					
	0.49	0.5	98	108	14.2	13.1		
2876	1.86	2.0	93					
	1.59	2.0	80					
	1.64	2.0	82					
	1.78	2.0	89					
	1.67	2.0	84	85	5.5	6.4		
2877	11.10	10.0	111					
	10.20	10.0	102					
	9.76	10.0	98					
	10.50	10.0	105					
	10.70	10.0	107	105	5.06	4.82		
		Overall:		105	16.0	15.2	73	137

Table 2. Method Validation Data (% recoveries) for the 1992 Sacramento River Study

Study: 117
Analyte: Dicamba
MDL: 0.1 ppb
Date of Report: 2/24/92

Sample Type: Surface Water
Labs: CDFA
Chemist: Paul Lee

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{x}$	SD	CV (%)	LCL	UCL
2870	0.12	0.1	120					
	0.12	0.1	120					
	0.09	0.1	90					
	0.12	0.1	120					
	0.10	0.1	100	110	14.1	12.8		
2875	0.46	0.5	92					
	0.46	0.5	92					
	0.49	0.5	98					
	0.47	0.5	94					
	0.47	0.5	94	94	2.4	2.6		
2876	2.25	2.0	113					
	1.96	2.0	98					
	2.04	2.0	102					
	2.24	2.0	112					
	2.05	2.0	103	106	6.6	6.21		
2877	12.0	10.0	120					
	10.8	10.0	108					
	10.4	10.0	104					
	11.1	10.0	111					
	11.6	10.0	116	112	6.34	5.66		
		Overall:		105	10.6	10.1	83	127

LCL = Lower Control Limit (mean - 2 SD)
UCL = Upper Control Limit (mean + 2 SD)

Table 3. Method Validation Data (% recoveries) for the 1992 Sacramento River Study

Study: 117
Analyte: 2,4-D
MDL: 0.1 ppb
Date of Report: 2/24/92

Sample Type: Surface Water
Labs: CDFA
Chemist: Paul Lee

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	x̄	SD	CV (%)	LCL	UCL
2878	0.083	0.1	83					
	0.096	0.1	96					
	0.100	0.1	100					
	0.080	0.1	80					
	0.106	0.1	106	93	11	12		
2879	0.60	0.5	120					
	0.49	0.5	98					
	0.50	0.5	100					
	0.55	0.5	110					
	0.53	0.5	106	107	8.79	8.21		
2876	2.11	2.0	106					
	1.90	2.0	95					
	1.80	2.0	90					
	2.23	2.0	112					
	2.17	2.0	109	102	9.45	9.26		
2881	10.1	10.0	101					
	9.17	10.0	92					
	9.15	10.0	92					
	9.52	10.0	95					
	9.36	10.0	94	95	3.70	3.89		
		Overall:		99	9.9	10	79	119

Table 4. CDFA's Continuing Quality Control Data (% recoveries) for the 1992 Sacramento River Study

Study: 117
Analyte: MCPA
MDL: 0.1 ppb
Date of Report: 7/15/92

Sample Type: Ground Water
Labs: CDFA
Chemist: Paul Lee

Extraction Set #	Lab #	Spike Level (ppb)	Results (ppb)	Recovery %	x̄	SD	CV (%)
29,30,62	3567	2.0	2.28	114			
21,64	3596	2.0	1.84	92			
93	4513	0.625	0.56	89.6			
100	4518	0.625	0.71	113.6			
76	4510	0.625	0.65	104			
2,4,6,8,10,12,14,16,20,24	4476	0.625	0.75	120			
26,28,38,34,36,38,40,42,44, 47,50,52	4506	0.625	0.51	81.6			
54,56,58,90,67,69,71,92, 115,117,125	4505	0.625	0.56	89.6			
73,75,103,105,107,109,145, 147,179	4502	0.625	0.58	92.8			
79,81,83,85,87,89,97,122, 124,140,142,143,180	4464	0.625	0.61	97.6			
99,133,135,137,187,191,205, 207,209,217,223,225	4466	0.625	0.68	106.9			
193,195,197,199,201,203,211, 213,215,219,227,230,232	4468	0.625	0.79	126			
51,153,155,157,159,161,163, 165,167,169,171,235,237	4472	0.625	0.71	113.6			
28,130,131,173,175,181,183, 185,239,248,250,252,242	4474	0.625	0.57	91.2			
254,256,258,260,262	4470	0.625	0.55	88			
				Overall:	102	13.5	13.2

Table 5. CDFA's Continuing Quality Control Data (% recoveries) for the 1992 Sacramento River Study

Study: 117
Analyte: Dicamba
MDL: 0.1 ppb
Date of Report: 7/15/92

Sample Type: Ground Water
Labs: CDFA
Chemist: Paul Lee

Extraction Set #	Lab #	Spike Level (ppb)	Results (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
29,30,62	3567	2.0	1.85	92.5			
21,64	3596	2.0	2.00	100			
93	4513	0.625	0.53	84.3			
100	4518	0.625	0.61	97.6			
76	4510	0.625	0.70	112			
2,4,6,8,10,12,14,16,20,24	4476	0.625	0.58	92.8			
26,28,38,34,36,38,40,42,44, 47,50,52	4506	0.625	0.56	89.6			
54,56,58,90,67,69,71,92, 115,117,125	4505	0.625	0.45*	72			
73,75,103,105,107,109,145, 147,179	4502	0.625	0.64	100			
79,81,83,85,87,89,97,122, 124,140,142,143,180	4464	0.625	0.63	101			
99,133,135,137,187,191,205, 207,209,217,223,225	4466	0.625	0.82**	131			
193,195,197,199,201,203,211, 213,215,219,227,230,232	4468	0.625	0.57	91.2			
51,153,155,157,159,161,163, 165,167,169,171,235,237	4472	0.625	0.73	117			
28,130,131,173,175,181,183, 185,239,248,250,252,242	4474	0.625	0.65	104			
254,256,258,260,262	4470	0.625	0.59	94.4			
				Overall:	99	14	14

* Recovery fell below lower control limit set at 83%

** Recovery fell below upper control limit set at 127%

Table 6. CDFA's Continuing Quality Control Data (% recoveries) for the 1992 Sacramento River Study

Study: 117
Analyte: 2,4-D
MDL: 0.1 ppb
Date of Report: 7/15/92

Sample Type: Ground Water
Labs: CDFA
Chemist: Paul Lee

Extraction Set #	Lab #	Spike Level (ppb)	Results (ppb)	Recovery %	$\bar{x}$	SD	CV (%)
29,30,62	3567	2.0	2.0	100			
21,64	3596	2.0	2.08	104			
93	4513	0.625	0.49*	78.0			
100	4518	0.625	0.67	107			
76	4510	0.625	0.65	104			
2,4,6,8,10,12,14,16,20,24	4476	0.625	0.77**	123			
26,28,38,34,36,38,40,42,44, 47,50,52	4506	0.625	0.56	89.6			
54,56,58,90,67,69,71,92, 115,117,125	4505	0.625	0.52	83.2			
73,75,103,105,107,109,145, 147,179	4502	0.625	0.62	99.2			
79,81,83,85,87,89,97,122, 124,140,142,143,180	4464	0.625	0.61	97.6			
99,133,135,137,187,191,205, 207,209,217,223,225	4466	0.625	0.68	107			
193,195,197,199,201,203,211, 213,215,219,227,230,232	4468	0.625	0.63	101			
51,153,155,157,159,161,163, 165,167,169,171,235,237	4472	0.625	0.71	114			
28,130,131,173,175,181,183, 185,239,248,250,252,242	4474	0.625	0.64	102			
254,256,258,260,262	4470	0.625	0.63	101			
				Overall:	101	11.1	10.9

* Recovery fell below lower control limit set at 79%

** Recovery fell below upper control limit set at 119%

Table 7. Storage Dissipation Data for the 1992 Sacramento River Study (refrigerated at 4°C, pH3)

Study: 117
Analyte: MCPA
MDL: 0.1 ppb
pH: 3

Sample Type: Surface Water
Labs: CDFA
Date of Report: 8/3/92
Chemist: Paul Lee

Day	Date Extracted	Date Analyzed	Spike Level (ppb)	Results (ppb)	% Recovery	$\bar{x}$	SD	CV (%)
0	2/20/92	2/26/92	2.0	2.11	106			
0	2/20/92	2/26/92	2.0	1.95	98	102	5.66	5.55
1	2/21/92	2/26/92	2.0	2.21	111			
1	2/21/92	2/26/92	2.0	2.25	113	112	1.41	1.26
4	2/24/92	2/26/92	2.0	2.27	114			
4	2/24/92	2/26/92	2.0	1.95	98	106	11.3	10.7
7	2/27/92	3/2/92	2.0	1.71	86			
7	2/27/92	3/2/92	2.0	1.92	96	91	7.1	7.8
12	3/3/92	3/10/92	2.0	1.93	97			
12	3/3/92	3/10/92	2.0	1.91	96	97	0.71	0.73
14	5/14/92	5/14/92	2.0	1.9	95			
14	5/14/92	5/14/92	2.0	1.54	77	86	13	15

Table 8. Storage Dissipation Data for the 1992 Sacramento River Study (refrigerated at 4°C, pH 8.5)

Study: 117
Analyte: MCPA
MDL: 0.1 ppb
pH: 8.5

Sample Type: Surface Water
Labs: CDFA
Date of Report: 8/3/92
Chemist: Paul Lee

Day	Date Extracted	Date Analyzed	Spike Level (ppb)	Results (ppb)	% Recovery	$\bar{x}$	SD	CV (%)
0	2/20/92	2/26/92	2.0	1.96	98			
0	2/20/92	2/26/92	2.0	1.94	97	98	0.71	0.72
1	2/21/92	2/26/92	2.0	2.08	104			
1	2/21/92	2/26/92	2.0	1.84	92	98	8.5	8.7
4	2/24/92	2/26/92	2.0	2.16	108			
4	2/24/92	2/26/92	2.0	2.11	106	107	1.41	1.32
7	2/27/92	3/2/92	2.0	1.88	94			
7	2/27/92	3/2/92	2.0	1.83	92	93	1.4	1.5
12	3/3/92	3/10/92	2.0	1.82	91			
12	3/3/92	3/10/92	2.0	2.22	111	101	14.1	14.0
14	5/14/92	5/14/92	2.0	1.58	97			
14	5/14/92	5/14/92	2.0	1.95	98	98	0.71	0.72

Table 9. Storage Dissipation Data for the 1992 Sacramento River Study (refrigerated at 4°C, pH 3)

Study: 117
Analyte: 2,4-D
MDL: 0.1 ppb
pH: 3

Sample Type: Surface Water
Labs: CDFA
Date of Report: 8/3/92
Chemist: Paul Lee

Day	Date Extracted	Date Analyzed	Spike Level (ppb)	Results (ppb)	% Recovery	x̄	SD	CV (%)
0	2/20/92	2/26/92	2.0	2.33	117			
0	2/20/92	2/26/92	2.0	2.06	103	110	9.90	9.0
1	2/21/92	2/26/92	2.0	2.53	127			
1	2/21/92	2/26/92	2.0	2.48	124	126	2.12	1.68
4	2/24/92	2/26/92	2.0	2.58	129			
4	2/24/92	2/26/92	2.0	2.02	101	115	19.8	17.2
7	2/27/92	3/2/92	2.0	1.87	93.5			
7	2/27/92	3/2/92	2.0	1.96	98	96	2.8	2.9
12	3/3/92	3/10/92	2.0	1.99	99.5			
12	3/3/92	3/10/92	2.0	2.07	104	102	2.83	2.75
14	5/14/92	5/14/92	2.0	2.18	109			
14	5/14/92	5/14/92	2.0	1.84	92	101	12.0	11.9

Table 10. Storage Dissipation Data for the 1992 Sacramento River Study (refrigerated at 4°C, pH 8.5)

Study: 117
Analyte: 2,4-D
MDL: 0.1 ppb
pH: 8.5

Sample Type: Surface Water
Labs: CDFA
Date of Report: 8/3/92
Chemist: Paul Lee

Day	Date Extracted	Date Analyzed	Spike Level (ppb)	Results (ppb)	% Recovery	X̄	SD	CV (%)
0	2/20/92	2/26/92	2.0	2.04	102			
0	2/20/92	2/26/92	2.0	2.04	102	102	0	0
1	2/21/92	2/26/92	2.0	2.2	110			
1	2/21/92	2/26/92	2.0	2.09	105	108	3.54	3.28
4	2/24/92	2/26/92	2.0	2.43	122			
4	2/24/92	2/26/92	2.0	2.4	120	121	1.41	1.17
7	2/27/92	3/2/92	2.0	1.88	94			
7	2/27/92	3/2/92	2.0	2.1	105	100	7.78	7.78
12	3/3/92	3/10/92	2.0	1.78	89			
12	3/3/92	3/10/92	2.0	2.33	117	103	19.8	19.2
14	5/14/92	5/14/92	2.0	1.99	99.5			
14	5/14/92	5/14/92	2.0	2.29	115	108	10.6	9.81

Table 11. Storage Dissipation Data for the 1992 Sacramento River Study (refrigerated at 4°C, pH 3)

Study: 117
Analyte: Dicamba
MDL: 0.1 ppb
pH: 3

Sample Type: Surface Water
Labs: CDFA
Date of Report: 8/3/92
Chemist: Paul Lee

Day	Date Extracted	Date Analyzed	Spike Level (ppb)	Results (ppb)	% Recovery	x̄	SD	CV (%)
0	2/20/92	2/26/92	2.0	2.2	110			
0	2/20/92	2/26/92	2.0	2.06	103	107	4.95	4.63
1	2/21/92	2/26/92	2.0	2.13	107			
1	2/21/92	2/26/92	2.0	2.16	108	108	0.71	0.66
4	2/24/92	2/26/92	2.0	1.66	83			
4	2/24/92	2/26/92	2.0	1.6	80	82	2.1	2.6
7	2/27/92	3/2/92	2.0	1.97	99			
7	2/27/92	3/2/92	2.0	2.19	110	105	7.78	7.41
12	3/3/92	3/10/92	2.0	2.21	111			
12	3/3/92	3/10/92	2.0	2.13	107	109	2.83	2.59
14	5/14/92	5/14/92	2.0	1.86	93			
14	5/14/92	5/14/92	2.0	1.54	77	85	11	13

Table 12. Storage Dissipation Data for the 1992 Sacramento River Study (refrigerated at 4°C, pH 8.5)

Study: 117
Analyte: Dicamba
MDL: 0.1 ppb
pH: 8.5

Sample Type: Surface Water
Labs: CDFA
Date of Report: 8/3/92
Chemist: Paul Lee

Day	Date Extracted	Date Analyzed	Spike Level (ppb)	Results (ppb)	% Recovery	x̄	SD	CV (%)
0	2/20/92	2/26/92	2.0	1.88	94			
0	2/20/92	2/26/92	2.0	2.08	104	99	7.1	7.2
1	2/21/92	2/26/92	2.0	1.96	98			
1	2/21/92	2/26/92	2.0	1.71	86	92	8.5	9.2
4	2/24/92	2/26/92	2.0	1.76	88			
4	2/24/92	2/26/92	2.0	1.55	78	83	7.1	8.6
7	2/27/92	3/2/92	2.0	2.13	107			
7	2/27/92	3/2/92	2.0	2.12	106	107	0.71	0.66
12	3/3/92	3/10/92	2.0	1.9	95			
12	3/3/92	3/10/92	2.0	2.33	117	106	15.6	14.7
14	5/14/92	5/14/92	2.0	1.53	77			
14	5/14/92	5/14/92	2.0	1.79	90	84	9.2	11

Table 13. Continuing quality control data (matrix blind spikes) for the 1992 Sacramento River Study.

Study: 117
Analytes: MCPA, 2,4-D, Dicamba
MDL: 0.1 ppb

Sample Type: Surface Water
Labs: CDFA
Date of Report: 6/4/92

Chemical	Lab No.	Spike Level (ppb)	Results (ppb)	% Recovery	x̄	SD	CV (%)
MCPA	62	0.5	0.55	110			
	64	0.5	0.4	80			
	125	0.3	0.28	93			
	179	0.3	0.26	87			
	180	0.3	0.31	103	95	12	13
2,4-D	62	0.5	0.52	104			
	64	0.5	0.4	80			
	125	0.3	0.33	110			
	179	0.3	0.21	70			
	180	0.3	0.28	93	91	17	19
Dicamba	62	0.5	0.4	80			
	64	0.5	0.49	98			
	125	0.3	0.22	73			
	179	0.3	0.23	77			
	180	0.3	0.31	103	86	13	15

CALIFORNIA DEPT. OF FOOD & AGRICULTURE
CHEMISTRY LABORATORY SERVICES
ENVIROMENTAL MONITORING SECTION
3292 Meadowview Road
Sacramento, CA 95832
(916) 262-2080
Fax (916) 262-2082

Original Date:March 1, 1992
Supersedes: none
Current Date:March 22, 1993
Method #:MCPA 92-1

MCPA, DICAMBA and 2,4-D in River Water by GC/MSD

SCOPE:

This method is for the determination of MCPA, DICAMBA and 2,4-D in River water. The detection limit of this method is 0.1 ppb for all three compounds.

PRINCIPLE:

The water sample is acidified below pH 1. The protonated MCPA, DICAMBA and 2,4-D are all extracted with diethyl ether. The residues are derivatized with diazomethane, and analyzed by gas chromatography on a capillary column using a mass selective detector (MSD).

REAGENTS AND EQUIPMENT:

1. ***Reagents:***

Petroleum ether, grade suitable for pesticide residue analysis.

Diethyl ether, grade suitable for pesticide residue analysis. (grade not suitable should be redistilled).

Sulfuric acid, concentrated, A.C.S. reagent grade.

Hydrochloric acid, concentrated, A.C.S. reagent grade.

Ethanol, 95%.

Potassium hydroxide, A.C.S reagent grade.

N-methyl-1-nitroso-p-toluenesulfonamide, Aldrich D2,800-0

Sodium sulfate, anhydrous, suitable for pesticide residue analysis.

Diazomethane (see below)

Reagents continued

PREPARATION OF DIAZOMETHANE:

Diazomethane is Explosive and Carcinogenic-use caution and protective measures (read MSDS)

Diazomethane is prepared from N-methyl-1-nitroso-p-toluenesulfonamide. Assemble a distillation apparatus according to the Aldrich Technical Information Bulletin number AL-131 (cat #Z10,025-0).

The reaction flask is placed in a 65°C water bath on a hot plate with a magnetic stirring control. A 0.5-inch stirring bar is placed in the reaction flask and a 1-inch stirring bar is placed in the water bath. Both magnetic bars should be stirring. Place a separatory funnel in the side arm of the Claisen adaptor. Add 10 mL of 95% ethanol to a solution of 5 g KOH in 8 mL water in the reaction flask. Five grams of N-methyl-1-nitroso-1-toluenesulfon amide crystals are carefully dissolved in 100 mL ether and transferred into the separatory funnel. The crystals are moderately soluble in ether. Carefully open the stopcock of the funnel to allow the solution to drain into the reaction flask at a slow rate of about 1 hour for the entire 100 mL solution. Add an additional 20 mL of ether to rinse the separatory funnel and drain it into the reaction flask.

Diazomethane formed in the reaction is distilled, condensed and collected into a 500 mL flask in an ice bath. After completing the distillation, transfer the diazomethane solution to a 4 ounce brown bottle with a teflon-lined cap and store it in the freezer. This solution should be good for about a month in the freezer.

2. *Equipment:*

Rotary evaporator (Büchi/Brinkmann, R110).

Nitrogen evaporator (Organomation Model #12).

Distillation kit (Aldrich Z 10025-0)

Hotplate with magnetic stirrer, 10"x10"

ANALYSIS:

Sample Preparation:

1. Wash all glassware with 1N HCl, rinse with deionized water and dry them in a 110°C oven.
2. Allow sample to equilibrate to ambient temperature. Measure 800 mL (or by weight) of the sample to be analyzed into a 1-liter separatory funnel and record the volume or the weight to one decimal point.
3. Add 2.5 mL of the concentrated sulfuric acid to the water slowly and mix well.
4. Add 150 mL of 1:1 petroleum ether : diethyl ether (v/v). Shake it vigorously for 1.5 minutes. ***Vent frequently as pressure builds rapidly.***
5. Allow the phases to separate. Drain the aqueous layer into a 1-liter beaker.
6. Pour the organic phase from the top of the separatory funnel into a 500-mL acid-washed beaker. Transfer the aqueous phase back to the separatory funnel.

ANALYSIS: *Sample Preparation: continued*

7. Repeat steps 4 through 6 twice. Combine the extracts.

8. Add approximately 20 mL of anhydrous sodium sulfate to the solvent extracts and immediately stir with a teflon rod to remove any water.

9. Pour the dried solvent to an acid-washed 500-mL boiling flask.

10. Rinse the beaker with 20 mL of the 1:1 ether mix and combine in the flask.

11. Evaporate the solvent to about 1-3 mL on a rotary evaporator at 35° C and 20 inches of vacuum.

Derivatization of the Residues:

1. Add 2 mL of the diazomethane solution to the residue in the 500-mL flask.

2. Allow the reagent to contact the inside surface of the flask by swirling gently and let the reaction mixture sit in fume hood covered with aluminum foil for 20 minutes. (If the brownish-yellow color has disappeared within 20 minutes, add additional diazomethane and let the reaction mixture sit for another 20 minutes.)

3. Evaporate the solvent and the excess reagent to just dryness at ambient temperature using a gentle stream of nitrogen.

4. Pipette 2 mL ethyl acetate into the flask and swirl. Make sure no significant solvent evaporation before transferring the sample to an autosampler vial. The extract is ready for GC analysis.

Instrument Conditions:

Hewlett-Packard Model 5890 Gas Chromatograph equipped with a series 5970 Mass Selective Detector Model 9000-340 Computer System and a Model 7673A Autosampler.
Column: HP-1 (cross-linked methyl silicon), 25 m X 0.2 mm X 0.33 um film.

Carrier:	Helium, 50 cm/sec
Column Temperature:	Initial 60°C 0.5 minute Program Rate 20°C/minute Final 250°C 5 minutes
Injector Temperature:	250°C
Detector Temperature:	250°C
Ions Selected for SIM Acquisition:	77, 125, 141, 188, 196, 198, 199, 200, 203, 205, 214, 216, 223, 225, 234, 236, 254, 256.
Retention time:	Dicamba, 9.3 min. MCPA, 9.4 min. 2,4-D, 10.0 min.

Volume Injected: **2 microliter**

CALCULATIONS:

Report data in ppb.

$$\text{Analyte (ppb)} = \frac{PA1}{PA2} \times \frac{FV}{W} \times SC \times 1000$$

Where:

PA1 = peak area of analyte from injected sample volume
PA2 = peak area of analyte standard
FV = final volume of sample extract (in mL)
W = sample weight (in grams)
SC = standard concentration (in ng/mL)

RESULTS and DISCUSSION:

Recovery:

Chemical Name	Spike Levels (ppb)	Recovery (%)	$\bar{x}$	Standard Deviation	n
Dicamba	0.1	92	0.11	0.014	5
	0.5	94	0.47	0.012	5
	2.0	106	2.11	0.130	5
	10.0	112	11.18	0.634	5
MCPA	0.1	122	0.122	0.011	5
	0.5	108	0.538	0.071	5
	2.0	85	1.708	0.110	5
	10.0	105	10.452	0.507	5
2,4-D	0.1	93	0.093	0.011	5
	0.5	107	0.534	0.044	5
	2.0	102	2.042	0.184	5
	10.0	95	9.460	0.388	5

Discussion: Our experience indicated that with this method all glassware must be rinsed with acid to ensure a decent recovery. We also noticed that the diethyl ether should be redistilled. The presence of many high background peaks were due to the impurity of the ether.

UP DATED BY: JIM ECHELBERRY

TITLE: LAB TECHNICIAN

WRITTEN BY: PAUL LEE

TITLE: AGRICULTURAL CHEMIST III

REVIEWED BY: CATHERINE COOPER

TITLE: SUPERVISING CHEMIST III

Appendix B. Dicamba concentration levels (ppb) for the seven sampling sites.

			SAMPLING SITES				
DATE	SR1	SR2	SR3	SR4	CBD	SS	FR
Feb 21, 1992	0	0	0	0	0	0	0
Feb 25, 1992	0	0	0	0	0	0	0
Feb 28, 1992	0	0	0	0	0	0	0
Mar 3, 1992	0	0	0	0	0	0	0
Mar 6, 1992	0	0	0	0	1.8	0	0
Mar 10, 1992	0	0	0	0	0.1	0	0
Mar 13, 1992	0	0	0	0	0	0	0
Mar 17, 1992	0	0	0	0	0	0	0
Mar 24, 1992	0	0	0	0	0	0	0
Mar 27, 1992	0	0	0	0	0	0	0
Mar 31, 1992	0	0	0	0	0	0	0
Apr 3, 1992	0	0	0	0	0	0	0
Apr 7, 1992	0	0	0	0	0	0	0
Apr 10, 1992	0	0	0	0	0	0	0
Apr 14, 1992	0	0	0	0	0	0	0

* MDL for Dicamba is 0.1 ppb

Appendix C. Daily application information for MCPA in the Sacramento River Basin.

Date	Acres Treated	Pounds of Active Ingredient	No. of Applications
Feb 1, 1992	210	128	3
Feb 2, 1992	5	3	1
Feb 3, 1992	601	331	9
Feb 4, 1992	775	492	18
Feb 5, 1992	1,621	1,222	28
Feb 6, 1992	321	223	14
Feb 7, 1992	987	475	15
Feb 8, 1992	271	176	4
Feb 9, 1992	283	147	4
Feb 10, 1992	250	190	3
Feb 12, 1992	20	12	1
Feb 17, 1992	518	313	7
Feb 18, 1992	383	241	4
Feb 20, 1992	2,062	1,285	22
Feb 22, 1992	1,212	901	20
Feb 23, 1992	608	472	9
Feb 24, 1992	6,319	3,992	94
Feb 25, 1992	5,753	4,167	83
Feb 26, 1992	5,294	4,793	70
Feb 27, 1992	5,959	4,444	86
Feb 28, 1992	5,343	3,685	87
Feb 29, 1992	5,118	3,419	85
Mar 1, 1992	808	584	17
Mar 2, 1992	1,561	1,332	22
Mar 3, 1992	3,604	2,827	61
Mar 4, 1992	2,782	2,369	33
Mar 5, 1992	263	230	3
Mar 6, 1992	394	341	5
Mar 7, 1992	1,601	1,348	17
Mar 8, 1992	1,782	1,313	29
Mar 9, 1992	2,911	2,418	46
Mar 10, 1992	2,847	2,343	41
Mar 11, 1992	1,674	1,199	36
Mar 12, 1992	1,164	1,054	22
Mar 13, 1992	866	875	19
Mar 14, 1992	38	20	3
Mar 17, 1992	648	510	13
Mar 18, 1992	1,029	894	19
Mar 19, 1992	503	449	8
Mar 20, 1992	1,694	1,279	22
Mar 21, 1992	473	308	9
Mar 22, 1992	445	301	4
Mar 23, 1992	875	562	7
Mar 24, 1992	1,333	1,131	16
Mar 25, 1992	1,352	946	14

Appendix C.(cont.) Daily application information for MCPA in the Sacramento River Basin.

Date	Acres Treated	Pounds of Active Ingredient	No. of Applications
Mar 26, 1992	731	577	17
Mar 27, 1992	544	327	8
Mar 28, 1992	402	265	9
Mar 29, 1992	84	33	2
Mar 31, 1992	833	559	9
Apr 1, 1992	86	75	3
Apr 2, 1992	561	380	8
Apr 3, 1992	419	338	6
Apr 4, 1992	188	132	6
Apr 7, 1992	485	208	6
Apr 8, 1992	84	45	1
Apr 9, 1992	150	122	2
Apr 11, 1992	93	79	2
Apr 14, 1992	81	73	2
Apr 20, 1992	870	267	2

Appendix D. Daily application information for 2,4-D in the Sacramento River Basin.

Date	Acres Treated	Pounds of Active Ingredient	No. of Applications
Feb 1, 1992	71	33	4
Feb 2, 1992	454	376	5
Feb 3, 1992	80	54	1
Feb 4, 1992	757	989	12
Feb 5, 1992	1,119	1,141	14
Feb 6, 1992	98	81	4
Feb 7, 1992	1,592	1,137	25
Feb 8, 1992	439	272	6
Feb 9, 1992	6	6	2
Feb 12, 1992	203	167	4
Feb 14, 1992	216	222	5
Feb 15, 1992	8	5	2
Feb 17, 1992	750	623	6
Feb 18, 1992	338	382	3
Feb 20, 1992	1,277	1,750	9
Feb 21, 1992	180	116	2
Feb 22, 1992	1,687	1,435	38
Feb 23, 1992	1,219	755	13
Feb 24, 1992	4,527	3,576	73
Feb 25, 1992	2,437	2,037	55
Feb 26, 1992	4,412	3,631	91
Feb 27, 1992	6,480	5,122	138
Feb 28, 1992	8,187	5,836	154
Feb 29, 1992	4,949	3,247	97
Mar 1, 1992	792	694	19
Mar 2, 1992	1,979	1,307	33
Mar 3, 1992	2,221	1,930	42
Mar 4, 1992	2,583	2,023	44
Mar 5, 1992	437	381	8
Mar 6, 1992	465	282	8
Mar 7, 1992	3,611	3,032	42
Mar 8, 1992	1,830	1,546	28
Mar 9, 1992	4,003	3,433	71
Mar 10, 1992	3,859	2,835	85
Mar 11, 1992	5,945	4,792	100
Mar 12, 1992	6,954	6,051	115
Mar 13, 1992	3,748	2,789	65
Mar 14, 1992	851	660	21
Mar 15, 1992	545	491	9
Mar 16, 1992	161	135	3
Mar 17, 1992	2,408	1,903	38
Mar 18, 1992	4,459	3,366	60
Mar 19, 1992	1,203	871	38
Mar 20, 1992	4,014	2,119	56
Mar 21, 1992	3,029	1,613	40

Appendix D(cont.). Daily application information for 2,4-D in the Sacramento River Basin.

Date	Acres Treated	Pounds of Active Ingredient	No. of Applications
Mar 22, 1992	612	520	8
Mar 23, 1992	864	712	17
Mar 24, 1992	2,217	1,476	37
Mar 25, 1992	2,357	1,554	37
Mar 26, 1992	2,935	1,668	58
Mar 27, 1992	2,388	1,449	40
Mar 28, 1992	1,562	1,347	34
Mar 29, 1992	468	357	17
Mar 30, 1992	1,226	928	19
Mar 31, 1992	858	358	22
Apr 1, 1992	1,298	851	28
Apr 2, 1992	2,177	1,893	55
Apr 3, 1992	1,332	1,327	35
Apr 4, 1992	1,169	662	26
Apr 5, 1992	418	192	7
Apr 6, 1992	566	230	17
Apr 7, 1992	1,456	1,063	30
Apr 8, 1992	629	308	16
Apr 9, 1992	917	311	26
Apr 10, 1992	1,325	528	18
Apr 11, 1992	223	84	7
Apr 12, 1992	270	6	2
Apr 13, 1992	899	66	11
Apr 14, 1992	453	118	17
Apr 15, 1992	184	101	12
Apr 16, 1992	266	184	11
Apr 17, 1992	105	63	8
Apr 18, 1992	4	3	2
Apr 19, 1992	12	10	2
Apr 20, 1992	364	199	7
Apr 21, 1992	336	268	13
Apr 22, 1992	1,598	611	23
Apr 23, 1992	510	157	13
Apr 24, 1992	473	239	19
Apr 25, 1992	504	149	10
Apr 26, 1992	1,498	351	16
Apr 27, 1992	1,550	1,027	19
Apr 28, 1992	954	438	15
Apr 29, 1992	911	549	15
Apr 30, 1992	2,628	859	37

Appendix E. Daily application information for dicamba in the Sacramento River Basin.

Date	Acres Treated	Pounds of Active Ingredient	No. of Applications
Feb 3, 1992	520	49	6
Feb 4, 1992	668	54	6
Feb 5, 1992	518	49	4
Feb 7, 1992	2,305	211	28
Feb 8, 1992	550	104	4
Feb 9, 1992	408	39	8
Feb 10, 1992	162	15	2
Feb 14, 1992	20	3	1
Feb 20, 1992	1,546	140	18
Feb 22, 1992	674	61	4
Feb 23, 1992	2,189	337	10
Feb 24, 1992	4,103	681	70
Feb 25, 1992	2,116	368	40
Feb 26, 1992	3,759	287	52
Feb 27, 1992	4,534	474	65
Feb 28, 1992	2,807	389	50
Feb 29, 1992	3,750	358	67
Mar 1, 1992	589	55	4
Mar 2, 1992	1,350	186	22
Mar 3, 1992	1,236	106	24
Mar 4, 1992	932	84	14
Mar 5, 1992	25	3	1
Mar 6, 1992	230	22	3
Mar 7, 1992	714	72	16
Mar 8, 1992	957	219	4
Mar 9, 1992	1,468	132	22
Mar 10, 1992	1,293	104	18
Mar 11, 1992	962	84	20
Mar 12, 1992	830	75	12
Mar 13, 1992	298	40	10
Mar 17, 1992	272	31	8
Mar 18, 1992	1,966	101	22
Mar 19, 1992	136	12	8
Mar 20, 1992	640	61	14
Mar 21, 1992	372	33	4
Mar 23, 1992	230	24	2
Mar 25, 1992	254	23	4
Mar 26, 1992	263	25	6
Mar 27, 1992	558	19	6
Mar 28, 1992	90	9	2
Mar 31, 1992	20	1	2
Apr 1, 1992	60	4	2
Apr 2, 1992	55	5	3
Apr 4, 1992	68	5	4
Apr 7, 1992	1,108	88	11
Apr 14, 1992	5	0	1
Apr 18, 1992	10	4	2
Apr 20, 1992	1,739	124	4
Apr 28, 1992	256	8	4

Appendix F. Rainfall (cm) at three meteorological stations representing the study area.

DATE	COLUSA	ZAMORA	NICOLAUS	AVERAGE
Feb. 14	4.3	2.9	3.6	3.6
Feb. 15	0.3	0.5	0.8	0.5
Feb. 16	---	0.1	0.3	0.1
Feb. 17	0.1	---	---	---
Feb. 18	2.0	1.1	0.8	1.3
Feb. 19	0.7	1.4	2.1	1.4
Feb. 20	---	---	0.1	---
Feb. 21	NA	0.7	0.9	0.8
Feb. 22	---	0.1	---	---
Feb. 27	---	---	1.6	0.5
Mar. 1	0.2	0.5	0.2	0.3
Mar. 2	---	0.1	---	---
Mar. 4	---	0.1	---	---
Mar. 5	3.0	3.7	2.7	3.1
Mar. 6	0.8	1.7	0.5	1.0
Mar. 12	0.5	---	---	0.2
Mar. 14	2.5	1.3	1.6	1.8
Mar. 15	1.1	0.6	0.4	0.7
Mar. 16	0.2	---	NA	0.1
Mar. 18	0.1	---	---	---
Apr. 11	0.8	0.7	0.5	0.7
Apr. 12	0.7	0.5	1.9	1.0
Apr. 13	0.1	0.1	---	0.1

--- = No measurable precipitation.
NA = Not Available

Appendix G. Colusa Basin Drain flow rate at Knights Landing gauging station.

State of California - Resources Agency
Department of Water Resources - Northern District
Station Number: A02945
COLUSA BASIN DRAIN AT KNIGHTS LANDING
(zero on gage = 0.00, used)

DAY	JAN	FEB	MAR	APR	MAY	JUN
1	287	NR	443	243	4.0	4.0
2	NR	NR	515	210	4.0	4.0
3	NR	NR	310	211	4.0	4.0
4	NR	NR	188	209	4.0	4.0
5	NR	NR	258	206	4.0	4.0
6	NR	NR	843	205	4.0	4.0
7	NR	NR	651	240	4.0	4.0
8	NR	NR	318	150	4.0	4.0
9	NR	NR	470	26	4.0	4.0
10	NR	NR	672	5.0	4.0	4.0
11	NR	NR	520	5.0	4.0	4.0
12	NR	NR	487	81	4.0	4.0
13	NR	0.0	410	106	4.0	4.0
14	NR	0.0	380	83	4.0	4.0
15	NR	0.0	575	59	4.0	4.0
16	NR	0.0	735	117	4.0	31
17	NR	0.0	132	62	4.0	450
18	NR	0.0	0.0	132	4.0	455
19	NR	0.0	0.0	5	4.0	442
20	NR	0.0	0.0	275	4.0	310
21	NR	0.0	244	222	4.0	183
22	NR	0.0	476	4.0	4.0	43
23	NR	0.0	583	4.0	4.0	60
24	NR	0.0	619	4.0	4.0	19
25	NR	0.0	537	4.0	4.0	4.0
26	NR	355	410	4.0	4.0	4.0
27	NR	497	342	4.0	4.0	4.0
28	NR	580	338	4.0	4.0	4.0
29	NR	598	311	4.0	4.0	4.0
30	NR		232	4.0	4.0	4.0
31	NR		263		4.0	
Mean	NR	NR	396	96.3	4.0	69.2
Max	NR	NR	843	275	4.0	455
Min	NR	NR	0.0	4.0	4.0	4.0

NR = No Records available for date

Appendix H. Sacramento Slough flow rate at Sacramento Slough gauging station.

State of California - Resources Agency
Department of Water Resources - Northern District
Station Number: A02925
SACRAMENTO SLOUGH AT SACRAMENTO RIVER
(zero on gage = 0.00, used)

DAY	JAN	FEB	MAR	APR	MAY	JUN
1	721	319	2650	381		NR
2	414	320	2090	405		NR
3	385	268	1530	398		NR
4	402	218	1050	339		NR
5	545	267	1030	364		NR
6	422	304	1450	338		NR
7	606	322	1740	272		NR
8	897	340	1160	300		NR
9	759	360	2000	468		NR
10	1040	399	2050	652	N	NR
11	923	666	1870	658	O	NR
12	350	735	1640	681		NR
13	528	0.0	1460	658	R	NR
14	322	1540	1360	544	E	NR
15	262	F	1320	434	C	NR
16	486	F	1070	586	O	NR
17	592	F	104	687	R	NR
18	620	F	989	689	D	NR
19	584	F	3460	544	S	274
20	419	F	4770	529		326
21	369	F	4390	638		394
22	399	F	3390	627		432
23	392	F	2490	524		419
24	401	F	1940	512		403
25	376	F	1640	495		432
26	363	F	1510	NR		375
27	373	5290	1400	NR		279
28	373	4450	1190	NR		299
29	348	3390	980	NR		390
30	285		788	NR		387
31	249		466			
Mean	490		1773	NR	NR	
Max	1040	F	4770	NR	NR	NR
Min	249	0.0	104	NR	NR	NR

Station located 0.5 miles above mouth, 4.6 miles southeast of Knights Landing. During low flows this represents combined flows of Sutter Bypass and Reclamation District 1500. During high flows (above gage height 26.0) the slough is entirely flooded.

NR = No Records available for date.
F = Gage flooded