

MONITORING FOR THE PRESENCE OF 2,4-D IN
THE AIR: A COOPERATIVE CALIFORNIA STUDY

by

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Acknowledgements and Participants

1. Field Sampling: The Contra Costa County Agricultural Commissioner's staff; the San Joaquin County Agricultural Commissioner's staff

2. Chemical Analysis: T. M. Mischke, California Department of Food and Agriculture

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Agricultural Commissioner of Sacramento County
Agricultural Commissioner of San Joaquin County
Agricultural Commissioner of Solano County

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

I. Introduction

The use of phenoxy herbicides for the control of broadleaf weeds has been widespread within California since World War II. Agriculture has utilized phenoxy herbicides, primarily 2,4-D and MCPA, for economical weed control in registered crops. The application methods and use of phenoxy herbicides are regulated by the California Department of Food and Agriculture and the county agricultural commissioners to protect sensitive crops from injury caused by improper application methods and off-target drift.

During previous growing seasons, including 1978, apparent phenoxy injury to grape vineyards has been reported within the Delta area east of San Francisco, specifically Contra Costa and San Joaquin Counties. The extent and severity of characteristic phenoxy-caused injury to grapes varied greatly from year to year. In response to this problem, each of the four Delta counties involved in this study, Contra Costa, Sacramento, San Joaquin and Solano, had previously developed their own restrictions on aerial herbicide applications.

Crop patterns and existing regulations in the Delta area make 2,4-D the suspected cause of phenoxy injury symptoms. There are several formulations of 2,4-D which have been used in California. The ester forms are classified as either "high volatile" or as "low volatile" based on their vapor pressure. Acid and amine forms are classed as "non-volatile" salts. All four counties heavily restrict the use of ester formulations of 2,4-D, but permit the use of "non-volatile" amine salt formulations. Prior to the grapes breaking dormancy all applications of 2,4-D are restricted and monitored to minimize potential injury. The date selected for this additional restriction is normally approximately the 15th of March.

Within San Joaquin County, existing state regulations prohibit the aerial application of 2,4-D in all but a small portion of the southwestern corner of the county. County personnel visually monitored all aerial applications in this region for applicator compliance with county and state regulations. Prior to 1979, Contra Costa and Sacramento County Agricultural Commissioners defined areas wherein their staff visually monitored aerial applications and/or they required a notice of intent to apply. Solano County, located furthest from the grape growing areas, had not required a notice of intent or assigned county personnel to visually monitor applications unless a crop sensitive to phenoxy herbicides was within two miles. Beginning 1 November 1978, the Solano County Agricultural Commissioner required notice of intent to apply for all restricted material including 2,4-D.

The objective of the study reported here was limited to establishing interagency cooperation for determination of the presence (quantitative) or absence of 2,4-D drift in selected vineyards within the four county area during the two month period, 15 March 1979 to 15 May 1979. Participation by the California Department of Food and Agriculture's Environmental Hazards Assessment Program (EHAP) in this study was limited to assisting the county agricultural commissioners. Such support was given by furnishing equipment, training, collection medium, and the chemical analysis of samples.

II. Materials & Methods

A. Study Design

The boundaries for the study were decided on during a preliminary meeting between the four county agricultural commissioners and EHAP (Figure 1).

Monitoring was performed within Contra Costa and San Joaquin Counties, with each county establishing their own sampling locations. Sites were located in or near vineyards where problems had been exhibited in previous years and which had access to 120V electrical power. The Environmental Hazards Assessment Program assisted the counties by inspecting the sites for possible sources of contamination which might affect later chemical analysis of collected air samples. Contra Costa County established three primary locations in the Antioch-Oakley area and San Joaquin established two sites on Mandeville Island and one site on Bacon Island (Figure 1).

To enable Contra Costa and San Joaquin Counties to make decisions as to when and where to monitor, a cooperative agreement was made between the four participating county agricultural commissioners. This agreement provided that from 15 March to 15 May 1979:

1. All four counties would institute a 24 hour notice of intent for all aerial applications of 2,4-D within the boundaries of the study area. Contra Costa and San Joaquin Counties would extend this restriction to cover ground rig applications also.
2. Upon receipt of a notice of intent, all counties would immediately forward this information to the Contra Costa Commissioner's office. Contra Costa County would in turn, notify San Joaquin County of any notices received.

The Environmental Hazards Assessment Program provided Contra Costa and San Joaquin Counties each with three air monitoring instruments, training

in their operation, collection tubes for thirty air samples, and freeze safes for the transportation of samples from sample sites to State chemistry laboratories in Sacramento.

B. Instrumentation

Instrumentation for this study were low volume air samplers incorporating a carbon **vaned** pump pulling through a critical orifice to establish a calibrated air flow rate of 5.5 **l/min.** through the collection tube. Sampler flowrates were calibrated prior to the delivery of samplers to the counties, at their field locations on 4 April 1979 and again after the termination of the study. The sampling apparatus is similar to that described by Robinson and Fox'. For the Delta study, 6" lengths of 19 mm O.D. glass tubing were packed with 60 to 80 mesh beads of precleaned Amberlite XAD-2, a solid adsorbant polystyrene-divinylbenzone **apolymer** purchased from Rohm & Haas. The resin was held in place using glass wool and 150 X '50 mesh/in stainless screen. The tubes were immediately sealed with plugs covered with Teflon film. At the sampling site, the tubes were unstoppered and inserted into Cajon Ultra Torr adaptors SS-12-UT-A-16 modified to accept a swagelock hose connector **SS-6-MHC-6S**. The hose connector was machined to hold the critical orifice plate. Collection and extraction efficiencies for 2,4-D esters and **amines** were performed at the Department of Food and Agriculture Chemistry Laboratory in Sacramento (Table 1). The percentage efficiencies compare favorable with the valued obtained by Robinson and Fox¹, Grover, et. al.² and Farwell, et. al.⁴, using similar solid adsorbant techniques.

TABLE 1. EXTRACTION AND RECOVERY EFFICIENCIES
FOR 2,4-D FROM THE XAD-2 RESIN TUBES

TUBE #	ISOBUTYL ESTER		DIETHYLAMINE SALT	
	AMOUNT SPIKED (μg)	AMOUNT RECOVERED (μg)	AMOUNT SPIKED (μg)	AMOUNT RECOVERED (μg)
1	10	8.1	10	9.0
2	10	9.2	10	9.5
3	10	8.2	10	9.3
4	10	9.0	10	9.2
MEAN VALUE		8.6 (86%)	9.3 (93%)	

C. Sampling

When a decision was made to monitor, county personnel would travel to the sampling site, load the collection tube, and plug in the instrument at the time the application was scheduled to begin. Before loading the collection tube, the date and time on, instrument number, and sampling site number **were** recorded.

Sampling was stopped after a minimum of three (3) hours sampling time. Date and time off were recorded, the tubes sealed again with Teflon covered plugs and immediately placed into polyfoam freeze safe mailers containing dry ice. The freeze safes were transported to the State chemistry laboratories at Sacramento, California. Once at the chemistry laboratory, the tubes were stored at -70°C prior to extraction and analysis.

Several control samples were collected at the Contra Costa sampling sites. These samples were collected on days when 2,4-D was not being applied

to aid the chemistry laboratory analysis to separate background contaminants in the event any were being given off by local chemical plants.

D. Chemical Analysis

The Amberlite XAD-2 resin was precleaned by a distilled water/hydrochloric acid (100:1) wash, then rinsed with distilled water until the rinse water did not turn cloudy upon the addition of a silver nitrate solution. The XAD-2 resin was then rinsed with acetone and extracted for 24 hours with nanograde methanol in a Soxhlet extractor. After drying in a vacuum oven, the XAD-2 was packed and sealed in the sampler tubes.

The collected 2,4-D compounds were removed from the XAD-2 resin by sequential solvent extraction. The 2,4-D esters were first removed from this resin by elution with 60 ml of nanograde hexane. The collected hexane elutant was then evaporated to a volume of 5 ml. Two microliters of the hexane solution was injected into the gas chromatographs for analysis.

The low volatility types of 2,4-D were next removed from the resin by eluting the tubes with 60 ml of a 0.05N KOH in 20% water/80% methanol solution. The collected elutant was then acidified to pH <2 with an aqueous sulfuric acid solution (1:1 vv). The solution volume was reduced, using a steam bath, to about 20 ml. Next, the solution was extracted with two 60 ml aliquots of diethyl ether. The combined ether aliquots were evaporated to near dryness on a steam bath and 0.5 to 1 ml of methanol was added. A solution of diazomethane in ether was then added until the

yellow color persisted (about 2 ml). The solution was then allowed to sit for at least 15 minutes. Finally the solution was evaporated to near dryness and the resulting **methyl ester** of 2,4-D was picked up in 1 ml nanograde hexane. Two microliters of this solution were used for the analysis.

Samples were analyzed on gas **chromatographs** equipped with **Ni⁶³** electron capture detectors. A 10" x ¼" O.D. glass column packed with 4% OV 101 on 100/120-mesh Gas Chrom Q was employed in all the GC/ECD analyses. The column was held isothermally at 170°C during the analysis of the derivatized non-volatile 2,4-D samples and operated at a programmed rate of 5°C/min from 180°C (held for three minutes) to a final temperature of 210°C (held for six minutes) during the analysis of the 2,4-D esters.

III. Results and Conclusions

The area-wide sampling methodology employed in this study had been utilized previously for 2,4-D sampling in Washington State^{1,3} and in Saskatchewan, **Canada**². Detectable levels of both high volatile and low volatile formulations of 2,4-D were found in the Washington and Saskatchewan studies, although the majority of usage was with the high volatile ester formulations in both locations.

For the four county 2,4-D study reported here, no 2,4-D diethylamine salt or isobutyl ester form was detected in any of the samples collected (Table 2). There also were no **incidences** of characteristic 'phenoxy injury' to grapes reported to the agricultural commissioners' offices during this growing season.

TABLE 2. 2,4-D CHEMICAL ANALYSIS RESULTS

DATE COLLECTED			SAMPLER LOCATION ¹	SAMPLE #	TIME ON	AIR VOLUME SAMPLED (LITERS)	2,4-D LEVELS DETECTED ($\mu\text{g}/\text{m}^3$)			
MO	DAY	YR					ESTER FORMS ²		AMINE FORMS ³	
03	19	79	2	01	07:15	1512	None	Detected	None	Detected
03	19	79	3	02	NA	1292	"	"	"	"
03	19	79	1	03	07:00	1402	"	"	"	"
03	20	79	2	25	11:00	1375	"	"	"	"
03	20	79	2	26	07:00	1320	"	"	"	"
03	20	79	3	27	06:45	1347	"	"	"	"
03	20	79	3	28	10:50	1320	"	"	"	"
03	20	79	1	29	07:15	1347	"	"	"	"
03	20	79	1	30	NA	1320	"	"	"	"
03	21	79	3	19	06:35	2172	"	"	"	"
03	21	79	2	20	06:40	2332	"	"	"	"
03	21	79	1	21	06:55	2337	"	"	"	"
03	23	79	2	04	09:25	1677 ⁴	"	"	"	"
03	23	79	1	05	09:40	1457 ⁴	"	"	"	"
03	23	79	5	31	08:00	1210	"	"	"	"
03	23	79	4	32	08:25	1320	"	"	"	"
03	23	79	5	33	11:50	1182	"	"	"	"
03	24	79	3	22	06:45	1815 ⁴	"	"	"	"
03	24	79	2	23	06:55	1776 ⁴	"	"	"	"
03	24	79	1	24	07:05	1787 ⁴	"	"	"	"
03	24	79	4	34	08:30	1017	"	"	"	"
03	24	79	5	35	08:55	1045	"	"	"	"
03	29	79	1	07	07:35	2035	"	"	"	"
03	29	79	2	08	08:00	1771	"	"	"	"
03	29	79	3	09	08:05	1705	"	"	"	"
03	29	79	4	36	07:10	1155	"	"	"	"
03	31	79	2	13	07:10	1485	"	"	"	"
04	02	79	4	37	08:30	1045	"	"	"	"
04	03	79	4	38	07:30	1210	"	"	"	"
04	04	79	4	39	08:00	1155	"	"	"	"
04	04	79	5	40	11:00	1155	"	"	"	"

TABLE 2. 2,4-D CHEMICAL ANALYSIS RESULTS (CONT.)

DATE			SAMPLER LOCATION ¹	SAMPLE #	TIME ON	AIR VOLUME SAMPLED (LITERS)	2,4-D LEVELS DETECTED ($\mu\text{g}/\text{m}^3$)			
MO	DAY	YR					ESTER	FORMS ²	AMINE	FORMS ³
04	04	79	4	41	11:30	1127	None	Detected	None	Detected
04	05	79	2	64	08:20	1567	"	"	"	"
04	05	79	1	65	08:35	1595	"	"	"	"
04	07	79	2	66	06:20	1595 ⁴	"	"	"	"
04	07	79	1	68	06:40	1567 ⁴	"	"	"	"
04	08	79	2	67	06:05	1980 ⁴	"	"	"	"
04	24	79	5	42	07:25	1182	"	"	"	"
05	05	79	1	14	06:45	1595	"	"	"	"
05	05	79	2	15	06:30	1595	"	"	"	"
05	12	79	2	16	07:45	3520	"	"	"	"
05	12	79	1	18	06:55	3245	"	"	"	"

1) Numbers correspond to locations on Figure 1.

2) Samples analyzed for Isopropyl, Isobutyl, Propylene Glycol Butyl Ether, Butoxyethanol, and Isooctyl ester forms with a minimum detectable level of 1 μg .

3) Samples analyzed with a minimum detectable level of 0.2 μg .

4) Control Sample

The study's objectives were met, with the mechanisms for coordination and communication between counties working well over the 60 day study period. The negative results of this study could be attributable to many factors. One possibility is that weather trends may have helped to prevent 2,4-D drift into the vineyards. Studies in Washington State by Robinson and Fox' over several yearshave shown major differences in both atmospheric 2,4-D levels and severity in 2,4-D damage symptoms to grapes in that region from year to year. These studies point out a general relationship between weather patterns and 2,4-D injury to grapes.

The unique weather situation in the San Francisco Delta area often produces a fanning out of prevalent westerly winds. It would not be unusual for wind direction to be southwesterly in Solano County, while across the river in Contra Costa and San Joaquin Counties, the wind direction would be northwesterly. Several wind data stations would have been necessary to properly document the wind patterns within the study area. It was not possible for the Environmental Hazards Assessment Program to incorporate the instrumentation and manpower required to determine local weather patterns at the time of this study.

Another possibility could have been a change in use patterns of 2,4-D for 1979; however, this does not appear to have been the case. Table 3 shows the use permit data for 1979 from the four participating counties. Comparison with permit data from previous years (not shown) indicates no apparent reduction in usage over previous years. The **spacial** relationships between application sites and sampling locations are indicated in Figure 2.

TABLE 3 2,4-D USE PERMITS GRANTED WITHIN FOUR COUNTY STUDY AREA
MARCH 15 - MAY 15, 1979

#	DATE OF APPLICATION			COUNTY	LOCATION	TOTAL ACRES TREATED	TOTAL AERIAL		CROP TREATED
	MON	DAY	YR				2,4-D APPLIED	OR GROUND RI G	
1	MAR	17	79	SJ	T.1N,R.5E,S.28	169	256	A	WHEAT
2	MAR	19	79	CC	T.1N,R.3E,S.01	130	192	A	WHEAT
3	MAR	19	79	SJ	T.1N,R.5E,S.10	50	75	A	WHEAT
4	MAR	19	79	SO	T.3N,R.1E,S.26	160	240	A	WHEAT
5	MAR	19	79	SO	T.4N,R.2E,S.21	250	376	A	OATS
6	MAR	19	79	SO	T.4N,R.2E,S.36	340	512	A	WHEAT
7	MAR	20	79	CC	T.1N,R.3E,S.34	100	200	A	WHEAT
8	MAR	20	79	SJ	T.1N,R.5E,S.07	67	200	G	ASPARAGUS
9	MAR	20	79	SJ	T.2N,R.4E,S.13	125	112	G	BARLEY
10	MAR	21	79	CC	T.1N,R.2E,S.31	145	217	A	GRAIN
11	MAR	21	79	SA	T.2N,R.2E,S.08	30	45	A	BARLEY
12	MAR	21	79	SA	T.3N,R.2E,S.28	100	150	A	WHEAT & BARLEY
13	MAR	21	79	SA	T.2N,R.2E,S.04	75	112	A	WHEAT
14	MAR	21	79	SA	T.2N,R.2E,S.04	235	352	A	WHEAT
15	MAR	21	79	SA	T.3N,R.2E,S.33	25	37	A	WHEAT
16	MAR	21	79	SA	T.3N,R.2E,S.33	80	120	A	WHEAT & BARLEY
17	MAR	21	79	SA	T.2N,R.2E,S.03	40	60	A	WHEAT
18	MAR	21	79	SA	T.3N,R.2E,S.36	55	78	A	WHEAT
19	MAR	21	79	SA	T.2N,R.2E,S.03	135	203	A	WHEAT
20	MAR	21	79	SA	T.3N,R.2E,S.36	150	225	A	WHEAT
21	MAR	21	79	SA	T.3N,R.2E,S.25	30	45	A	BARLEY
22	MAR	21	79	SJ	T.1N,R.5E,S.07	67	200	G	ASPARAGUS
23	MAR	21	79	SJ	T.2N,R.5E,S.28	130	96	A	WHEAT
24	MAR	22	79	CC	T.1N,R.3E,S.03	8	64	G	ALFALFA
25	MAR	22	79	CC	T.1S,R.2E,S.**	545	409	A	BARLEY
26	MAR	22	79	CC	T.2N,R.2E,S.33	250	315	A	GRAIN
27	MAR	22	79	SJ	T.1N,R.5E,S.07	66	200	G	ASPARAGUS
28	MAR	23	79	CC	T.1N,R.2E,S.**	***	805	A	GRAIN
29	MAR	24	79	SJ	T.2N,R.4E,S.27	125	164	A	WHEAT
30	MAR	25	79	CC	T.1N,R.3E,S.34	410	824	A	WHEAT
31	MAR	25	79	SJ	T.1N,R.4E,S.27	70	144	A	WHEAT
32	MAR	25	79	SJ	T.2N,R.4E,S.27	125	164	A	WHEAT
33	MAR	26	79	CC	T.1N,R.2E,S.01	35	56	A	BARLEY
34	MAR	29	79	SO	T.3N,R.2E,S.04	88	136	A	WHEAT
35	MAR	29	79	SO	T.3N,R.2E,S.02	100	152	A	WHEAT
36	MAR	29	79	SO	T.3N,R.1E,S.03	30	48	A	WHEAT
37	MAR	29	79	SO	T.3N,R.2E,S.15	110	168	A	WHEAT
38	MAR	29	79	SO	T.3N,R.2E,S.16	360	544	A	WHEAT
39	MAR	30	79	CC	T.1N,R.2E,S.06	230	345	A	GRAIN
40	APR	01	79	SJ	T.1N,R.5E,S.17	30	48	G	BARLEY
41	APR	01	79	SJ	T.2N,R.5E,S.31	290	382	A	BARLEY
42	APR	02	79	SJ	T.2N,R.4E,S.13	125	112	G	BARLEY
43	APR	02	79	SJ	T.1N,R.5E,S.24	40	60	A	WHEAT
44	APR	02	79	SJ	T.2N,R.5E,S.29	5	10	G	DITCH BANKS

TABLE 3 (cont.)

#	DATE OF APPLICATION			COUNTY	LOCATION	TOTAL ACRES TREATED	TOTAL	AERIAL	CROP TREATED
	MON	DAY	YR				PINTS	OR	
#	MON	DAY	YR	COUNTY	LOCATION	TREATED	2, 4-D APPLIED	GROUND RI G	TREATED
45	APR	02	79	SO	T. 4N, R. 2E, S. 35	40	64	A	WHEAT
46	APR	02	79	SO	T. 4N, R. 1E, S. 27	174	264	A	WHEAT
47	APR	03	79	CC	T. 2N, R. 3E, S. 25	60	180	G	PASTURE
48	APR	03	79	SJ	T. 1N, R. 5E, S. 24	40	60	A	WHEAT
49	APR	04	79	CC	T. 2N, R. 3E, S. 26	60	180	G	PASTURE
50	APR	04	79	CC	T. 1S, R. 4E, S. 01	123	240	A	WHEAT
51	APR	04	79	CC	T. 1N, R. 4E, S. 32	165	328	A	ASPARAGUS
52	APR	04	79	SJ	T. 1N, R. 4E, S. 24	4	8	A	WHEAT
53	APR	04	79	SJ	T. 1N, R. 5E, S. 16	2	3	A	WHEAT
54	APR	04	79	SJ	T. 2N, R. 5E, S. 33	8	12	A	WHEAT
55	APR	04	79	SJ	T. 2N, R. 4E, S. 14	35	48	A	BARLEY
56	APR	04	79	SJ	T. 1N, R. 4E, S. 21	100	160	A	WHEAT
57	APR	05	79	CC	T. 1S, R. 2E, S. 03	20	3	A	BARLEY
58	APR	05	79	CC	T. 1N, R. 3E, S. 12	423	***	A	WHEAT
59	APR	05	79	CC	T. 1N, R. 4E, S. 07	254	***	A	WHEAT
60	APR	05	79	CC	T. 1N, R. 4E, S. 07	214	***	A	WHEAT
61	APR	05	79	SJ	T. 1N, R. 5E, S. 04	70	112	A	BARLEY
62	APR	05	79	SJ	T. 1N, R. 5E, S. 10	5	8	A	WHEAT
63	APR	05	79	SO	T. 4N, R. 1E, S. 26	10	16	A	PASTURE
64	APR	05	79	SO	T. 3N, R. 2E, S. 07	75	112	A	WHEAT
65	APR	06	79	CC	T. 1S, R. 4E, S. 30	55	80	A	GRAIN
66	APR	06	79	CC	T. 2N, R. 4E, S. 17	70	105	A	WHEAT
67	APR	06	79	CC	T. 2N, R. 4E, S. 07	40	60	A	WHEAT
68	APR	06	79	CC	T. 1N, R. 3E, S. 02	110	165	A	GRAIN
69	APR	08	79	SA	T. 2N, R. 2E, S. 09	100	150	A	WHEAT
70	APR	12	79	SJ	T. 1N, R. 5E, S. 02	8	16	A	WHEAT
71	APR	12	79	SJ	T. 2N, R. 5E, S. 26	12	19	A	WHEAT
72	APR	13	79	SJ	T. 1N, R. 5E, S. 17	80	120	A	BARLEY
73	APR	13	79	SJ	T. 2N, R. 5E, S. 26	13	21	A	WHEAT
74	APR	13	79	SJ	T. 2N, R. 5E, S. 33	10	16	A	BARLEY
75	APR	14	79	CC	T. 1N, R. 3E, S. 36	47	96	A	BARLEY
76	APR	15	79	CC	T. 1N, R. 2E, S. 04	75	200	A	BARLEY
77	APR	18	79	SJ	T. 1N, R. 4E, S. 23	80	120	G	ASPARAGUS
78	APR	20	79	SJ	T. 2N, R. 5E, S. 29	40	60	A	WHEAT
79	APR	20	79	SJ	T. 2N, R. 5E, S. 31	20	32	A	WHEAT
80	APR	30	79	SJ	T. 2N, R. 4E, S. 28	85	174	A	BARLEY
81	MAY	02	79	SJ	T. 1N, R. 4E, S. 12	68	72	A	BARLEY
82	MAY	05	79	CC	T. 3N, R. 3E, S. 34	60	120	A	GRAIN

CC = CONTRA COSTA, SA=SACRAMENTO, SJ =SAN JOAQUIN, SO = SOLANO

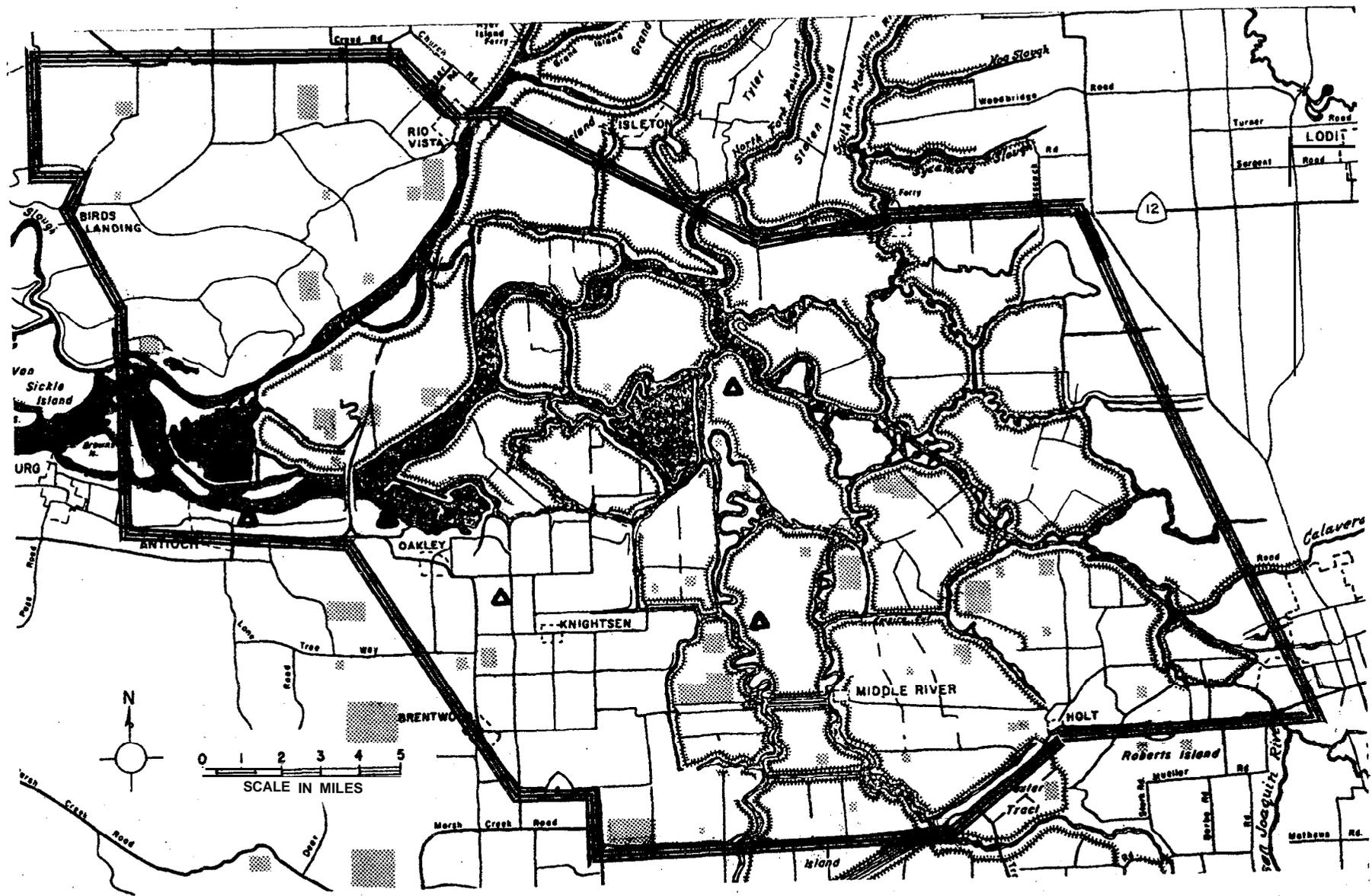


Figure 2. Applications of 2,4-D within study area from 15 March, 1979 to 15 May, 1979

▲ = Sampler location, ■ = Approximate acreage and location of 2,4-D applications listed on Table 3 .

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