State of California

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Memorandum

To : Clare Berryhill, Director
Department of Food and Agriculture

Date : February 26, 1987

Subject : ARB Monitoring of Ethyl Parathion

From : James D. Boyd
Executive Officer
Air Resources Board

In response to your request of February 13, 1985, the ARB has conducted air monitoring for pesticidal uses of ethyl parathion. This request was made by the Department of Food and Agriculture (DFA) pursuant to Division 7, Chapter 3, Article 1.5, Section 14021. The results of the ARB's monitoring efforts and additional background information are included in the summary table of this memorandum and in Attachments I-IV. By memorandum dated, December 5, 1985, your staff recommended changes to the sampling schedule. To compensate for this change in schedule, your staff requested that the monitoring results be submitted by February 1987. We have included these memorandums in Attachment I for your reference.

To narrow down possible sampling sites, several actions were taken by the ARB staff. These actions included numerous meetings with DFA staff, meetings with representatives of the Agricultural Commissioner's Office of the appropriate counties, aerial and ground surveys of possible site locations, and preliminary modeling to estimate areas of high concentrations. A chronology of these events has been included as Attachment II.

Several locations in both the San Joaquin Valley and Imperial County were selected as sampling sites. Sampling was conducted January through February 1986 in the San Joaquin Valley while sampling in Imperial County occurred from late September through October of 1986. The results of the ARB's sampling are shown in the following summary table. Maps of the sampling sites and complete data reports regarding the sampling and analysis are included as Attachment III to this memo.

Quality assurance and quality control procedures were established to ensure the integrity of the samples collected. The objectives and procedures which were established are outlined in the Quality Assurance Plan which is included in Attachment IV. Sampling precision was established by the use of collocated samplers. Precision of the samplers was found to be within 17 and 11 percent for the San Joaquin Valley and Imperial County sites, respectively. Field and laboratory audits were also conducted to ensure that the sampling was being conducted properly. The results of these audits are also included in Attachment IV.

Summary Table

Ethyl Parathion Sampling Results

Site	Ambient Concentration (ppt) Max 1	Max 2	Avg	Total No. of Samples	No. of Samples Above MDL
San Joaquin Valley					
Sanger	16.05	8.24	6.03	13	7
Parlier*	69.09	57.45	13.44	31	22
Reedley	34.00	29.64	15.68	13	13
Selma	22.91	21.64	12.62	13	8
Dinuba	31.09	24.00	10.07	13	13
Earlimart	5.04	4.16	4.60	6	2
Delano*	1.29	1.24	1.26	21	2
McFarland	7.34	6.04	3.53	7	5
Wasco	5.69	1.98	2.72	8	4
Shafter	< MDL	< MDL	<MDL	8	0
Bakersfield**	3.40	0.84	1.27	30	6
Fresno**	1.70	1.70	1.27	39	10
Sacramento**	0.84	0.84	0.84	28	2
Imperial County					
Heber	7.6	6.4	2.7	14	9
Holtville	2.4	2.2	1.4	13	7
Brawley-Swing School	3.3	2.7	1.7	13	8
Brawley-APCD Trailer	2.9	2.1	1.5	14	12
Calipatria*	12.0	3.8	3.6	13	8
El Centro**	1.2	0.82	1.0	14	2

MDL = Minimum detection limit, which is 0.8 ppt.

* These sites had collocated 24-hour samplers.

** Background sampling site.

In addition to quality assurance tests, testing was conducted to determine the effect of heavy fog and high temperature on the XAD-2 resin of the samplers. The results of the fog test showed that high humidity or fog did not affect the collection efficiency of the resin for ethyl parathion. The results of the conversion study in a high temperature environment showed minimal conversion to paraoxon, the breakdown product of ethyl parathion. These test results are also included in Attachment IV for your information.

If you have any questions, please contact me at 5-4383 or have your staff contact Bill Loscutoff at 2-6023.

Attachments

cc: Dr. Steven Book, DHS

ATTACHMENTS TO THE
TRANSMITTAL MEMORANDUM ON
ETHYL PARATHION MONITORING DATA

February 26, 1987

Attachment I: Correspondence Regarding Request and Transmittal of Data

Attachment II: Chronology of Events

Attachment III: Monitoring Data Reports

Attachment IV: Background Information Regarding Quality Assurance

Attachment I

Correspondence Regarding Request and
Transmittal of Data

Memorandum

To : Gordon Duffy, Chairman
Air Resources Board
1102 Q Street
Sacramento, CA 95814

RECEIVED
FEB 15 1985

Date : February 13, 1985

Place : Sacramento

From : Department of Food and Agriculture

Subject: Department Selection of First Candidate Pesticide for Evaluation in 1984-85 Under Tanner AB 1807/AB 3219 - Toxic Air Contaminants

The Department has completed the selection process for the first candidate pesticide from the list of pesticides sent to you on July 26, 1984. This letter is a formal request to the State Air Resources Board to begin documenting levels of airborne emissions and levels of public exposure to the pesticides parathion and methyl parathion.

Discussions between our staffs have resulted in the agreement that a complete documentation of levels throughout all seasons of usage will require up to a fifteen (15) month timeframe. Therefore, we will require this data on or before May 13, 1986.

My staff will be in contact with yours to identify usage areas and patterns as well as supply technical information on analytical procedures currently used by our Department.

Clare Berryhill
Director
(916) 445-7126

cc Stanley Cubanski, Acting Director, DHS
Emil Mrak, Chairman/Scientific Review Committee

State of California

Memorandum

To Bill Loscutoff, Chief
Toxic Pollutants Branch
Air Resources Board
1102 Q Street
Sacramento, CA 95814

Date : December 5, 1985

Place : Sacramento

From : Department of Food and Agriculture - 1220 N Street
Sacramento, CA 95814

Subject: ARB Monitoring for Ethyl Parathion (Reference 2301)

Ethyl parathion is an organic phosphate insecticide-acaricide that has been in use since the late 1940's. It is an active ingredient in 84 currently registered pesticide products and is generally formulated into granules, dusts, wettable powders and emulsifiable concentrates. Wettable powder formulations and emulsifiable concentrates are preferred for use on dormant orchards and on field and orchard crops, respectively.

Ethyl parathion is sold under many different trade names, some of which include: Bac E-M Parathion 6-3, Phoskil 25 Spray, Parathion 4 Emulsifiable, Prokil Parathion 4, Helena Parathion 8E, Parathion 2 Dust, Clean Crop Vegethion 45, Coastox Parathion 4-E, and Red-top Parathion 8 Flowable. Such products are used on a wide range of orchard, row and field crops, many of which may receive multiple applications on an as-needed basis. Depending upon crop and application rate, commodities treated with ethyl parathion may not be harvested for one to three weeks following treatment.

Since ethyl parathion is highly toxic to mammals (LD_{50} of 3-8 mg/kg) and is readily absorbed through the skin, prolonged contact with treated foliage should be avoided. Despite this relative high toxicity, some insects have developed resistance to ethyl parathion, but it is still considered a useful pesticide; its popularity is due in part to the fact that it is relatively economical to use. Where beneficial insects are at work and selectivity is important, however, newer materials have replaced ethyl parathion even when they are more costly.

Ethyl parathion is a category one restricted material and may only be used under permit and use conditions administered by the County Agricultural Commissioner. Regulatory procedures require users to file a pesticide use report with the county when this material is applied; information contained in the annual Pesticide Use Report published by CDFA is based on these individual reports to the counties. Table 1, Ethyl Parathion Use, summarizes use report data for 1981, 1982, and 1983. Table 2, Ethyl Parathion Use Pattern, contains information on application rates, tank mixtures, application methods and timing, and counties with major crop acreages which require ethyl parathion application.

SURNAME
SO-100

Recommendations

Use patterns of this pesticide suggest that sampling would be most productive either in the winter months when the amounts used are highest, or in the summer months when higher temperatures increase volatility. Based on consultations with Dr. James Seiber, Department of Environmental Toxicology at U.C. Davis and Dr. Dwight Glotfelty of the Agricultural Environmental Quality Institute, USDA, our staff has determined that there is no definitive information on which to choose one period over the other. Therefore, we recommend that you monitor at both times as follows:

County	Crop	Month
Winter Sampling		
Fresno, Tulare and Kings	Deciduous Orchards-almonds, peaches, nectarines, etc.	January or February
Summer Sampling		
Imperial	Sugar beets	September or October

Ronald J. Oshima
Branch Chief
Environmental Monitoring and
Pest Management, Room A-149
(916) 324-8921

Attachments

cc: Peter Venturini
Bob Barham
Peter Stoddard

TABLE 1. ETHYL PARATHION USE

	1981		1982		1983	
	Total Pounds Ai[1/]		Total Pounds Ai[1/]		Total Pounds Ai[1/]	
	755,302		663,336		663,364	
		% Use		% Use		% Use
Almond	207,264		187,643		192,953	
Apricot	11,528		16,863		15,870	
Nectarine	38,674		33,824		33,127	
Peach	59,040		58,839		67,999	
Plum	12,222		21,504		25,178	
Prune	32,993		39,488		36,072	
TOTAL	361,721	47.9	TOTAL 358,161	54	TOTAL 371,199	56
Grapefruit	23,537		3,091		1,330	
Lemon	16,622		20,196		37,434	
Orange	55,676		54,171		36,799	
Citrus	1,171		1,125		2,581	
TOTAL	95,835	12.7	TOTAL 78,583	11.8	TOTAL 77,144	11.6
Grape	23,537		26,517		46,023	
TOTAL	23,537	3.1	TOTAL 26,517	4.0	TOTAL 46,023	6.9
Broccoli	2,940		3,903		1,810	
Lettuce(head)	37,434		20,196		23,654	
Lettuce(leaf)	38,067		39,177		530	
TOTAL	78,441	10.4	TOTAL 53,576	8.1	TOTAL 65,994	3.9
Alfalfa	17,819		14,009		21,337	
TOTAL	17,819	2.4	TOTAL 14,009	2.1	TOTAL 21,337	3.2
Cotton	35,140		22,480		11,087	
TOTAL	35,140	4.7	TOTAL 22,480	3.4	TOTAL 11,087	1.7
Rice	25,397		15,230		7,419	
TOTAL	25,397	3.4	TOTAL 15,230	2.3	TOTAL 7,419	1.1
Sugarbeet	32,020		15,137		23,461	
TOTAL	32,020	4.2	TOTAL 15,137	2.3	TOTAL 23,461	3.5
Tomato	17,028		19,389		16,137	
TOTAL	17,028	2.3	TOTAL 19,389	2.9	TOTAL 16,137	2.4
	Cumulative %=91		Cumulative %=90.9		Cumulative %=90.3	

1/ Active ingredient

Source: 1981, 1982 and 1983 Pesticide Use Reports

TABLE 2. ETHYL PARATHION USE PATTERN

	Application Rate in AI/AC 1/	Tank Mixture	Application Method	Application Timing	Counties with Highest Acreages 2/
Almonds	2#Ai/Ac	400-600 gal. water 2-8 gal. oil/AC	Orchard fan sprayer	Dormant spray Jan - Feb.	Kern, Stanislaus, Merced, San Joaquin, Butte, Fresno
Apricot	" " "	" " " " " " "	" " " "	" " " " " "	Stanislaus, San Joaquin, San Benito
Nectarine	" " "	" " " " " " "	" " "	" " " " " " Note: Some May use-thrips, Fresno Tulare, Stanislaus	Fresno, Tulare, Kern, Kings
Peach	" " "	" " " " " "	" " " "	" " " " " " Note: Some May use-thrips, Fresno Tulare, Stanislaus	Fresno, Stanislaus, Sutter Merced
Plum	" " "	" " " " " "	" " " "	" " " " " "	Fresno, Tulare, Kern, Kings
Prune	" " "	" " " " " "	" " " "	" " " " " "	Sutter, Yuba, Butte, Tehama
Grapefruit	4#AI/Ac Max.	Wide range 600-2000 gal water water + 1-1/2 gal oil	Orchard fan sprayer or vertical boom sprayer	Scale Pest phenology May-June	Riverside, Kern, San Diego
Lemon	" " "	" " " " " " " "	" " " " " "	Late summer Aug-Sept	Ventura, Riverside, Tulare
Orange	" " "	" " " " " " " "	" " " " " "		Tulare, Kern, Fresno
Grape	2-1/2 Ai/Ac	200-300 gal water 1 gal oil	Overvine boom sprayer	Dormant spray Jan-March mealybug	Fresno, Tulare, Kern, Madera

Table 2 (Cont'd)

	Application Rate in AI/AC 1/	Tank Mixture	Application Method	Application Timing	Counties with Highest Acreages 2/
Broccoli	1#	5-14 gal water 40-70 gal water	Aircraft boom sprayer	Varies spring/late summer aphid	Monterey, S.Barbara, Imperial, Ventura
Lettuce	1#	5-15 gal water 40-70 gal water	Aircraft boom sprayer	Varies Spring/late summer	Imperial, Monterey
Lettuce	2#-6	10 gal water	Boom sprayer incorporated	Preplant Minor soil pest use	Monterey
Rice	1/5# Ai/Ac	5-10 gal water	Aircraft	May	Colusa, Butte, Sutter, Glenn
Cotton	1# Ai	10-25 gal water 5-10 gal water	Boom sprayer Aircraft	July-Aug in in S. Joaquin	Fresno, Kern, Kings, Tulare
Sugarbeet	1#-1-1/2#	20-50 gal water 5-15 gal water	Boom sprayer Aircraft	Varies Sept-Oct in	Imperial, S. Joaquin Solano, Merced
Alfalfa	1/2#-1-1/2#	20-50 gal water 5-15 gal water	Boom sprayer Aircraft	Throughout season	Imperial, Tulare, Fresno
Tomato	1#-2#	20-50 gal water 5-15 gal water	Boom sprayer Aircraft	Varies July-Aug.	Fresno, Yolo San Joaquin, Solano

1/ Pounds active ingredient per acre
2/ Ranked in descending order

Source: 1983 California Crop & Livestock Reporting Service: County Agricultural Commissioner Report

emorandum

: Bill Loscutoff
Chief
Toxic Pollutants Branch
Air Resources Board
1102 Q Street
Sacramento, CA 95814

Date : December 12, 1985

Place : Sacramento

m : Department of Food and Agriculture - 1220 N Street
Sacramento, CA 95814

ject : Extension of the Ethyl Parathion Sampling Period

In view of recent changes in our recommended sampling schedule, we feel February 15, 1987, and April 15, 1987 would now be appropriate for your submittal of ethyl and methyl parathion monitoring data, respectively. In the case of ethyl parathion, this is an extension of nine months to insure that initial monitoring effects are successful in view of the two distinct but widely spaced periods of recommended monitoring (Attachment).

Also, because the EPA may withdraw the federal pesticide registrations of both ethylene dichloride (EDC) and carbon tetrachloride on January 1, 1986, and because ARB monitoring of canceled compounds will not be required, supplemental schedule changes may follow the EPA determination.

If you have any questions, please feel free to contact Peter Stoddard at 324-8916.

Ronald Oshima
Branch Chief
Environmental Monitoring and
Pest Management, Room A-149
(916) 324-8921

Attachment

cc: Lori Johnston
Peter Venturini
Bob Barham
Peter Stoddard

DEC 17 1985

Attachment II

Chronology of Events

ATTACHMENT II

Ethyl Parathion Monitoring
Chronology of Major Events

Date	Event
June 28, 1984	Initial meeting of ARB and DFA staff regarding pesticide monitoring. ARB/DFA staff continue to meet on a monthly or bi-weekly basis depending on need.
July 26, 1984	DFA transmits list of Candidate Pesticides.
February 13, 1985	DFA requests ARB to monitor ethyl parathion.
July 31, 1985	ARB completes San Joaquin Valley modeling analysis for ethyl parathion.
August 30, 1985	Parathion monitoring protocol is transmited to DFA.
August 1985	ARB staff meets with representatives of Imperial County APCD and Agricultural Commissioner's Office regarding parathion use and sampling.
September 1985	ARB conducts trial parathion sampling in Imperial County.
October 1985	Background parathion sampling begins at Sacramento, Bakersfield and Fresno.
December 1985	ARB staff meets with representatives from Fresno, Tulare, and Kern County APCD's and Agricultural Commissioner's Offices regarding parathion use and sampling.
December 27, 1985	ARB completes study of effects of heavy fog on parathion sampling.
January 6 - February 14, 1986	Parathion sampling is conducted at San Joaquin Valley sites.
January 1986	Aeromatic Data Division of ARB completes field evaluation of San Joaquin Valley samplers.
March 1986	Sampling is discontinued at background sites.

July 1986	ARB staff meets with representatives of Imperial County APCD and Agricultural Commissioner's Office regarding parathion use and sampling.
September 29 - October 24, 1986	Parathion sampling is conducted at Imperial County sites.
October 1986	Aeromatic Data Division of ARB completes field audit of Imperial County samplers.
October 1986	Aeromatic Data Division of ARB completes laboratory audit of parathion analysis.
February 1987	ARB transmits results of ethyl parathion monitoring to DFA.

Attachment III

Monitoring Data Reports

~~State of~~ California

Memorandum

To: Bill Loscutoff, Chief
Toxic Pollutants Branch

Date: January 29, 1987

Subject: EEB Project C-86-072
Parathion, Monitoring

Dean C. Simeroth, Chief
Engineering Evaluation Branch
Stationary Source Division

From: Air Resources Board

At the request of the Toxic Pollutants Branch, EEB staff conducted an ambient parathion sampling program from September 23 through October 22, 1986 in Imperial County. A total of six monitoring sites, one collocated, were selected for this program. Participants of the test program are identified below.

Name	Affiliation
Tom Parker	ARB/TPB
Lynn Baker	ARB/TPB
Al Jenkins	ARB/EEB
Bud Thoma	ARB/EEB
Jack LaBrue	ARB/EEB
Dwight Warner	ARB/EEB
Jack Rogers	ARB/EEB
Mike Poore	ARB/ADD
Dave Hartman	ARB/ADD
Gasper Torres	Imperial County APCD

Sampling Locations

Six monitoring sites, either a city or town in the vicinity of El Centro, were selected for ambient sampling and are listed below.

City/Town	Street Address	Sampling Location Code
El Centro	(See Attachment 1)[1/]	ELC
Calipatria[2/] - 1,-2	"	CAL
Brawley (APCD)	"	BRA
Brawley (Swing)	"	BRS
Holtville	"	HOL
Heber	"	HEB

1/ Sampling site criteria are shown in Attachment 1.
2/ Calipatria, collocated site.

Information specific to each sampling location is presented in Attachment 1:

(i) street address locating the sampling site within the city or town,

(ii) location of field to be sprayed with parathion with respect to the sampling site,

(iii) set up of the sampling equipment.

Sampling Methods

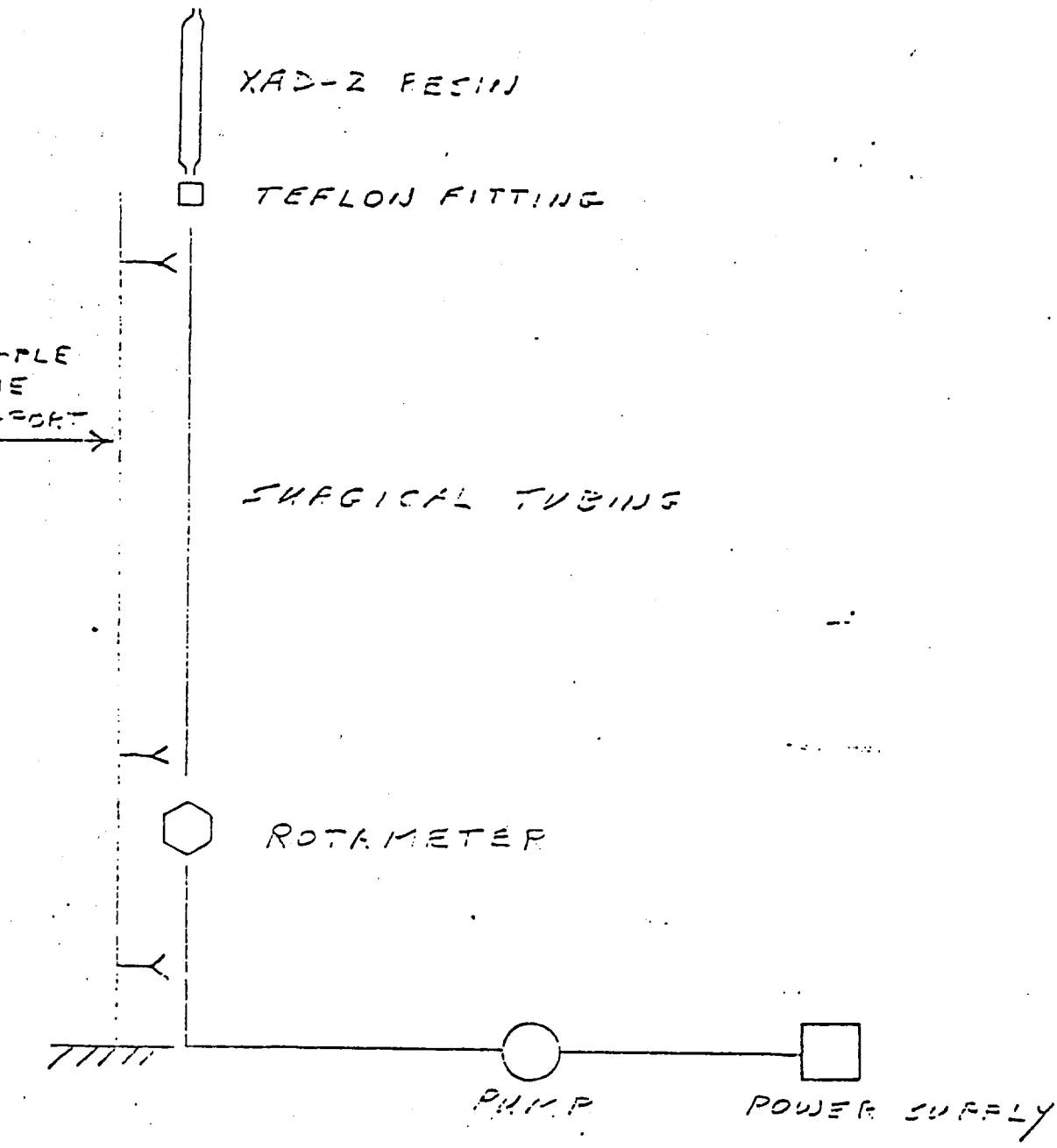
1. Measured quantities of ambient air were drawn through XAD-2 resin tubes.

   Calibrated rotameters were used for determining flowrates.

   The sampling train schematic is shown in Figure 1.

FIGURE 1

SAMPLING TRAIN SCHEMATIC



Laboratory Analysis

The Air Resources Board's Aerometic Data Division (ADD) laboratory performed sample analyses using their procedure entitled "Method ADDL003 for the Determination of Selected Organophosphate Pesticides in Ambient Air." The text of the method is presented in Attachment 2.

Test Conditions

All tests performed at each sampling site were of 24-hour duration. Sampling rates were set at 2-4 liters per minute.

XAD-2 resin tube changes were made every 24-hours yielding 4 samples per week per site.

The following is an example Weekly Schedule.

1. Monday A.M. - travel
2. Monday P.M. to Tuesday P.M. - Sample 1
3. Tuesday P.M. to Wednesday P.M. - Sample 2
4. Wednesday P.M. to Thursday P.M. - Sample 3
5. Thursday P.M. to Friday P.M. - Sample 4
6. Friday P.M. - travel

Figure 2 is an example of the data sheets filled out by test personnel to collect and organize field test data.

Also, daily observations of local meteorological conditions were made by test personnel and recorded in field notebooks as they visited each sampling site.

FIGUR 2

EXAMPLE OF FIELD DATA SHEET

START DATE	SAMPLE ID NO.	TUBE LOT NO.	TIME (START/STOP)	Measured Flow, (lpm) Start	Measured Flow, (lpm) Stop	Average Flow, (lpm)	SAMPLE TIME (MINUTES)	TOTAL VOLUME (l)	SAMPLE WT. (ug)	PARATHION CONC. (μg/l)	PAR CON (PPM

mments:

* $ppm = \frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

Chain of Custody

All sample labels contained the job number, the date the sample was taken, the sample or run number, the sample location, the type of sample, the log number for the person labeling the sample and the labeler's initials.

Each sample custodian was responsible for insuring sample integrity until the sample was transferred to another person. Also each laboratory was required to maintain a chain-of-custody record of all samples received for this project.

If any samples were damaged or the integrity questionable, a note was made and initialed by the person delivering the sample on the receiver's log book. Examples of log book notations and chain-of-custody forms are presented in Attachment 3.

Quality Control

Procedures to document the precision and accuracy of reported sampling and analytical results have been established by the ARB for most of the sampling procedures to be used and are contained in the ARB document entitled "Air Monitoring Quality Assurance Volume VI, Standard Operating Procedures for Stationary Source Emission Monitoring and Testing." Additional quality control procedures specific to pesticide monitoring are documented in "Quality Assurance Plan for Pesticide Monitoring". These quality assurance (QA) procedures include the use of referee audit samples provided by independent laboratories, duplicate sampling, siting criteria for ambient sampling, field and laboratory blank samples and calibration procedures.

Several quality assurance measures were taken during the course of the sampling program.

1. Resin blanks were taken into the field, kept with the sampling train, and later analyzed.
2. Samples of resin were spiked with known concentrations of parathion and later analyzed.

Sampling precision was calculated from a comparison of the collocated samplers at Calipatria. Sampling precision was within 22%.

Sampling accuracy was calculated from a field comparison of indicated flows obtained from rotameters readings and true flows obtained from an NBS traceable mass flow meter. Sampling accuracy was within 1%.

Test Results

The amounts and calculated concentrations of parathion collected over each 24-hour sampling period during the regularly scheduled field sampling are shown in Table 1. The laboratory test data are presented in Attachment 4. The concentrations of parathion in parts per trillion, PPT, shown in Table 1 were calculated using the equation shown below.

$$\text{concentration in PPT} = \frac{(24.05)\times(\text{ug}/\text{l})}{\text{Molecular Weight}} \times 10^{+6}$$

Field sampling with spiked and blank resin cartridges was conducted during the week of September 23, 1986 on the roof of the Imperial County APCD office building. Three samplers, were operated for 24 hours, one with an XAD-2 resin tube

spiked with 2.0 micrograms of parathion, one spiked with 0.5 micrograms, and one blank. This procedure was followed for three successive days. The percent recovery for parathion is shown in Table 2 and ranged from 86 to 98 percent. Parathion conversion to paraoxon during this test period was less than 6 percent and is shown in Table I, Attachment 4.

Meteorological observations are shown in Table 3.

Table 1

Field Sample Test Results

Date[1/]	HEBER Sample Volume, l	HEBER ug/l	HEBER PPT	HOLTVILLE Sample Volume, l	HOLTVILLE ug/l	HOLTVILLE PPT	BRAWLEY SWING SCHOOL Sample Volume, l	BRAWLEY SWING SCHOOL ug/l	BRAWLEY SWING SCHOOL PPT	BRAWLEY APCD TRAIL Sample Volume, l	BRAWLEY APCD TRAIL ug/l	BRAWLEY APCD TRAIL PPT	CALIPATRIA #1 (PRIMARY) Sample Volume, l	CALIPATRIA #1 (PRIMARY) ug/l	CALIPATRIA #1 (PRIMARY) PPT	CALIPATRIA #2 (DUPLICATE) Sample Volume, l	CALIPATRIA #2 (DUPLICATE) ug/l	CALIPATRIA #2 (DUPLICATE) PPT	EL CENTRO Sample Volume, l	EL CENTRO ug/l	EL CENTRO PPT
9-29	4270	LOQ	-	4453	2.9E-5	2.4	4226	3.3E-5	2.7	4302	2.9E-6	2.9	4573	2.2E-5	1.8	4399	2.8E-5	2.3	4438	LOQ	-
9-30	4802	LOQ	-	4757	1.3E-5	1.0	5010	4.0E-5	3.3	4974	1.4E-5	1.2	5012	2.0E-5	1.6	5012	2.2E-5	1.8	4940	LOQ	-
10-1	5117	LOQ	-	5098	LOQ	-	4977	LOQ	-	5013	1.4E-5	1.2	4893	LOQ	-	4959	LOQ	-	4648	LOQ	-
10-2	4813	LOQ	-	4928	LOQ	-	4716	LOQ	-	4767	1.5E-5	1.2	4732	LOQ	-	4817	LOQ	-	4708	LOQ	-
10-6	4414	1.8E-5	1.5	4324	9.3E-6	0.76	4123	9.7E-6	0.80	4186	1.9E-5	1.6	4809	1.5E-4	12.0	4207	N/D	-	4221	LOQ	-
10-7	5037	3.2E-5	2.6	4951	2.6E-5	2.2	5023	1.6E-5	1.3	5002	2.2E-5	1.8	4901	4.6E-5	3.8	4909	4.3E-5	3.5	4970	1.4E-5	1.2
10-8	4984	1.2E-5	0.99	N/D	-	-	4998	2.2E-5	1.8	4998	2.6E-5	2.1	5007	3.7E-5	3.1	5041	3.8E-5	3.1	5023	1.0E-5	0.82
10-9	5328	1.5E-5	1.2	5328	1.5E-5	1.2	N/D	-	-	4177	1.4E-5	1.2	N/D	-	-	N/D	-	-	4935	LOQ	-
10-14	4744	LOQ	-	4916	LOQ	-	4760	1.7E-5	1.4	4810	1.5E-5	1.2	4655	LOQ	-	4655	LOQ	-	4580	LOQ	-
10-15	4634	1.0E-4	6.4	4697	1.3E-5	1.1	4599	2.0E-5	1.6	4589	2.0E-5	1.6	4582	2.2E-5	1.8	4582	2.6E-5	2.2	4530	LOQ	-
10-16	4897	1.0E-4	7.6	4900	LOQ	-	4995	LOQ	-	4925	LOQ	-	4960	LOQ	-	4967	LOQ	-	5013	LOQ	-
10-20	4399	2.3E-5	1.9	4463	LOQ	-	4463	LOQ	-	4463	LOQ	-	4550	LOQ	-	4533	1.3E-5	1.1	4449	LOQ	-
10-21	4935	1.8E-5	1.5	4883	LOQ	-	4935	LOQ	-	4935	1.0E-5	0.84	4865	2.5E-5	2.0	4865	4.1E-5	3.4	4865	LOQ	-
10-22	4813	1.0E-5	0.86	4830	1.4E-5	1.2	4830	8.3E-6	0.68	4830	2.1E-5	1.7	4830[2/]	3.1E-5	2.6	4830[2/]	3.9E-5	3.3	4830	LOQ	-

1/ Date on which 24 hour sampling began.

2/ Estimated

LOQ: Below level of quantitation.

N/D Not determined

Table 2

Recovery Efficiencies of Parathion, Using Spiked XAD-2 Resin Cartridges at the El Centro Monitoring Station

Date[1/]	Amount Spiked, ug	Parathion Measured, ug	Percent Recovery
9-23-86	2.0	1.76	88
9-23-86	0.5	0.45	90
9-23-86	0	0.04	N/A
9-24-86	2.0	1.88	94
9-24-86	0.5	0.43	86
9-24-86	0	0.04	N/A
9-25-86	2.0	1.95	98
9-25-86	0.5	0.46	92
9-25-86	0	0.04	N/A

1/ Date on which 24-hour sampling began.
N/A not applicable

Table 3

C-86-072

METEOROLOGICAL OBSERVATIONS

DATE	Barometric Pressure in Hg	COMMENT
9-23	29.80	Clear
9-24	29.80	Clear
9-25	29.92	Clear and windy (westerly)
9-29	29.94	Clear and windy
9-30	29.94	Clear and hot
10-1	29.73	Clear and sunny
10-2	29.72	Clear and windy, cool
10-6	29.96	-
10-7	29.96	Clear and hot
10-8	29.97	Clear and hot, rain overnight
10-9	29.95	Cloudy and hot
10-14	30.12	Clear and hot
10-15	30.02	Partly cloudy
10-16	30.06	Clear
10-20	30.07	Clear and hot
10-21	30.10	-
10-22	29.94	Cloudy, overcast

Attachment 1

Sampling Site Information

NOTE: All sampling stations are in Imperial County

1. El Centro, APCD site, 150 S. 9th Street
   Phil Shafer, Telephone: 339-4314

2. Calipatria, Fire Station, 101 N. Lake Street
   Chris Hall, Fireman, Telephone: (619) 348-2886
   Margaret Hatfield, City Clerk, Telephone: 348-2293

3. Brawley, APCD trailer, No. on 111 just south of golf course
   Phil Shafer, Telephone: 339-4314

4. Brawley, Phil D. Swing School
   N. Western Avenue and A St., Felix Duarte,
   Telephone: 344-8686

5. Holtville, Meadow Union School (west of Holtville)
   S-80 at Bowker Road
   Jose Gastelum, Telephone: 352-7512

6. Heber, Rogelio E. Rodriguez Jr. High
   1052 Heber Avenue
   Jesse Silva, 353-3040

Table 1. Pesticide Monitor Siting Criteria

The following probe siting criteria apply to pesticide monitoring and are summarized from the EPA ambient monitoring criteria (40 CFR 58 Appendix E) which are used by the ARB.

Height above ground, meters	Distance from supporting structure, m		Other spacing criteria
	Vert.	Horiz.	
2-15	>1	>1	1. Should be >20 m from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. No furnace or incineration flues should be within 10 m.

Pesticide Monitoring in the Imperial Valley

Pesticide: Ethyl Parathion

Monitoring period: 9/29 - 10/24/86

Site address: Brawley
Phil D. Swing School
N. Western at A St.

Contact at site: Filex Duarte, School District Maintenance

Direction from site to fields which may be sprayed: W

Distance from site to fields which may be sprayed: 1/2 mile

Sampling method (power source AC or DC): (AC) XAD-2 resin tubes at 3 l/min, 24 hr.

Height of monitoring probe: 5' above roof
20' total above ground

Distance to obstructions:
None

Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: 9/29 – 10/24/86 (conversion study 9/23 - 25)

Site address: El Centro - APCD office roof
150 S. 9th St.

Contact at site: Phil Shafer, Deputy APCO
Harry Dillon
Gaspar Torres

Direction from site to fields which may be sprayed: Midtown background site

Distance from site to fields which may be sprayed: ——

Sampling method (power source AC or DC): (AC) XAD-2 resin tubes at 3 l/min., 24 hr.

Height of monitoring probe: 4' above roof
30' total above ground

Distance to obstructions: None

Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: 9/25 – 10/24/86

Site address: Calipatria – Fire Station roof (Collocated)
101 N. Lake St.

Contact at site: Chris Hall, Fireman
Margaret Hatfield, City Clerk

Direction from site to fields which may be sprayed: N, W

Distance from site to fields which may be sprayed: 1/4 mile

Sampling method (power source AC or DC): (AC) XAD-2 resin tubes at 3 ℓ/min, 24 hr.

Height of monitoring probe: 8' above roof
25' total above ground

Distance to obstructions: None

Pesticide Monitoring [illegible] Description

Pesticide: Ethyl Parathion

Monitoring period: 9/29 - 10/24/86

Site address: Brawley - APCD monitoring trailer
Hwy. 111 on south edge of Del Rio Golf Course
at Shank Rd.

Contact at site: Phil Shafer, Deputy APCO
Harry Dillon
Gaspar Torres

Direction from site to fields which may be sprayed:

Distance from site to fields which may be sprayed:

Sampling method (power source AC or DC): (AC) XAD-2 resin tubes
at 3 l/min, 24 hr.

Height of monitoring probe: 4' above trailer roof
15' total above ground

Distance to obstructions:
Tree to west

Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: 9/29 - 10/24/86

Site address: Heber
Felipe and Ramon Primary School
10th St. & Heber St.

Contact at site: Jesse Silva, Superintendent

Direction from site to fields which may be sprayed: W

Distance from site to fields which may be sprayed: 200 yd.

Sampling method (power source AC or DC): (AC) XAD-2 resin tubes
at 2 l/min, 24 hr.

Height of monitoring probe: 8' above roof
20' total

Distance to obstructions:
None

Pesticide Monitoring : [illegible]

Pesticide: Ethyl Parathion

Monitoring period: 9/29 - 10/24/86

Site address: Holtville (west on Hwy S-80)
Meadows Union School
S-80 at Bowker Rd.

Contact at site: Jose Gastélum, Custodian

Direction from site to fields which may be sprayed: All directions

Distance from site to fields which may be sprayed: Within 100 yd.

Sampling method (power source AC or DC): (AC) XAD-2 resin tubes at 3 l/min, 24 hr.

Height of monitoring probe: 4' above roof.
14' total

Distance to obstructions:
None

Attachment 2

Method ADDL003

Method for the Determination of Selected Organophosphate Pesticides in, Ambient Air

METHOD ADDL003

METHOD FOR THE DETERMINATION OF SELECTED ORGANOPHOSPHATE PESTICIDES IN AMBIENT AIR

1. Scope

This document describes a method for the sampling and analysis of parathion, methyl parathion, paroxon, malathion, and diazinon at concentrations normally found in ambient air. The method was developed based on NIOSH, EPA and the California Department of Food and Agriculture published methods.

2. Summary of Method

After sampling using a low-volume system comprising pump, controller, glass fiber pre-filter, and purified XAD-2 absorbant trap, the exposed filter and absorbant are desorbed with 2.0 milliliters of 80/20 isoctane/acetone mixture. Two microliters of the extract are injected using splitless mode technique into a gas chromatographic system equipped with a 30 meter DB-5 capillary column, thermionic detector (TSD), and data system. The resultant peaks are identified by characteristic retention times and quantitated in reference to external standards. The identity of a component may be confirmed by use of a column with different characteristics, a second detector system, or by GC/MS.

3. Interferences/Limitations

3.1 Components having similar GC retention times will interfere, causing misidentification and/or erroneous quantitation.

3.2 Extreme care must be taken to insure that sample losses do not occur due to leaks in the sampling system or to sample handling within the laboratory. All glassware must be thoroughly cleaned to insure that cross-contamination does not occur between samples. Samples are to be protected from sunlight during sampling and storage.

4. Apparatus

4.1 Varian Model 3300 Gas Chromatograph equipped with thermionic detector (TSD) and a Vista 402 Data System.

4.2 DB-5 fused silica capillary column, 30 meters x 0.35 mm i.d., 1 μm film thickness.

4.3 Amber vials, 3.7 ml capacity, with teflon-lined septum caps.

4.4 Sample agitator with timer and sample rack.

4.5 Microliter syringes, 5-50 µl sizes.

4.6 Low-volume sampler pump and flow controller capable of maintaining preset flow rates of 6 lpm over a 24 hour period. Sampling system must have an accurate timer system to control sampling interval and to indicate total sampling elapsed time.

4.7 Sampling head capable of containing a 37 mm glass fiber filter in-line with a 6" x 1/4" absorption tube containing XAD-2 absorbant.

4.8 Glass fiber filters, 37 mm diameter, type A/E, with teflon holder.

4.9 Glass absorption tubes, 6" x 1/4", containing purified XAD-2 absorbant; 400 mg primary section, 200 mg secondary section. Absorbant must be demonstrated to be free of interfering substances by analysis of unused absorbants (analytical blanks).

5. Reagents

5.1 80/20 iso-octane/acetone desorbant solvent: Mix 80 ml pesticide grade iso-octane (trimethyl pentane) and 20 ml pesticide grade acetone in a clean glass bottle equipped with teflon-lined screw cap. CAUTION: Flammable - DO NOT expose to heat or oxidizers.

5.2 Stock Standards: Individual 1000 µg/ml certified stock standards containing diazion, parathion, methyl parathion, malathion, and paraoxon may be obtained from Nanogens, Inc. CAUTION: Toxic - Use protective gloves in handling these materials.

5.3 Working Standards: Dilute 20 µl of each stock standard into 50/50 isoctane/acetone solvent and dilute to 10.0 ml. This corresponds to 2.0 µg/ml standard.

6. Instrument Conditions.

Column: 30 m x 0.37 mm i.d. DB-5 fused silica capillary column

Temperature - Injector: 250°C
Detector: 300°C
Oven: 50°C, initial, hold for 1 minute, ramp at 50°C/min to 140°C/min; ramp at 4°C/min to 260°C, 4 min hold

Flow Rates: Carrier - He, 50 cc/min at splitter, 0.5 min splitless hold, carrier velocity after splitter opens: 25 cm/sec

Detector: TSD - Range 11, Attenuation x 32
Hydrogen Flow: 4.5 cc/min
Air Flow: 180 cc/min
Heater: 3.4 amp

7. Sample Collection

7.1 Sampling flow controllers and indicators must be calibrated by trained personnel before the unit can be installed in the field. The flow rate calibration must be verified monthly at the flow rate used for sampling.

7.2 The 37 mm glass fiber filter and holder, as received from the laboratory, is placed in the sampling head compartment. The compartment is then assembled, taking care that the unit is completely sealed. The filter holder may be handled, but care must be taken not to touch or contaminate the filter itself. If any question of contamination is present, the filter is discarded and a new filter is installed.

7.3 The sealed XAD-2 absorbant tube is prepared for use by snapping off the sealed ends with the tool provided. The open tube is then placed in the sampling train using 1/4" polyethylene tubing fittings, making sure that the flow indicator arrow printed on the tube points in the direction of the flow. The tubing fittings must be tightened sufficiently to insure the system is leak-free.

7.4 After starting the pump system, the flow must be adjusted to approximately 6 lpm. The time, indicated flow reading, and the true flow (read from the calibration graph) must be recorded. The filter and absorbant trap numbers must be recorded. The elapsed time meter is reset to zero. The system is leak-checked by sealing the sampler inlet and insuring that the flow is zero.

7.5 After a 24 hour sampling period, the indicated flow and true flow rates must be recorded. The sampler system is deactivated, the elapsed time and actual time is recorded, and the filter and absorbant tube removed. The filter and cassette holder is placed into a plastic shipping container. The tube is sealed using the red end caps provided. The filter and tube are immediately sent to the laboratory with all sampling information and chain of custody.

8. Instrument Calibration Procedure

8.1 Before a standard solution may be injected, a system blank must be analyzed. This is done by injecting 2.0 µl of 80/20 iso-octane/acetone solvent for analysis. If the subsequent analysis indicates interferences or contamination, the solvent must be replaced.

8.2 A method blank must be analyzed for every 10 samples. This is done by randomly selecting a "blank" (unused) filter and absorbant tube, desorbing (extracting) the "blank" filter and absorbant, and injecting 2.0 µl of the resultant extract into the instrument for analysis. If interferences or contamination is noted, the source must be found and, if possible, eliminated.

8.3 Instrument calibration is performed by injection of 2.0 µl of 2.0 µg/ml mixed standard. The resultant chromatogram and calculated concentrations must be inspected to insure proper integration and consistency with previous analyses. The data is then used to calibrate the method. The instrument data system will not accept updated response factors which are not within 10 percent of historic data.

8.4 If the analyses are to be made daily, a weekly analysis of three standards (2.0, 0.4, 0.08 µg/ml) must be made to insure that the method exhibits linear response. In addition, a weekly "spiked" sample of 0.8 micrograms per absorbant tube of individual pesticides must be taken through the entire analytical scheme to insure that the method is in control. The results of these analyses must be entered on the method control charts.

9. Analysis of Samples

9.1 After removal of the glass fiber filter from the teflon filter holder using stainless steel forceps, the filter is carefully rolled and placed in a 3.7 ml vial. The filter must be forced into the bottom of the vial to insure tht the entire filter is in contact with the solvent.

9.2 After removal of the red end-caps from the absorbant tube, the tube is scored using a glass cutter above the location of the retainer spring. Using the tool provided, the tube is then broken and the retainer spring removed. The glass wool plug and the primary (400 mg) section of XAD-2 is placed in a 3.7 ml vial. Similarly, the secondary section (200 mg) of XAD-2 is placed in a second vial. Make sure all vials are properly identified.

9.3 Place 2.0 ml desorbing solvent (80/20) into the vials, cap tightly, and place on vial agitator for 45 minutes.

9.4 After desorption, 2.0 µl of each extract is injected into the chromatographic system for analysis. The data generated from the glass fiber filter extract is recorded as "filterable". The combined results are recorded as "total".

9.5 The results are recorded in micrograms/m^3 and are calculated as follows:

$$\mu g/m^3 = \frac{\mu g/ml \text{ (found)} \times 2 \times 1000}{\text{average flow (lpm)} \times \text{time sampled (minutes)}}$$

10. Method Sensitivity, Precision, and Accuracy

10.1 The method sensitivity, precision, and accuracy are outlined in Table I. The data was generated using standards.

11. Desorption Efficiencies and Sample Stability

11.1 The primary section of the XAD-2 sampling tube was "spiked" with 10 µl of solutions containing known amounts of the five organophosphate pesticides of interest. The tubes were then sealed, placed in a refrigerator for storage, and tested after intervals to test the stability of the materials on the sorbent. Table II presents the results of this study. Note that the samples are stable for over a period of two weeks.

11.2 The primary section of the XAD-2 sampling tube was "spiked" with 10 µl of solutions containing known amounts of the five pesticides of interest. The "spiked" tubes were then placed in the low vlume sampling device and sampled at a flow rate of 7.5 lpm for differing lengths of time. Both the primary and secondary sections of the sampling tubes were desorbed and analyzed. The results are presented in Table III. Note that at the sampling rate of 7.5 lpm, the breakthrough volume of all the pesticides tested is greater than 14 m^3.

Table I

Compound	Conc. 1 µg/ml	S.D.* (percent)	Conc. 2 µg/ml	S.D. (percent)	Conc. 3 µg/ml	S.D. (percent)	MDL µg/ml
Diazinon	2.0	11.6	0.4	14	0.08	7	0.04
Methyl Parathion	2.0	2.3	0.4	8	0.08	7	0.02
Paroxon	2.0	11	0.4	12	0.08	11	0.04
Malathion	2.0	9.6	0.4	10	0.08	8	0.04
Parathion	2.0	8.3	0.4	8	0.08	9	0.02

Compound	Correlation Coefficient	Slope	Intercept (µg/ml)
Diazinon	0.998	0.980	0.031
Methyl Parathion	0.998	0.988	0.016
Paroxon	0.997	0.996	0.026
Malathion	0.997	0.991	0.032
Parathion	0.998	1.003	-0.015

* S.D. = Relative Standard Deviation

Table II

ORGANO-PHOSPHATE PESTICIDE STABILITY STUDY

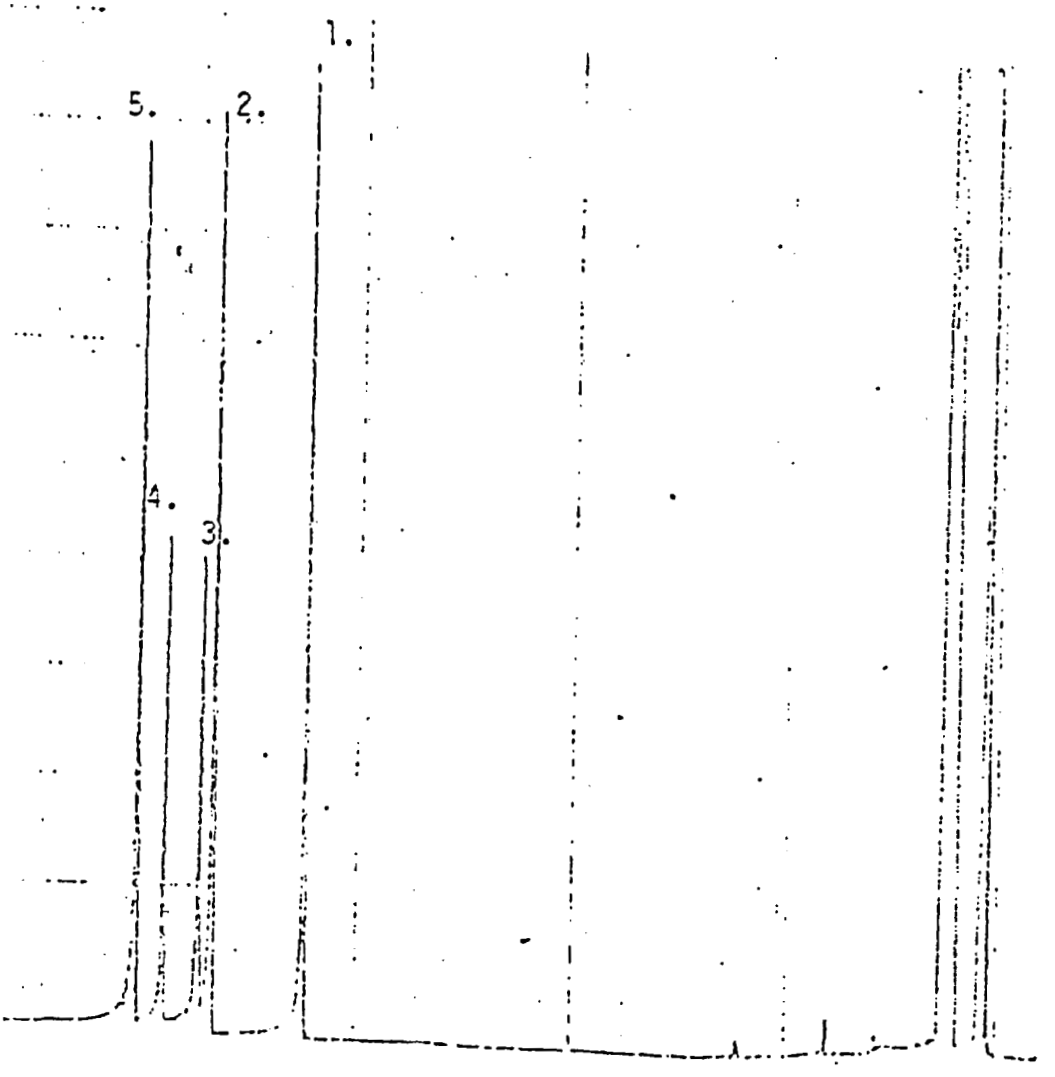
Storage Time, Hrs:	0	24	48	96	192	384
Compound	Amount Recovered, µg (Percent)					
Diazinon	1.68 (98)	1.60 (93)	1.70 (99)	1.58 (92)	1.64 (95)	1.62 (94)
Methyl Parathion	1.45 (83)	1.42 (82)	1.50 (86)	1.40 (80)	1.42 (82)	1.35 (78)
Paroxon	1.42 (97)	1.40 (96)	1.48 (101)	1.38 (94)	1.40 (96)	1.41 (96)
Malathion	1.42 (91)	1.38 (88)	1.50 (96)	1.40 (90)	1.42 (91)	1.48 (95)
Parathion	1,50 (88)	1.52 (89)	1.60 (94)	1.46 (86)	1.50 (88)	1.42 (84)

Table III

ORGANO-PHOSPHATE PESTICIDE SAMPLING AND BREAKTHROUGH STUDY

Volume Sampled (7.5 lpm), m^3	3.6	7.2	10.8	14
Compound	Amount Recovered, µg (percent) Primary/µg (percent) Secondary			
Diazinon	1.60 (93)/0 (0)	1.66 (96)/0 (0)	1.56 (91)/0 (0)	1.92 (100)/0 (0)
Methyl Parathion	1.47 (84)/0 (0)	1.55 (89)/0 (0)	1.44 (83)/0 (0)	1.62 (93)/0 (0)
Paroxon	1.40 (96)/0 (0)	1.48 (101)/0 (0)	1.38 (94)/0 (0)	1.50 (103)/0 (0)
Malathion	1.44 (93)/0 (0)	1.48 (95)/0 (0)	1.40 (90)/0 (0)	1.50 (96)/0 (0)
Parathion	1.52 (89)/0 (0)	1.56 (92)/0 (0)	1.42 (84)/0 (0)	1.56 (92)/0 (0)

CHROMATOGRAPHIC ANALYSIS OF ORGANOPHOSPHATE PESTICIDES



STANDARD: 1.0 ug/ml Mixed Standard
CONDITIONS: DB-5 Capillary Column, 30m, 50°C(1 min.), 50°C/min to 140°C, 4°C/min to 260°C(4 min.); TSD, 3.4 A, Range 11; Helium carrier, 26 cm/sec, splitless.

1. Diazinon
2. Methyl Parathion
3. Paroxon
4. Malathion
5. Parathion

Attachment 3

Example of Chain-of-Custody Form and Log Book Notations

APPROVED: _____

LOG BOOK

#	Sample/ Run #	Lab #	Action Taken	Date	Time	Given By	Taken By

Resin Train DT - Dioxin Train WF - Waste Fuel GV - Gas Van

HCl Train PS - Pan Sample CW - Cooling Water

Attachment 4

Laboratory Data

emorandum

: Bob Barham, Manager
Source Evaluation Section
Stationary Source Division

Date : November 17, 1986

Subject : Imperial Valley Parathion Study - October 1986

Bob Kuhlman, Manager
Laboratory Services Section
Aerometric Data Division

m : Air Resources Board

RECEIVED

NOV 18 1986

Stationary Source Division
Air Resources Board

The analyses of Imperial Valley parathion samples submitted by Stationary Source Division staff during the month of October have been completed. The results are presented in two tables. Table I includes field samples into which parathion was initially spiked at nominal levels of 2.0 and 0.5 micrograms. The purpose was to determine the extent of breakdown of parathion during sampling. Table II includes the results of analyses on all other field samples submitted to the laboratory.

Note that while several incoming samples were received with identical sample codes, all samples were reidentified by the laboratory, as received, with a sequential Lab I.D. number.

All quality control procedures were in effect during the period of analysis. The analytical system was audited by the Quality Assurance Section and the results of that audit will be reported by them.

Attachments

bcc: Mike Poore
Tom Parker
Lynn Baker
Dave Hartmann

TABLE I

(Spiked Field Samples)

Sample Code	Lab I.D. No.	Parathion Spike Added µg	Parathion Measured µg	Paraoxon Measured µg
ELC-1S	6394	2.0	1.76	0.09
ELC-1AS	6395	0.5	0.45	< 0.08
ELC-1	6396	--	< 0.04	< 0.08
ELC-2S	6397	2.0	1.88	0.10
ELC-2AS	6398	0.5	0.43	< 0.08
ELC-2	6399	--	< 0.04	< 0.08
ELC-3S	6400	2.0	1.95	0.11
ELC-3AS	6401	0.5	0.46	< 0.08
ELC-3	6402	--	< 0.04	< 0.08

TABLE II

(Regular Field Samples)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
HEB-1	6403	0.39	*	*	0.35	*
HOL-1	6404	*	*	*	*	0.13
BRS-1	6405	*	*	*	*	0.14
BRA-1	6406	0.11	*	*	*	0.15
CAL1-1	6407	*	*	*	*	0.10
CAL2-1	6408	*	*	*	*	0.12
ELC-1	6409	*	*	*	*	*
BLANK	6410	*	*	*	*	*
HEB-2	6411	*	*	*	*	*
HOL-2	6412	*	*	*	*	0.06
BRS-2	6413	0.11	*	*	*	0.20
BRA-2	6414	*	*	*	*	0.07
CAL1-2	6415	*	*	*	*	0.10
CAL2-2	6416	*	*	*	*	0.11
ELC-2	6417	*	*	*	*	*
HEB-3	6418	*	*	*	*	*
HOL-3	6419	*	*	*	*	*
BRS-3	6420	*	*	*	*	*
BRA-3	6421	*	*	*	*	0.07
CAL1-3	6422	*	*	*	*	*
CAL2-3	6423	*	*	*	*	*
ELC-3	6424	*	*	*	*	*
HEB-4	6425	*	*	*	*	*

TABLE II
(continued)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
HOL-4	6426	*	*	*	*	*
BRS-4	6427	*	*	*	*	*
BRA-4	6428	*	*	*	*	0.07
CAL1-4	6429	*	*	*	*	*
CAL2-4	6430	*	*	*	*	*
ELC-4	6431	*	*	*	*	*
HEB-1	6432	*	*	*	*	0.08
BRS-1	6433	*	*	*	*	0.04
HOL-2	6434	0.09	0.06	*	*	0.13
BRA-1	6435	0.15	*	*	*	0.08
CAL1-1	6436	0.13	0.15	*	*	0.72
CAL2-1	6437	VIAL BROKEN IN TUBE				
ELC-1	6438	*	*	*	*	*
HEB-2	6439	0.08	*	*	*	0.16
HOL-1	6440	0.10	*	*	*	0.04
BRS-2	6441	0.08	*	*	*	0.08
BRA-2	6442	0.28	*	*	*	0.11
CAL1-2	6443	*	*	*	*	0.23
CAL2-2	6444	*	*	*	*	0.21
ELC-2	6445	*	*	*	*	0.07
BLANK	6446	*	*	*	*	*
HEB-3	6447	*	*	*	*	0.06
HOL-3	6448	*	*	*	*	*

TABLE II
(continued)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
BRS-3	6449	0.19	*	*	*	0.11
BRA-3	6450	0.08	*	*	*	0.13
CAL1-3	6451	*	*	*	*	0.19
CAL2-3	6452	*	*	*	*	0.19
ELC-3	6453	*	*	*	*	0.05
BLANK	6454	*	*	*	*	*
HEB-4	6455	*	*	*	*	0.08
BRS-4	6456	*	*	*	*	0.04
BRA-4	6457	*	*	*	*	0.06
CAL1-4	6458			TEST FAILURE		
CAL2-4	6459			TEST FAILURE		
ELC-4	6460	*	*	*	*	*
HEB-5	6461	*	*	*	*	*
HOL-5	6462	*	*	*	*	*
BRS-5	6463	0.10	*	*	*	0.08
BRA-5	6464	0.13	*	*	*	0.07
CAL1-5	6465	*	*	*	*	*
CAL2-5	6466	*	*	*	*	*
ELC-5	6467	*	*	*	*	*
HEB-6	6468	0.55	*	*	*	0.36
HOL-6	6469	*	*	*	*	0.06
BRS-6	6470	*	*	*	*	0.09
BRA-6	6471	*	*	*	*	0.09

TABLE II
(continued)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
CAL1-6	6472	*	*	*	*	0.10
CAL2-6	6473	*	*	*	*	0.12
ELC-6	6474	*	*	*	*	*
HEB-7	6475	0.42	*	*	*	0.45
HOL-7	6476	*	*	*	*	*
BRS-7	6477	*	*	*	*	*
BRA-7	6478	*	*	*	*	*
CAL1-7	6479	*	*	*	*	*
CAL2-7	6480	*	*	*	*	*
ELC-7	6481	*	*	*	*	*
BLANK	6482	*	*	*	*	*
ELC-8	6752	*	*	*	*	*
HEB-8	6753	*	*	*	*	0.10
HOL-8	6754	*	*	*	*	*
BRS-8	6755	*	*	*	*	*
BRA-8	6756	*	*	*	*	*
CAL-1-8	6757	*	*	*	*	*
CAL-2-8	6758	*	*	*	*	0.06
BLANK	6759	*	*	*	*	*
ELC-9	6760	*	*	*	*	*
HEB-9	6761	0.17	*	*	*	0.09
HOL-9	6762	*	*	*	*	*
BRS-9	6763	*	*	*	*	*

TABLE II
(continued)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
BRA-9	6764	*	*	*	*	0.05
CAL-1-9	6765	*	*	*	*	0.12
CAL-2-9	6766	*	*	*	*	0.20
ELC-10	6767	*	*	*	*	*
HEB-10	6768	*	*	*	*	0.05
HOL-10	6769	*	*	*	*	0.07
BRS-10	6770	*	*	*	*	0.04
BRA-10	6771	*	*	*	*	0.10
CAL-1-10	6772	*	*	*	*	0.15
CAL-2-10	6773	0.09	*	*	*	0.19

* Not detected

Detection Limits:

Diazinon:	0.08 µg
Methyl Parathion:	0.04 µg
Paraoxon:	0.08 µg
Malathion:	0.08 µg
Parathion:	0.04 µg

State of California

Memorandum

To : Bill Loscutoff, Chief
Toxic Pollutants Branch

Date : January 22, 1987

Subject : EEB Project C-85-063
Parathion Monitoring

From : Dean C. Simeroth, Chief
Engineering Evaluation Branch
Stationary Source Division
Air Resources Board

At the request of the Toxic Pollutants Branch, EEB staff conducted an ambient air sampling program in the central valley for ethyl parathion. Sampling was conducted during the months of January and February, 1986 at ten sampling sites located in the Fresno and Bakersfield areas.

Attached is a description of the test program and a summary of test data.

Study No. C-85-063B

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I ADDL 003

II Modeling Results

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IV Complete Data Set

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I. INTRODUCTION

As the result of a request from the Director of the California Department of Food and Agriculture (DFA) to conduct ambient monitoring for ethyl parathion, the Engineering Evaluation Branch conducted field sampling in the Fresno and Bakersfield areas during the months of January and February 1986. This study was a coordinated effort between various Air Resources Board staff and personnel from DFA and was conducted subsequent to the requirements of AB 1807. The timing and location of collected samples, was based on information in the 1983 and 1984 Pesticide Use Reports (PUR) data base, and modeling performed by ARB staff to predict expected high impact areas. Table 1 shows a list of the various agency personnel involved with this project and their general duties.

Table 1

Study Contact List

Contact	Agency	Phone #	Duties
Greg Allen	ARB	323-8452	Field Engineer
Paul Allen	ARB	322-7278	Modeling
Lynn Baker	ARB	322-8278	Plan Development and Meteorological Data
Dick Lundquist	ARB	322-6049	Quality Assurance
Mike Poore	ARB	324-1970	Sample Analysis
Ralph Propper	ARB	322-8284	Interagency Coordination
Bill Fabre	DFA	322-2395	Application & Use Data
Cheryl Langley*	DFA	324-8916	Interagency Coordination
Tom Mischke	DFA	324-8916	Monitoring Methods
Lisa Ross	DFA	324-8916	Plan Development (Stat. Analysis)
Bill House	FCAPCD	(209) 445-3239	Coordination w/Dist.
Robert Koster	TCAPCD	(209) 733-6438	Coordination w/Dist.
Phil Powers	KCAPCD	(805) 861-3655	Coordination w/Dist.

*ARB's main contact with DFA

II. PROCESS DESCRIPTION

Ethyl parathion is an organic phosphate insecticide - acaricide that has been in use since the late 1940's. It is an active ingredient in many different pesticide products which are generally formulated into granules, dusts, wettable powders and emulsifiable concentrates. Wettable powder and emulsifiable concentrate formulations are those preferred for use on dormant orchards and on field and orchard crops, respectively. Such products are used on a wide variety of orchard, row and field crops, many of which may receive multiple applications.

Since ethyl parathion is highly toxic to mammals and is readily absorbed through the skin, prolonged contact should be avoided. Ethyl parathion is a restricted material and may only be applied under permit and use conditions administered by the local county agricultural commissioner. Regulatory procedures require users to file pesticide use reports with the county whenever parathion or other restricted materials are applied. This information is then used by DFA in publishing annual Pesticide Use Reports (PUR's) which summarize state-wide use. Table 2, "Ethyl Parathion Use." summarizes ethyl parathion use data published in the 1981, 1982, and 1983 PUR's. Table 3, "Ethyl Parathion Use Pattern," contains information on application rates, tank mixtures, application methods and timing, and counties with major crop acreages requiring ethyl parathion application. In general, the application rate varies from one half pound per acre to four pounds per acre in the geographical areas covered by this study. The methods of application include orchard fan sprayers, boom sprayers, and aircraft.

Table 2[1]/
ETHYL PARATHION USE

	1981			1982			1983	
	Total Pounds Active Ingredient			Total Pounds Active Ingredient			Total Pounds Active Ingredient	
	755,302	% Use		663,336	% Use		663,364	% Use
Almond	207,264			187,643			192,953	
Apricot	11,528			16,863			15,870	
Nectarine	38,674			33,824			33,127	
Peach	59,040			58,839			67,999	
Plum	12,222			21,504			25,178	
Prune	32,993			39,488			36,072	
TOTAL	361,721	47.9	TOTAL	358,161	54	TOTAL	371,199	56
Grapefruit	23,537			3,091			1,330	
Lemon	16,622			20,196			37,434	
Orange	55,676			54,171			36,799	
Citrus	1,171			1,125			2,581	
TOTAL	95,835	12.7	TOTAL	78,583	11.8	TOTAL	77,144	11.6
Grape	23,537			26,517			46,023	
TOTAL	23,537	3.1	TOTAL	26,517	4.0	TOTAL	46,023	6.9
Broccoli	2,940			3,903			1,810	
Lettuce(head)	37,434			20,196			23,654	
Lettuce(leaf)	38,067			39,177			530	
TOTAL	78,441	10.4	TOTAL	53,576	8.1	TOTAL	65,994	3.9
Alfalfa	17,819			14,009			21,337	
TOTAL	17,819	2.4	TOTAL	14,009	2.1	TOTAL	21,337	3.2
Cotton	35,140			22,480			11,087	
TOTAL	35,140	4.7	TOTAL	22,480	3.4	TOTAL	11,087	1.7
Rice	25,397			15,230			7,419	
TOTAL	25,397	3.4	TOTAL	15,230	2.3	TOTAL	7,419	1.1
Sugarbeet	32,020			15,137			23,461	
TOTAL	32,020	4.2	TOTAL	15,137	2.3	TOTAL	23,461	3.5
Tomato	17,028			19,389			16,137	
TOTAL	17,028	2.3	TOTAL	19,389	2.9	TOTAL	16,137	2.4
	Cumulative %=91			Cumulative %=90.9			Cumulative %=90.3	

Source: 1981, 1982 and 1983 Pesticide Use Reports

1/ Reference: Dec. 5, 1985 Memo from DFA to Loscutoff, ARB, Subject: ARB Monitoring for Ethyl Parathion (Reference: 2301)

TABLE 3[3/]

ETHYL PARATHION USE PATTERN

	Application Rate in AI/AC [1/]	Tank Mixture	Application Method	Application Timing	Counties with Highest Acreages[2/]
Almonds	2#	400-600 gal. water 2-8 gal. oil/AC	Orchard fan sprayer	Dormant spray Jan. - Feb.	Kern, Stanislaus, Merced, San Joaquin, Butte, Fresno
Apricot	" " "	" " " " " " " " "	" " " " " "	" " " " " "	Stanislaus, San Joaquin, San Benito
Nectarine	" " "	" " " " " " " " "	" " " " " "	" " " " " " Note: Some May use-thrips, Fresno, Tulare, Stanislaus	Fresno, Tulare, Kern, Kings
Peach	" " "	" " " " " " " " "	" " " " " "	" " " " " " Note: Some May use-thrips, Fresno, Tulare, Stanislaus	Fresno, Stanislaus, Sutter, Merced
Plum	" " "	" " " " " " " " "	" " " " " "	" " " " " "	Fresno, Tulare, Kern, Kings
Prune	" " "	" " " " " " " " "	" " " " " "	" " " " " "	Sutter, Yuba, Butte, Tehama
Grapefruit	4# Max.	Wide range 600-2000 gal. water water + 1-1/2 gal. oil	Orchard fan sprayer or vertical boom sprayer	Scale Pest phenology May - June	Riverside, Kern, San Diego
Lemon	" " "	" " " " " " " " "	" " " " " "	Late summer Aug. - Sept.	Ventura, Riverside, Tulare
Orange	" " "	" " " " " " " " "	" " " " " "		Tulare, Kern, Fresno
Grape	2-1/2	200-300 gal. water 1 gal. oil	Overvine boom sprayer	Dormant spray Jan. - March mealybug	Fresno, Tulare, Kern, Madera

TABLE 3[3/] (cont.)

ETHYL PARATHION USE PATTERN

	Application Rate in AI/AC [1/]	Tank Mixture	Application Method	Application Timing	Counties with Highest Acreages[2/]
Broccoli	1#	5-14 gal. water 40-70 gal. water	Aircraft boom sprayer	Varies spring/late summer aphid	Monterey, S. Barbara, Imperial, Ventura
Lettuce	1#	5-15 gal. water 40-70 gal. water	Aircraft boom sprayer	Varies spring/late summer	Imperial, Monterey
Lettuce	2#-6	10 gal. water	Boom sprayer incorporated	Preplant Minor soil pest use	Monterey
Rice	1/5#	5-10 gal. water	Aircraft	May	Colusa, Butte, Sutter, Glenn
Cotton	1#	10-25 gal. water 5-10 gal. water	Boom sprayer Aircraft	July Aug. in S. Joaquin	Fresno, Kern, Kings, Tulare
Sugarbeet	1#-1-1/2#	20-50 gal. water 5-15 gal. water	Boom sprayer Aircraft	Varies Sept. - Oct. in	Imperial, S. Joaquin Solano, Merced
Alfalfa	1/2#-1-1/2#	20-50 gal. water 5-15 gal. water	Boom sprayer Aircraft	Throughout season	Imperial, Tulare, Fresno
Tomato	1#-2#	20-50 gal. water 5-15 gal. water	Boom sprayer Aircraft	Varies July - Aug.	Fresno, Yolo San Joaquin, Solano

1/ Pounds active ingredient per acre
2/ Ranked in descending order

Source: 1983 California Crop & Livestock Reporting Service: County Agricultural Commissioner Report

3/ Ref: December 5, 1985 memo from DFA to Loscutoff, ARB,
Subject: ARB Monitoring for Ethyl Parathion (Reference 2301)

III. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through two, primary and backup, XAD-2 resin tubes. Parathion present in the sampled ambient air was captured by the XAD adsorbent contained in the resin tubes. Subsequent to field sampling, the resin tubes were transported to the ARB's Aerometric Data Division (ADD) Laboratory facilities in Sacramento for sample recovery and analysis using Method ADDL 003 (Attachment I).

Sampling trains designed to operate 24 hours were set up at ten selected sites identified in Section V of this report. In addition to these ten 24-hour samplers, two additional sampling trains were set up, one in the Fresno area and one in the Bakersfield area. These two additional samplers were used to collect 3-hour samples twice per day for a one week period.

In general, each week's sampling began on Monday afternoon with XAD-2 resin tube changes being made every 24 hours, except on 3-hour samplers, yielding four samples per week per site. The following schedule shows the typical weekly sampling time frame.

1. Monday A.M. - travel
2. Monday A.M. to Tuesday A.M. - Sample 1
3. Tuesday A.M. to Wednesday A.M. - Sample 2
4. Wednesday A.M. to Thursday A.M. - Sample 3
5. Thursday A.M. to Friday A.M. - Sample 4
6. Friday P.M. - travel

Each sample train consisted of two XAD-2 resin tubes, tube covers, teflon fittings and tubing, rain shield, flowmeter, train support, and a 110 VAC

carbon vane pump (Figure 1). On a daily basis, resin tubes were prepared for use by breaking off each sealed glass end and then inserting the tubes into the teflon fittings. The tubes were oriented according to a small arrow printed on each resin tube. Tube covers were installed to protect the adsorbent from exposure to sunlight, and rain shields were used to minimize any chance of water intrusion.

Sample pumps were left on continuously during mid-week sampling and turned off over the weekends. Upon daily sample initiation the flow rate was adjusted with the flowmeter metering valve to an indicated reading of three liters per minute (lpm). A daily leak check was performed by blocking off the sample inlet (with thumb) and watching the indicated flow on the flowmeter drop to zero (successful leak check). Upon completion of a successful leak check, the beginning indicated flow rate was set at 3 lpm. The date, time, tube lot number, site location and sample log number were then entered into the field data log book.

Sampling duration was approximately twenty four hours for each sample. In addition to the 24 hour samples, a limited number of three hour samples were taken in an attempt to quantify peak exposure. A timer was used during the 3 hour sampling periods to automatically shut off the sample pump. These samples were collected each morning and each afternoon.

Upon completion of each sampling period the final indicated flow rate and time observations were entered into the field data log book. The XAD-2 resin tubes were then removed from the sample train, end caps were installed on both ends and I.D. labels affixed to each resin tube. Each tube was then placed in a capped culture tube and stored in a cool, dark, ice chest until delivered to the ADD Lab for analysis. (Note; tube covers and rain shields were considered part of the sample train and were only in place on the XAD-2 resin tubes during sampling.)

Parathion Sampler

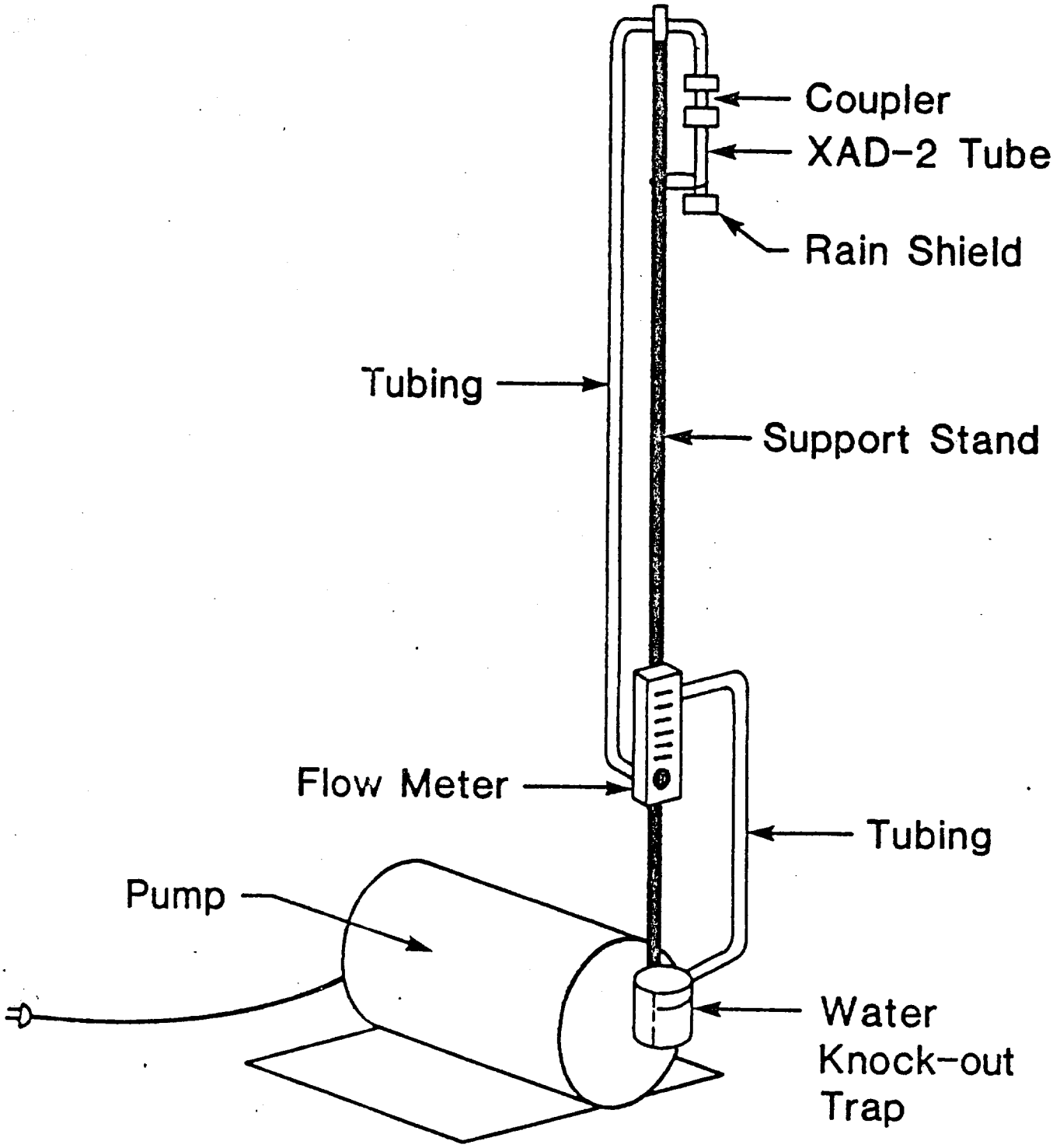


Figure 1

IV. SAMPLING SITES

In order to predict when, and where, high short term ambient concentrations of parathion could be expected to impact populated areas in California, staff analyzed 1983 Pesticide Use Report data to determine areas of high usage and the timing of application. This data, along with historical meterological data from local airports, was used with EPA's Industrial Source Complex Short Term (ISCST) air quality model to determine the locations which would be expected to have the highest ambient parathion concentrations. The complete results of this modeling study are included as Attachment II.

As a result of the modeling study, ten agricultural communities were selected for ambient monitoring. Due to the historical timing of applications (based on PUR's), the ten communities were separated into two groups, North and South. Accordingly, ambient monitoring in the Northern, or Fresno, area was conducted primarily during January; and monitoring in the Southern, or Bakersfield, area was conducted primarily during February.

The specific location of each monitoring site within each of the ten selected communities was chosen in accordance with ambient monitoring siting criteria outlined in 40 CFR 58. The criteria applied is summarized in Table 4. Monitoring sites in each community were chosen considering proximity to application areas (stone fruit orchards and vineyards), population exposure,and availability of a reasonably accessable site which met applicable siting criteria where monitoring equipment could be safely left unattended. The selected monitoring sites, along with contact information, are presented in Table 5. Figure 2 shows a map of the entire study area and the ten selected communities. Individual site descriptions are presented in Attachment III.

Table 4

Pesticide Monitor Siting Criteria

The following probe siting criteria apply to pesticide monitoring and are summarized from the EPA ambient monitoring criteria (40 CFR 58) which are used by the APB.

Height above ground, meters	Distance from supporting structure, m Vert.	Horiz.	Other spacing criteria
2-15	1	1	1. Should be 20 m from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 m apart.

Table 5

Ethyl Parathion Monitoring Sites and Contacts

County Designation: Fresno = F

Tulare = T

Kern = K

North

1) Selma — Selma Community Health Center
(F) — 1041 Rose Ave.
Contact: Maxime Helman, Manager, (209) 896-6660

2) Sanger — Jefferson School
(F) — Tucker Ave. & Annadale Ave.
Contact: Dallon Ragland, (209) 875-4591

3) Parlier — Kearney Agri. Research Field Station
(F) — Manning Road & Riverbend
Contact: Dr. Bob Brewer (209) 888-2537

4) Reedley — Monte Vista School
(F) — 1221 E. Duff Ave.
Contact: Kent Tanaka, Principal, (209) 888-2840

5) Dinuba — Water Pump Station
(T) — E. Kamm Ave. near Greene (near Wilson School)
Contact: Stan Moore, Public Works, (209) 591-3725

Table 5 (Continued)

South

6) Earlimart Intermediate School
(T) State Road
Contact: Vic Sylvester, (805) 849-2631

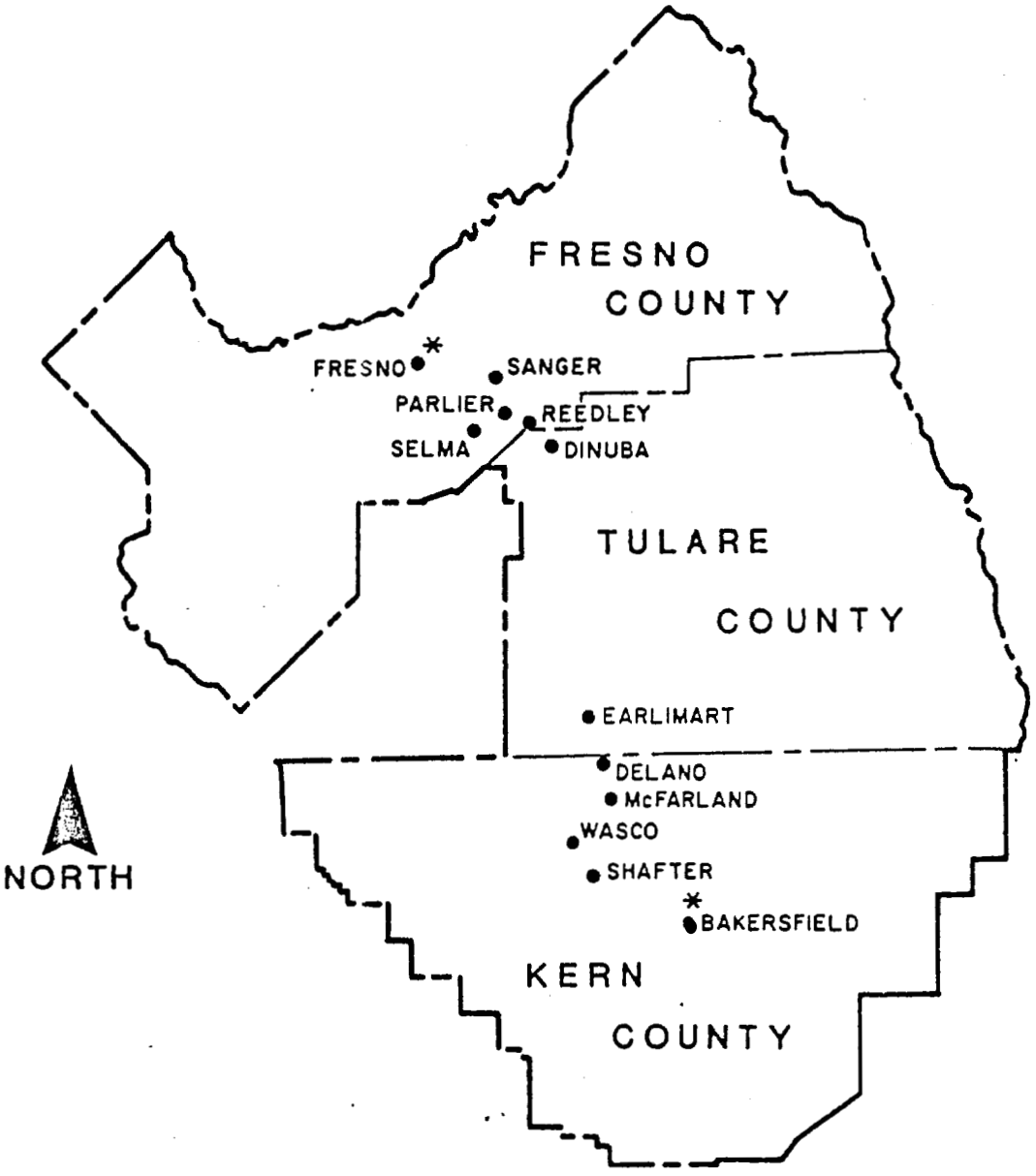
7) Delano City Works Bldg.
(K) 725 S. Lexington St.
Contact: Eddie Ahumada, Superint., (805) 725-2147

8) McFarland City Hall
(K) Kern Ave. & 4th
Contact: Mike O'Haver, City Planner, (805) 793-3091

9) Wasco North Kern Hospital
(K) 2101 7th St. (at Palm)
Contact: Scott Blakley, Administrator, (805) 758-5123

10) Shafter Richland School District Office
(K) 331 N. Shafter Ave. (at Richland Dr.)
Contact: Dr. Vera Stone, (805) 746-3904

San Joaquin Valley
Sampling Sites



* Denotes background sampling site. Sacramento was also included as a background site, but is not included on this map.

Figure 2

V. Summary of Results

Ambient concentrations of parathion were monitored in the Fresno area from January 7 through January 31 with a total of 146 samples taken. Monitoring in the Bakersfield area was conducted from January 28 through February 13 with a total of 102 samples taken. Measurable quantities of parathion were found at all but one of ten sampling sites during the study period. A summary of the completed field operations is presented in Table 6.

Table 6

Sample Collection Summary

Number of Samples Collected*

SITE	Week 1 (24 Hr)	Week 2 (24 Hr)	Week 2 (3 Hr)	Week 3 (24 Hr)	Week 4 (3 Hr)	Week 5 (24 Hr)	Week 5 (3 Hr)	Week 6 (24 Hr)
Sanger	6	8	-	4	6	-	-	-
Parlier**	12	16	8	8	6	-	-	-
Reedley	6	8	-	4	6	-	-	-
Selma	6	8	-	4	6	-	-	-
Dinuba	6	8	-	4	6	-	-	-
Earlimart	-	-	-	-	4	6	-	2
Delano**	-	-	-	-	4	16	14	8
McFarland	-	-	-	-	4	6	-	4
Wasco	-	-	-	-	4	6	-	6
Shafter	-	-	-	-	4	8	-	6

* Represents the number of exposed XAD-2 resin tubes.
** These sites were used for both collocated and 3 hr. samples in addition to primary 24-hr. samples.

A summary of the results of this study is presented in Table 7, which includes the highest, and second highest, recorded ambient concentration of parathion at each site. For each site, the average daily concentration, the total number of daily samples, and the total number of daily samples which resulted in concentration above the Minimum Detection Limit (MDL) of the analytical technique (0.02 ug) are also presented. A complete set of laboratory results is enclosed as Attachment V. It should be noted that none of the 3 hr. samples captured measurable quantities of parathion. A complete set of monitoring data is enclosed as Attachment IV.

Table 7

Summary of Results*

Site	Ambient Concentration (ppt) Max 1	Max 2	Avg.	Total No. of Samples	No. of Samples Above MDL
Sanger	16.05	8.24	6.03	13	7
Parlier**	69.09	57.45	13.44	31	22
Reedley	34.0	29.64	15.68	13	13
Selma	22.91	21.64	12.62	13	8
Dinuba	31.09	24.0	10.07	13	13
Earlimart	5.04	4.16	4.6	6	2
Delano**	1.29	1.24	1.26	21	2
McFarland	7.34	6.04	3.53	7	5
Wasco	5.69	1.98	2.72	8	4
Shafter	NA	NA	NA	8	0

*24-hr. samples only (since no measurable quantities were captured during 3 hr. sampling.) Average concentrations represent samples above MDL.
**These sites had collocated 24-hr. samplers, only the highest daily value at each site was used in preparing this table.

VI. DISCUSSION

The two main objectives of this study were to (1) monitor ambient concentrations of parathion in order to establish a "source/receptor" relationship, and (2) to compare monitoring results with that which had been predicted by modeling. Although an in depth analysis of the monitoring results to establish a source/receptor relationship has not been performed, it does appear that the modeling approach used to predict high impact areas was applicable. Modeling results had indicated that Reedley was probably the best location to find high ambient parathion concentrations in Fresno County, and after sampling was completed Reedley was the only Fresno County site which resulted in measurable quantities of parathion every day that samples were taken. Similarly, modeling had predicted that Wasco and McFarland were the best locations to monitor in Kern County, and after sampling was completed were the only Kern County sites which resulted in measurable quantities of parathion on at least half of the days that samples were collected.

Developing a source/receptor relationship based on the results of this ambient air monitoring study will require the use of additional information which is beyond the scope of this report. In addition to PUR's, appropriate meteorological data will also be required. Meteorological data may be obtained from nearby airports which have been selected as being representative for each monitoring site (Table 8). This data is currently available, however, complete data sets are quite voluminous.

Table 8

Meteorological Stations Applicable to

Jan. - Feb. 1986 Parathion Monitoring Sites

Monitoring Site	Airport Meteorological Station		
	Fresno	Visalia	Bakersfield
Sanger	x		
Selma	x		
Parlier	x		
Reedley	x		
Dinuba		x	
Earlimart		x	
Delano			x
McFarland			x
Wasco			x
Shafter			x

In general, meteorological conditions observed during ambient monitoring included foggy mornings, overcast afternoons, and intermittent rain. Due to the time of year, these conditions were anticipated which resulted in two operational concerns. The first concern was that parathion is not generally applied while it is raining, therefore, ambient samples were never initiated in the rain.

The second concern was with the effectiveness of XAD-2 resin in sampling the ambient atmosphere for organo-phosphate pesticides during periods of heavy fog. To address this concern, the ADD laboratory conducted a study to evaluate the sampling technique's capabilities while operating in high relative humidity. The conclusion of the study was that there was no indication that the presence of fog significantly affects the collection efficiency of the XAD-2 resin for the pesticides studied. A summary of this study is presented in Attachment VI.

VII. QUALITY ASSURANCE

Several Quality Assurance (QA) measures were taken during the course of the sampling program. Precision calculations will be possible based on data obtained from the two collocated samplers. The samplers were collocated between two and four meters apart. Blank XAD-2 resin tubes were submitted to the lab for analysis with each week's batch of samples collected. Only the field operator knew the log numbers of these blank tubes, information provided to the lab was limited to individual sample log numbers.

The QA Section of ADD performed a "flow check" on eight of the ten sites during the week of January 27, 1986. Siting of each sampler was also compared against applicable siting criteria. In general, the siting of each monitor was in accordance with guidelines. The one siting concern was that

the sample intake probes did not extend the required two meters minimum from the supporting structure at any of the sites. However, obstructions to flow should not have been a problem because of the relatively small size of the supporting structure (approximately one to two inches effective diameter).

The "flow check" performed measured true flow through the XAD-2 tubes with a standard limiting orifice combined with an appropriately calibrated magnehelic pressure gauge. The result of these flow checks was the realization that the indicated flow on each of the sample train flowmeters was considerably low. That is to say, indicated flow may have been 3 lpm, but actual flow was 1.6 lpm. When this type of flowmeter is used in a vacuum application, which was the case during this study, the indicated flow is not true flow and must be corrected for pressure. However, this was not realized until after the completion of field sampling and the necessary pressure data for accurate flow correction was not obtained. Therefore, subsequent to field sampling, the sampling train was operated in the laboratory to simulate actual operating conditions and determine minimum and maximum correction factors. During field sampling, two extremes were observed with regards to flowmeter metering valve adjustments necessary to set an indicated flow of 3 lpm. At some sites it was necessary to limit the flow considerably with the metering valve (indicating a "strong" pump) causing a significant pressure drop across the valve. Yet at other sites it was necessary to have the metering valve almost completely open (indicating a "weak" pump) causing minimal pressure drop across the valve. Therefore, both of these extremes were simulated in the lab and corresponding correction factors were determined. The "worst case" regarding data correction is for maximum pressure drop. It was therefore necessary to correct each ambient concentration for this worst case scenario.

Using what was determined to be one of the strongest pumps which had been used during the field monitoring, the sampling train was modified by the addition of a pressure guage and auxiliary metering valve. Maximum pressure drop was determined by opening the auxiliary metering valve and controlling the flow with the flowmeter metering valve. Minimum pressure drop was determined by opening the flowmeter metering valve and controlling the flow with the auxiliary metering valve. The sampling train used in the lab simulation is depicted in Figure 3, and the relationship between line pressure and true flow is presented in Figure 4.

As a result of these flow related problems the sampling train is being redesigned for future use. The new design may incorporate a critical orifice flow controller to provide consistent flows over the 24-hr sampling period. However, if a flow controller is not used, the use of a flowmeter with a "top mounted" metering valve should be considered.

MODIFIED
Parathion Sampler

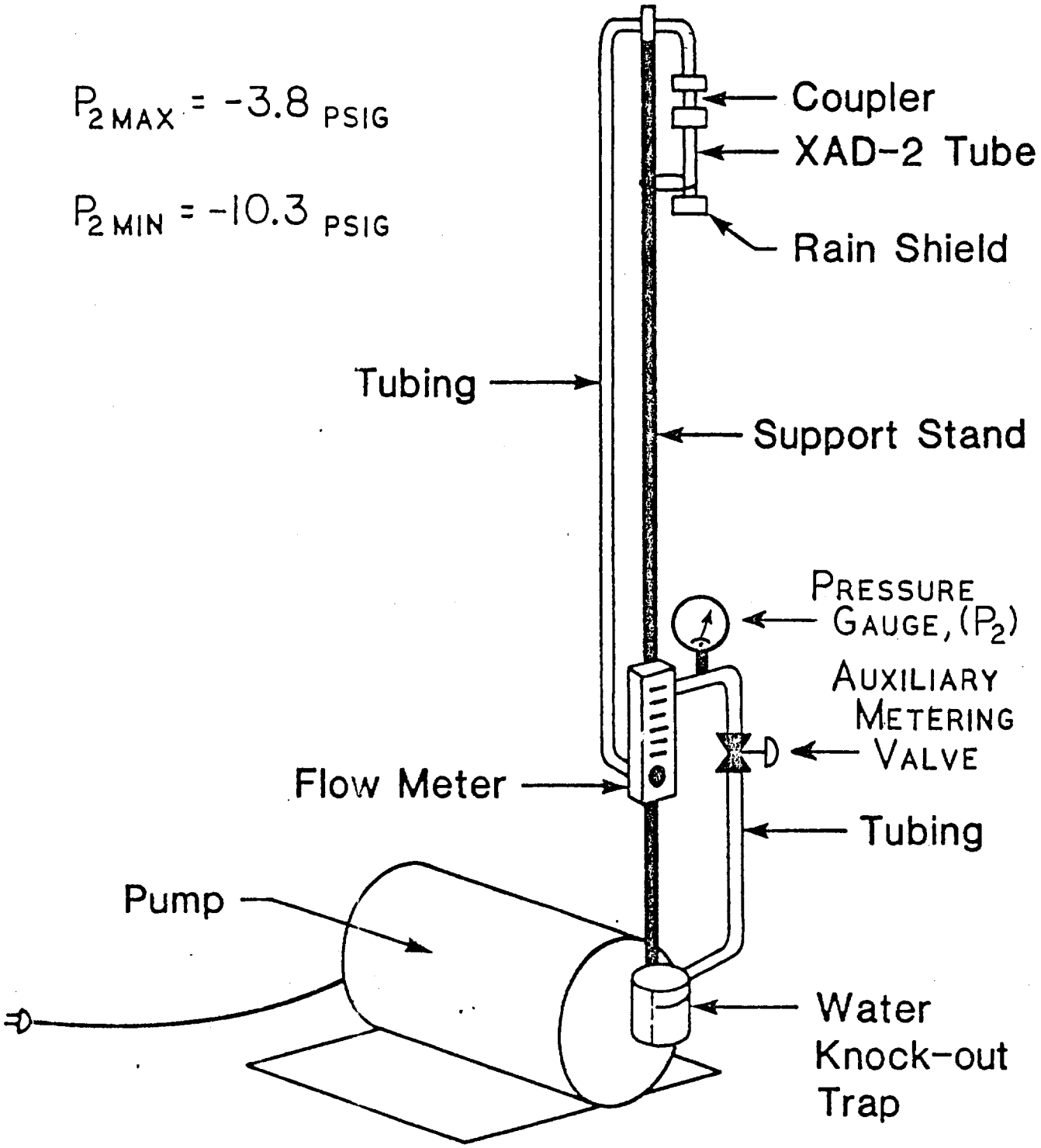


Figure 3

Figure 4

Actual Gas Flow Corrected

for Pressure

$$Q_2 = Q_1 \sqrt{P_2/P_1}$$

Q_2 = Actual flow corrected for pressure

Q_1 = Indicated flowmeter reading

P_2 = Actual pressure inside flowmeter (psia)*

P_1 = Standard atmospheric pressure (14.7 psia)

*Minimum and maximum expected values for P_2 were established in the laboratory using a sample train which had been slightly modified to simulate a range of operating parameters.

Results:

Q_2 max = $Q_1 \sqrt{P_2 \text{ max}/P_1}$ where P_2 max = 14.7 - 3.8

= Q_1 x 0.86 = 10.9

= 86% of indicated flow

Q_2 min = $Q_1 \sqrt{P_2 \text{ min}/P_1}$ where P_2 min = 14.7 - 10.3

= Q_1 x 0.55 = 4.4

= 55% of indicated flow

ATTACHMENT I

Method ADDL 003

METHOD ADDL003

METHOD FOR THE DETERMINATION OF SELECTED ORGANOPHOSPHATE PESTICIDES IN AMBIENT AIR

1. Scope

This document describes a method for the sampling and analysis of parathion, methyl parathion, paraoxon, malathion, and diazinon at concentrations normally found in ambient air. The method was developed based on NIOSH, EPA and the California Department of Food and Agriculture published methods.

2. Summary of Method

After sampling using a low-volume system comprising pump, controller, glass fiber pre-filter, and purified XAD-2 absorbant trap, the exposed filter and absorbant are desorbed with 2.0 milliliters of 80/20 isoctane/acetone mixture. Two microliters of the extract are injected using splitless mode technique into a gas chromatographic system equipped with a 30 meter DB-5 capillary column, thermionic detector (TSD), and data system. The resultant peaks are identified by characteristic retention times and quantitated in reference to external standards. The identity of a component may be confirmed by use of a column with different characteristics, a second detector system, or by GC/MS.

3. Interferences/Limitations

3.1 Components having similar GC retention times will interfere, causing misidentification and/or erroneous quantitation.

3.2 Extreme care must be taken to insure that sample losses do not occur due to leaks in the sampling system or to sample handling within the laboratory. All glassware must be thoroughly cleaned to insure that cross-contamination does not occur between samples. Samples are to be protected from sunlight during sampling and storage.

4. Apparatus

4.1 Varian Model 3300 Gas Chromatograph equipped with thermionic detector (TSD) and a Vista 402 Data System.

4.2 DB-5 fused silica capillary column, 30 meters x 0.35 mm i.d., 1 μm film thickness.

4.3 Amber vials, 3.7 ml capacity, with teflon-lined septum caps.

4.4 Sample agitator with timer and sample rack.

4.5 Microliter syringes, 5-50 µl sizes.

4.6 Low-volume sampler pump and flow controller capable of maintaining preset flow rates of 6 lpm over a 24 hour period. Sampling system must have an accurate timer system to control sampling interval and to indicate total sampling elapsed time.

4.7 Sampling head capable of containing a 37 mm glass fiber filter in-line with a 6" x 1/4" absorption tube containing XAD-2 absorbant.

4.8 Glass fiber filters, 37 mm diameter, type A/E, with teflon holder.

4.9 Glass absorption tubes, 6" x 1/4", containing purified XAD-2 absorbant; 400 mg primary section, 200 mg secondary section. Absorbant must be demonstrated to be free of interfering substances by analysis of unused absorbants (analytical blanks).

5. Reagents

5.1 80/20 iso-octane/acetone desorbant solvent: Mix 80 ml pesticide grade iso-octane (trimethyl pentane) and 20 ml pesticide grade acetone in a clean glass bottle equipped with teflon-lined screw cap. CAUTION: Flammable - DO NOT expose to heat or oxidizers.

5.2 Stock Standards: Individual 1000 µg/ml certified stock standards containing diazion, parathion, methyl parathion, malathion, and paraoxon may be obtained from Nanogens, Inc. CAUTION: Toxic - Use protective gloves in handling these materials.

5.3 Working Standards: Dilute 20 µl of each stock standard into 50/50 isoctane/acetone solvent and dilute to 10.0 ml. This corresponds to 2.0 µg/ml standard.

6. Instrument Conditions

Column: 30 m x 0.37 mm i.d. DB-5 fused silica capillary column

Temperature - Injector: 250°C
Detector: 300°C
Oven: 50°C, initial, hold for 1 minute, ramp at 50°C/min to 140°C/min; ramp at 4°C/min to 260°C, 4 min hold

Flow Rates: Carrier - He, 50 cc/min at splitter, 0.5 min splitless hold, carrier velocity after splitter opens: 25 cm/sec

Detector: TSD - Range 11, Attenuation x 32
Hydrogen Flow: 4.5 cc/min
Air Flow: 180 cc/min
Heater: 3.4 amp

7. Sample Collection

7.1 Sampling flow controllers and indicators must be calibrated by trained personnel before the unit can be installed in the field. The flow rate calibration must be verified monthly at the flow rate used for sampling.

7.2 The 37 mm glass fiber filter and holder, as received from the laboratory, is placed in the sampling head compartment. The compartment is then assembled, taking care that the unit is completely sealed. The filter holder may be handled, but care must be taken not to touch or contaminate the filter itself. If any question of contamination is present, the filter is discarded and a new filter is installed.

7.3 The sealed XAD-2 absorbant tube is prepared for use by snapping off the sealed ends with the tool provided. The open tube is then placed in the sampling train using 1/4" polyethylene tubing fittings, making sure that the flow indicator arrow printed on the tube points in the direction of the flow. The tubing fittings must be tightened sufficiently to insure the system is leak-free.

7.4 After starting the pump system, the flow must be adjusted to approximately 6 lpm. The time, indicated flow reading, and the true flow (read from the calibration graph) must be recorded. The filter and absorbant trap numbers must be recorded. The elapsed time meter is reset to zero. The system is leak-checked by sealing the sampler inlet and insuring that the flow is zero.

7.5 After a 24 hour sampling period, the indicated flow and true flow rates must be recorded. The sampler system is deactivated, the elapsed time and actual time is recorded, and the filter and absorbant tube removed. The filter and cassette holder is placed into a plastic shipping container. The tube is sealed using the red end caps provided. The filter and tube are immediately sent to the laboratory with all sampling information and chain of custody.

8. Instrument Calibration Procedure

8.1 Before a standard solution may be injected, a system blank must be analyzed. This is done by injecting 2.0 µl of 80/20 iso-octane/acetone solvent for analysis. If the subsequent analysis indicates interferences or contamination, the solvent must be replaced.

8.2 A method blank must be analyzed for every 10 samples. This is done by randomly selecting a "blank" (unused) filter and absorbant tube, desorbing (extracting) the "blank" filter and absorbant, and injecting 2.0 µl of the resultant extract into the instrument for analysis. If interferences or contamination is noted, the source must be found and, if possible, eliminated.

8.3 Instrument calibration is performed by injection of 2.0 µl of 2.0 µg/ml mixed standard. The resultant chromatogram and calculated concentrations must be inspected to insure proper integration and consistency with previous analyses. The data is then used to calibrate the method. The instrument data system will not accept updated response factors which are not within 10 percent of historic data.

8.4 If the analyses are to be made daily, a weekly analysis of three standards (2.0, 0.4, 0.08 µg/ml) must be made to insure that the method exhibits linear response. In addition, a weekly "spiked" sample of 0.8 micrograms per absorbant tube of individual pesticides must be taken through the entire analytical scheme to insure that the method is in control. The results of these analyses must be entered on the method control charts.

9. Analysis of Samples

9.1 After removal of the glass fiber filter from the teflon filter holder using stainless steel forceps, the filter is carefully rolled and placed in a 3.7 ml vial. The filter must be forced into the bottom of the vial to insure tht the entire filter is in contact with the solvent.

9.2 After removal of the red end-caps from the absorbant tube, the tube is scored using a glass cutter above the location of the retainer spring. Using the tool provided, the tube is then broken and the retainer spring removed. The glass wool plug and the primary (400 mg) section of XAD-2 is placed in a 3.7 ml vial. Similarly, the secondary section (200 mg) of XAD-2 is placed in a second vial. Make sure all vials are properly identified.

9.3 Place 2.0 ml desorbing solvent (80/20) into the vials, cap tightly, and place on vial agitator for 40 minutes.

9.4 After desorption, 2.0 µl of each extract is injected into the chromatographic system for analysis. The data generated from the glass fiber filter extract is recorded as "filterable". The combined results are recorded as "total".

9.5 The results are recorded in micrograms/m^3 and are calculated as follows:

$$\mu g/m^3 = \frac{\mu g/ml \text{ (found)} \times 2 \times 1000}{\text{average flow (lpm)} \times \text{time sampled (minutes)}}$$

10. Method Sensitivity, Precision, and Accuracy

10.1 The method sensitivity, precision, and accuracy are outlined in Table I. The data was generated using standards.

11. Desorption Efficiencies and Sample Stability

11.1 The primary section of the XAD-2 sampling tube was "spiked" with 10 µl of solutions containing known amounts of the five organophosphate pesticides of interest. The tubes were then sealed, placed in a refrigerator for storage, and tested after intervals to test the stability of the materials on the sorbent. Table II presents the results of this study. Note that the samples are stable for over a period of two weeks.

11.2 The primary section of the XAD-2 sampling tube was "spiked" with 10 µl of solutions containing known amounts of the five pesticides of interest. The "spiked" tubes were then placed in the low volume sampling device and sampled at a flow rate of 7.5 lpm for differing lengths of time. Both the primary and secondary sections of the sampling tubes were desorbed and analyzed. The results are presented in Table III. Note that at the sampling rate of 7.5 lpm, the breakthrough volume of all the pesticides tested is greater than 14 m^3.

Table I

Compound	Conc. 1 µg/ml	S.D.* (percent)	Conc. 2 µg/ml	S.D. (percent)	Conc. 3 µg/ml	S.D. (percent)	MDL µg/ml
Diazinon	2.0	11.6	0.4	14	0.06	7	0.04
Methyl Parathion	2.0	2.3	0.4	8	0.08	7	0.02
Paroxon	2.0	11	0.4	12	0.08	11	0.04
Malathion	2.0	9.6	0.4	10	0.08	8	0.04
Parathion	2.0	8.3	0.4	8	0.08	9	0.02

Compound	Correlation Coefficient	Slope	Intercept (µg/ml)
Diazinon	0.998	0.980	0.031
Methyl Parathion	0.998	0.988	0.016
Paroxon	0.997	0.996	0.026
Malathion	0.997	0.991	0.032
Parathion	0.998	1.003	-0.015

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*S.D. = Relative Standard Deviation

Table II

ORGANO-PHOSPHATE PESTICIDE STABILITY STUDY

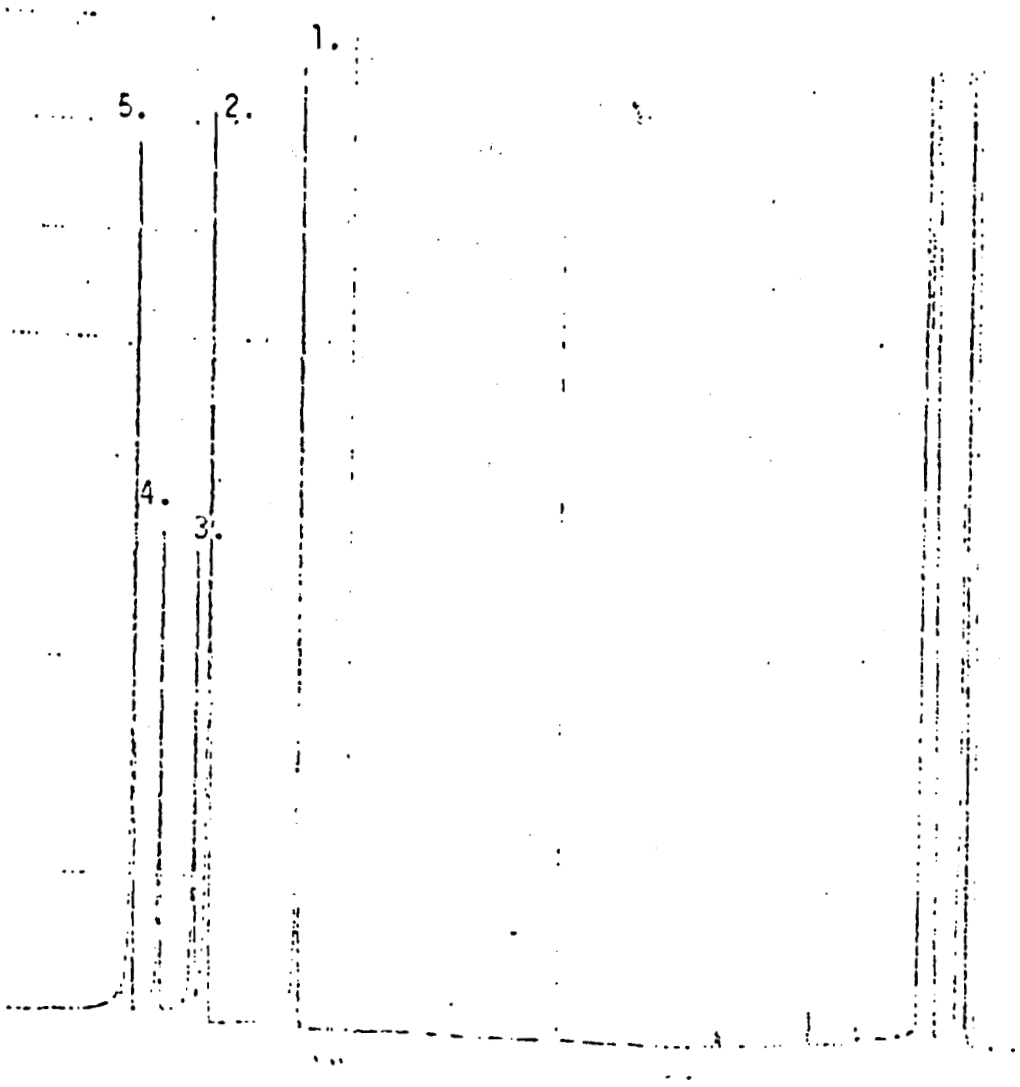
Storage Time, Hrs:	0	24	48	96	192	384
Compound	Amount Recovered, µg (Percent)					
Diazinon	1.68 (98)	1.60 (93)	1.70 (99)	1.58 (92)	1.64 (95)	1.62 (94)
Methyl Parathion	1.45 (83)	1.42 (82)	1.50 (86)	1.40 (80)	1.42 (82)	1.35 (78)
Paroxon	1.42 (97)	1.40 (96)	1.48 (101)	1.38 (94)	1.40 (96)	1.41 (96)
Malathion	1.42 (91)	1.38 (88)	1.50 (96)	1.40 (90)	1.42 (91)	1.48 (95)
Parathion	1.50 (88)	1.52 (89)	1.60 (94)	1.46 (86)	1.50 (88)	1.42 (84)

Table III

ORGANO-PHOSPHATE PESTICIDE SAMPLING AND BREAKTHROUGH STUDY

Volume Sampled (7.5 lpm), m^3	3.6	7.2	10.8	14
Compound	Amount Recovered, µg (percent) Primary/µg (percent) Secondary			
Diazinon	1.60 (93)/0 (0)	1.66 (96)/0 (0)	1.56 (91)/0 (0)	1.92 (100)/0 (0)
Methyl Parathion	1.47 (84)/0 (0)	1.55 (89)/0 (0)	1.44 (83)/0 (0)	1.62 (93)/0 (0)
Paroxon	1.40 (96)/0 (0)	1.48 (101)/0 (0)	1.38 (94)/0 (0)	1.50 (103)/0 (0)
Malathion	1.44 (93)/0 (0)	1.48 (95)/0 (0)	1.40 (90)/0 (0)	1.50 (96)/0 (0)
Parathion	1.52 (89)/0 (0)	1.56 (92)/0 (0)	1.42 (84)/0 (0)	1.56 (92)/0 (0)

CHROMATOGRAPHIC ANALYSIS OF ORGANOPHOSPHATE PESTICIDES



STANDARD: 1.0 ug/ml Mixed Standard
CONDITIONS: DB-5 Capillary Column, 30m, 50°C(1 min.), 50°C/min to 140°C, 4°C/min to 260°C(4 min.); TSD, 3.4 A, Range 11; Helium carrier, 26 cm/sec, splitless.

1. Diazinon
2. Methyl Parathion
3. Paroxon
4. Malathion
5. Parathion

ATTACHMENT II

Modeling Results

Memorandum

To : William V. Loscutoff, Chief
Toxic Pollutants Branch
Stationary Source Division

Date : July 31, 1985

Subject : Recommendations for Parathion Monitoring Locations

From : Don McNerny, Chief
Analysis and Modeling Branch
Technical Support Division
Air Resources Board

You asked us to recommend times and sites where high short term ambient concentrations of diethyl parathion (hereafter parathion) would be expected to impact populated areas in California. To accomplish this we have analyzed the 1983 Pesticide Use Report to determine areas with high usage and used EPA's ISCST air quality model to determine the locations which would be expected to have high parathion concentrations. We stress here that the main purpose of the modeling is to determine locations where high concentrations are expected to be found based on historical meteorology. The actual magnitude of the concentrations are based on hourly flux rates that approximate emission fluxes during monitoring studies made by U.C. Davis. The modeled concentrations should represent approximate levels for each specified averaging time. Since future applications may be different, the number of actual applications and their locations may vary considerably from scenarios studied here.

Table 1 summarizes 1983 parathion applications by township and month. Based on this table it appears that Tulare, Kern, and Fresno counties would be good choices to conduct emission modeling. Even though Tulare county was ranked first in Table 1, the application data were suspect and could not be immediately verified by DFA staff. We then decided to focus our efforts on Fresno and Kern counties. With agreement from SSD and DFA staff we then decided to study January parathion applications in Fresno county and February applications in Kern county.

Recommendations on sampling locations are for populated areas where the highest short term concentrations can be expected. The individual application data were surveyed to choose typical application areas and usage rates for each county. These data for the highest townships are shown in Tables 2 and 3. As noted on Table 2, there are probably errors in the data for Fresno. Since the corrected total is still high, we decided to retain Fresno in the analysis.

The application scenarios chosen for modeling are somewhat arbitrary. Using application data for the highest townships in each county, typical sizes of fields and usage rates were selected for both counties. For Fresno, the parathion applications scenario was selected to be five simultaneous applications in the highest three townships during January. These modeled applications are shown in Table 4. All Fresno applications were modeled as 50 acre fields with usage rates set at 2 pounds active ingredient per acre. The parathion was reported as used on fruit trees and 2 pounds per acre is reasonable. The ISCST model was used with historical meteorological data from the Fresno Airport during 1960 - 1964 during January to determine approximate magnitudes and locations of worst-case concentrations of parathion for 3-hour, 6-hour, 24-hour, and monthly average concentrations. The estimated actual concentrations should be within an order of magnitude of that estimated for the chosen scenario.

The same approach was used for modeling ambient parathion levels in Kern county during February. Applications tend to be larger than for Fresno with higher usasge rates. Usage rates were as high as 5 pounds active ingredient per acre on almond trees. Four applications in the high use areas were modeled. They ranged from 50 to 200 acres. Modeled application data for Kern county townships are also shown in Table 4. The same years of meteorological data were used as reported for the Bakersfield Airport.

Again, we stress that these calculations are screening estimates based on available data. Hourly flux rates are approximate and could be refined using available literature if more accurate modeling estimates are required. These estimates are designed only to choose sample collection sites, they are not intended to document ambient exposures to parathion.

The locations and approximate amounts of the highest concentrations for all averaging times are shown in Figures 1 through 8. All figures were based on 1960 meteorological data which is representative of the five year period studied. The two overlays show the respective locations of the towns nearest the areas of highest expected concentrations. The predominant winds for both January and February are light with a relatively low persistance. The predominant winds give the same basic result as far as locations as the ISCST modeling results.

Since actual dates of applications are up to the farmers, an attempt to capture an ambient short term episode requires sample collection when both the meteorology and applications combine to produce episodes. Realistically, this means collecting samples over a three to four week period at each location to increase the chances of capturing an episode.

Figures 1 through 4 indicate that Reedley is probably the best location to find high parathion concentrations in Fresno county during January. Parlier and possibly Sanger are alternate choices. During February in Kern county, Figures 5 through 8 indicate that Wasco and McFarland are about equally good choices for collecting samples. There are other small towns shown on road maps that may be closer to the areas of expected high concentrations. If exposure for very small populations needs consideration, these figures can be used in conjunction with any road map to choose locations closer to the peak concentrations.

It may also be important to conduct ambient monitoring during a warm weather high use period. The usage is lower than during winter months but this may be partially offset by higher volatization rates. Imperial county may be a good choice if the parathion sampling can begin by September of October.

Parathion conversion to paraoxon was not considered in this study. Actual conversion rates probably vary from a few percent at night to as much as 50% or more during the day depending on downwind distance. The concentrations in Figures 1 through 8 represent parathion plus paraoxon concentrations for all locations. In general, conversion rates are higher in summer than winter and increase as the plume moves downwind from the application.

At this time we are preparing to analyze the 1984 Pesticide Use Report to determine if winter applications show the same trend and locations as 1983. These results will be reported to you in early August.

Should you have any questions do not hesitate to contact Paul Allen of my staff at 2-7278.

cc: Bob Barham (w/attachments)
Ralph Propper (w/attachments)
Paul Allen (w/attachments)

TABLE 1

TOWNSHIPS WITH HIGHEST MONTHLY PARATHION USE
DURING 1983

Rank	Month of Application	County	Township	Range	Base Meridian	Total Applied (Pounds)
1	February	Tulare	24S	25E	M	27,353
2	January	Fresno	14S	23E	M	10,247
3	January	Kern	26S	19E	M	8,500
4	January	Kern	32S	29E	M	6,330
5	February	Kern	25S	26E	M	5,218
6	January	Tulare	21S	26E	M	4,992
7	December	Kern	11N	19W	S	4,832
8	February	Kern	26S	19E	M	4,320
9	January	Kern	11N	19W	S	4,071
10	February	Fresno	15S	22E	M	4,002
11	January	Kern	27S	26E	M	3,905
12	January	San Joaquin	3S	6E	M	3,729
13	January	Merced	6S	12E	M	3,324
14	December	Kern	26S	25E	M	3,222
15	May	Tulare	16S	24E	M	3,204
16	January	Yuba	15N	4E	M	2,866
17	December	Merced	7S	15E	M	2,856
18	September	Imperial	13S	15E	S	2,631
19	January	Sutter	14N	3E	M	2,605
20	September	Imperial	14S	15E	S	2,582
21	January	Yuba	16N	3E	M	2,565
22	January	Glenn	22N	2W	M	2,559
23	July	Yuba	14N	5E	M	2,492
24	January	Fresno	15S	23E	M	2,486
25	December	Merced	6S	12E	M	2,485

Table 2

Diethyl Parathion Summary
Township 14S Range 23E
January 1983 - Fresno County

Day	Acres	Lbs/acre	Parathion (lbs)	
3	200	2.5	500.0	
3	45	2.5	112.5	
4	25	2.4	60.0	
9	6	2.0	12.1	
9	.3	202.0	68.7	*
10	27	1.9	51.5	
10	16	1.4	22.9	
10	25	1.2	31.0	
11	19	1.4	27.2	
12	74	2.0	145.0	
13	35	145.2	5,081.2	*
13	24	2.4	58.0	
14	38	1.5	57.0	
14	91	1.5	136.0	
14	10	1.4	14.3	
14	24	1.4	34.4	
14	16	138.7	2,218.6	*
17	3	6.5	19.4	
17	140	2.3	320.0	
17	60	2.5	152.0	
17	5	15.5	77.6	
17	17	1.7	28.6	
17	17	11.4	193.9	
18	27	1.4	37.9	
18	30	2.5	76.3	
18	30	17.2	517.1	
18	22	1.5	33.0	
20	62	2.6	160.0	
Total			10,246.8	
Corrected total (suspected data removed)			2,878.3	

* = suspected incorrect data

Table 3

Diethyl Parathion Summary
Township 25S Range 26E
February 1983 - Kern County

	Day	Acres	Lbs/acre	Parathion (lbs)
	4	75	1.7	124.4
	10	77	1.7	127.7
	17	315	5.1	1,591.7
	18	125	5.0	630.0
	21	182	5.1	928.5
	22	150	5.1	762.7
	24	50	5.3	265.3
	25	315	2.5	788.0
Total				5,218.1

Table 4

Applications Used in ISCST Parathion Modeling Scenarios

Grid Location (origin in miles)	Application Area (acres)	Use Rate (lbs/acre)
Fresno County		
26.1, 29.2	50	2.0
28.3, 26.2	50	2.0
29.4, 20.1	50	2.0
25.5, 23.6	50	2.0
32.0, 22.1	50	2.0
Kern County		
12.2, 21.2	200	5.0
34.2, 20.3	100	2.5
24.1, 21.1	100	2.0
22.6, 25.6	50	2.0

Figure 1

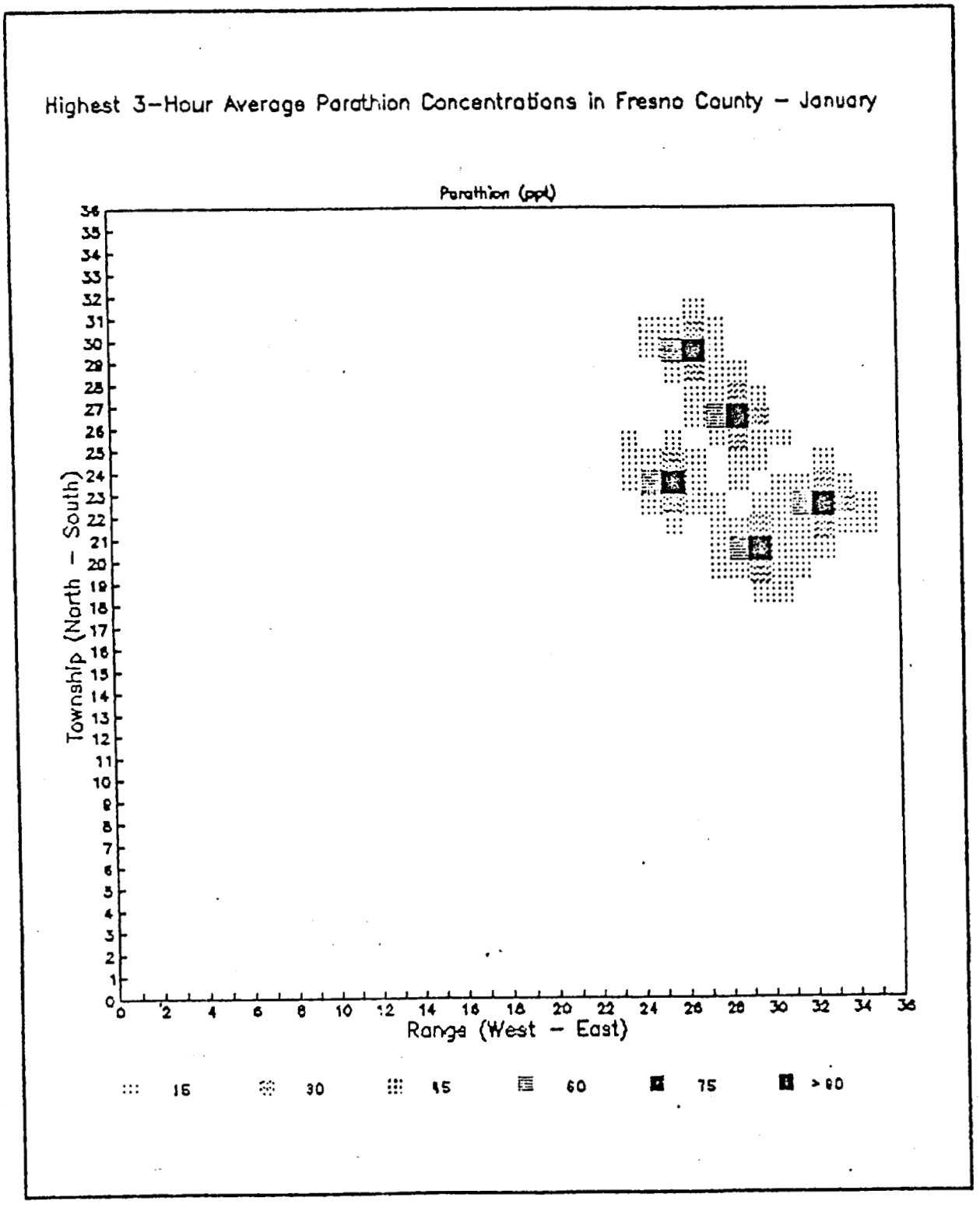

Highest 3-Hour Average Parathion Concentrations in Fresno County – January
Parathion (ppt)
Township (North – South)
Range (West – East)
15
30
45
60
75
> 90

Figure 2

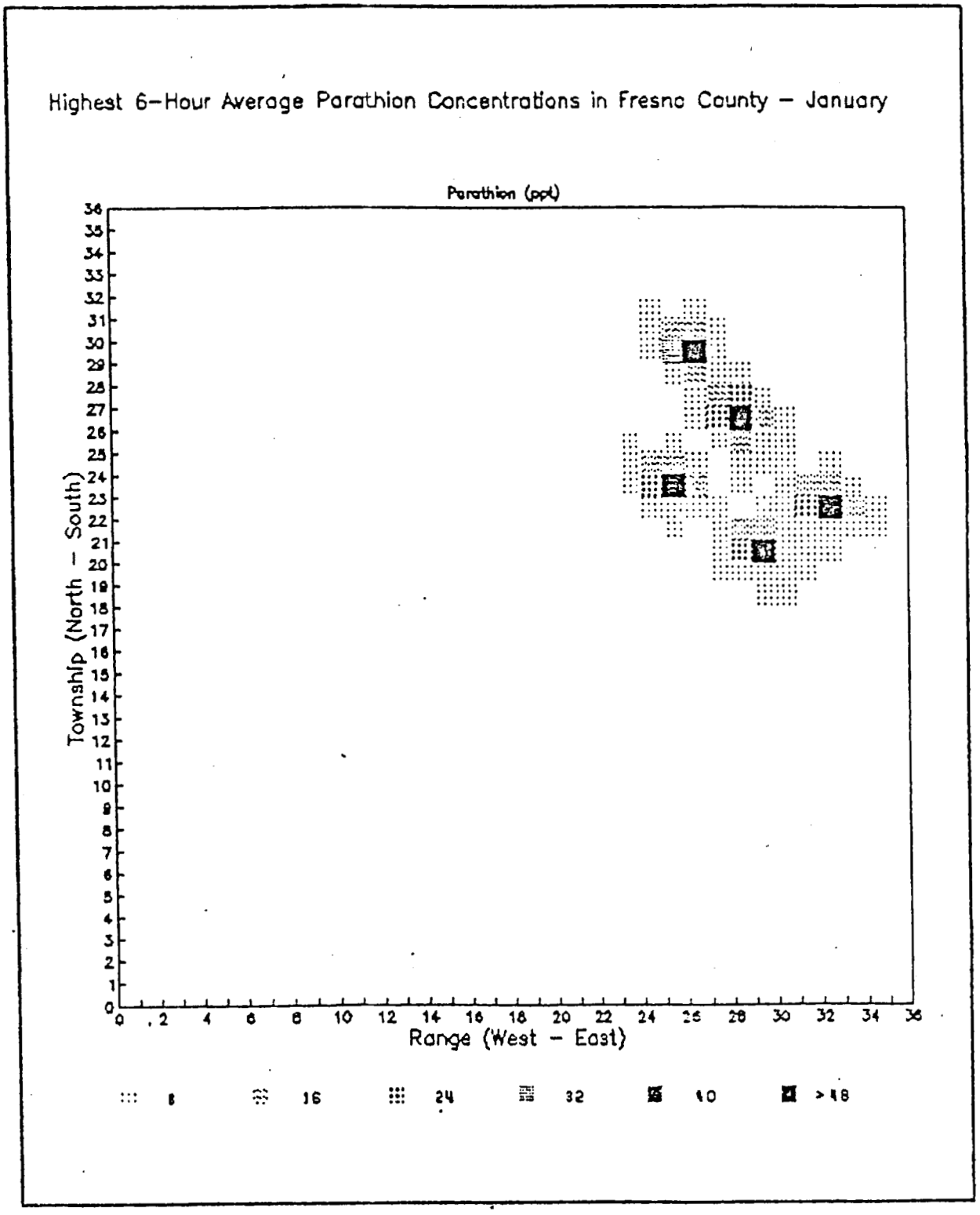

Highest 6-Hour Average Parathion Concentrations in Fresno County – January
Parathion (ppt)
Township (North – South)
Range (West – East)
8
16
24
32
40
>48

Figure 3

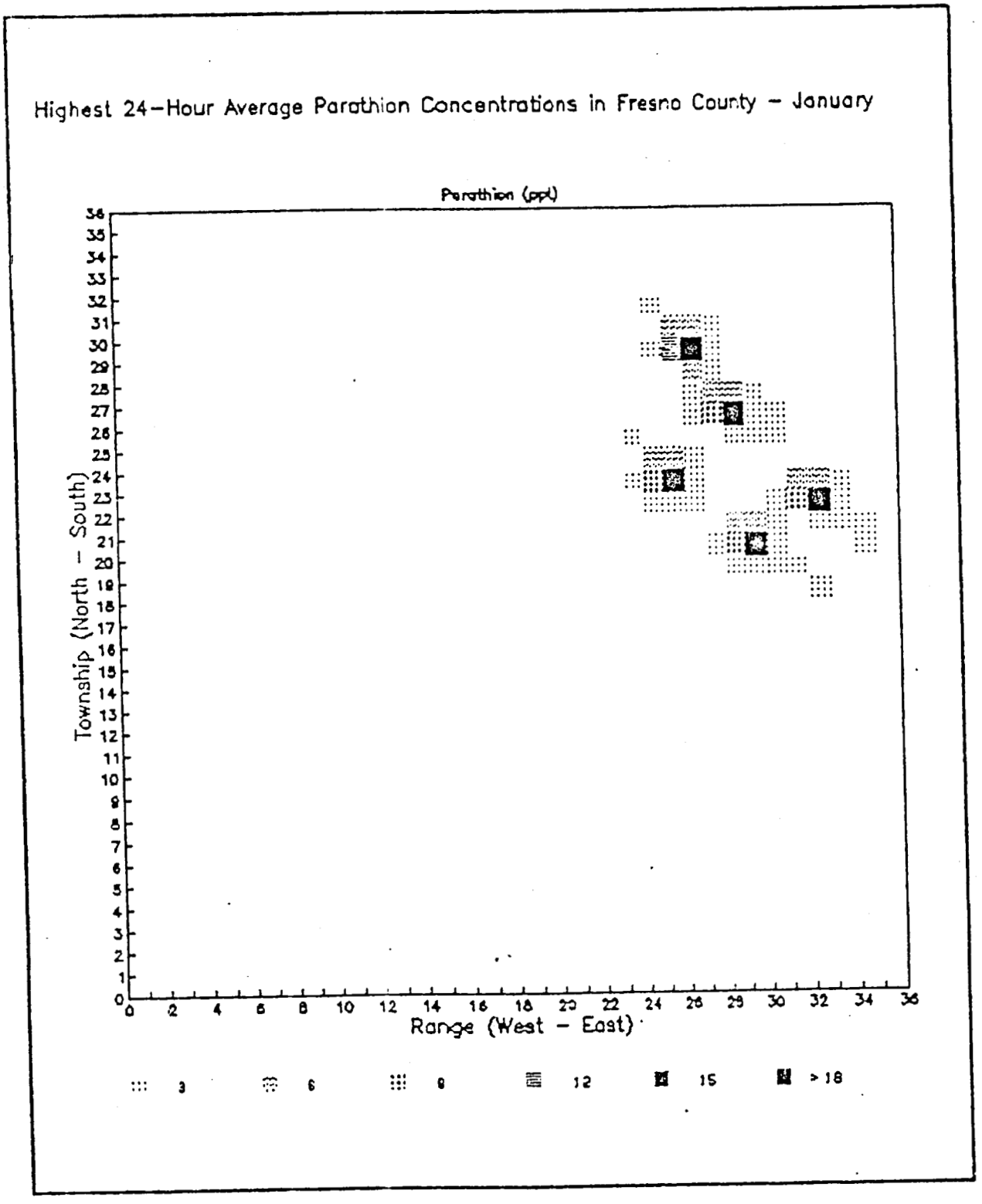

Highest 24-Hour Average Parathion Concentrations in Fresno County - January
Parathion (ppt)
Township (North - South)
Range (West - East)
3
6
9
12
15
> 18

Figure 4

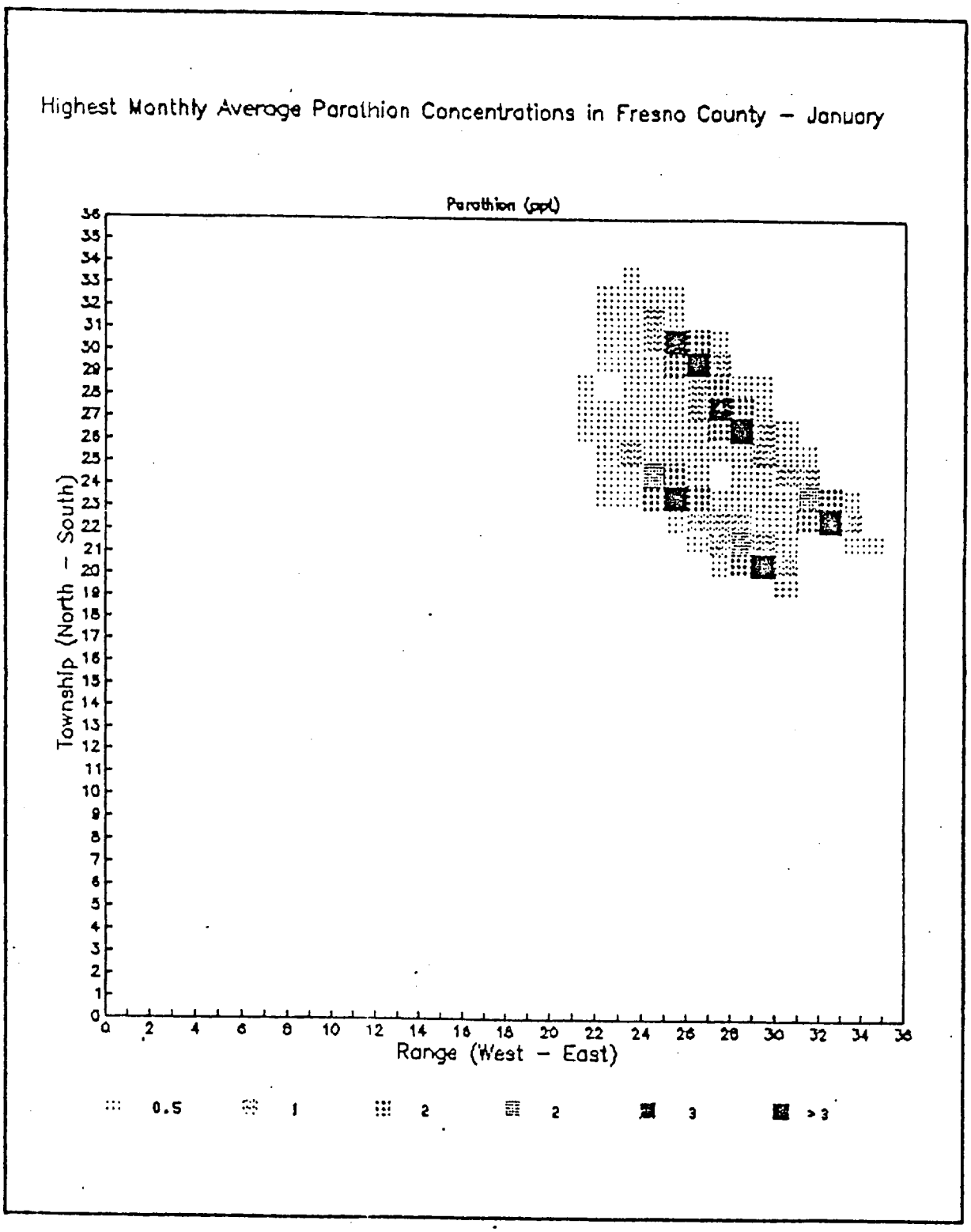

Highest Monthly Average Parathion Concentrations in Fresno County – January
Parathion (ppb)
Township (North – South)
Range (West – East)
0.5
1
2
2
3
> 3

Figure 6

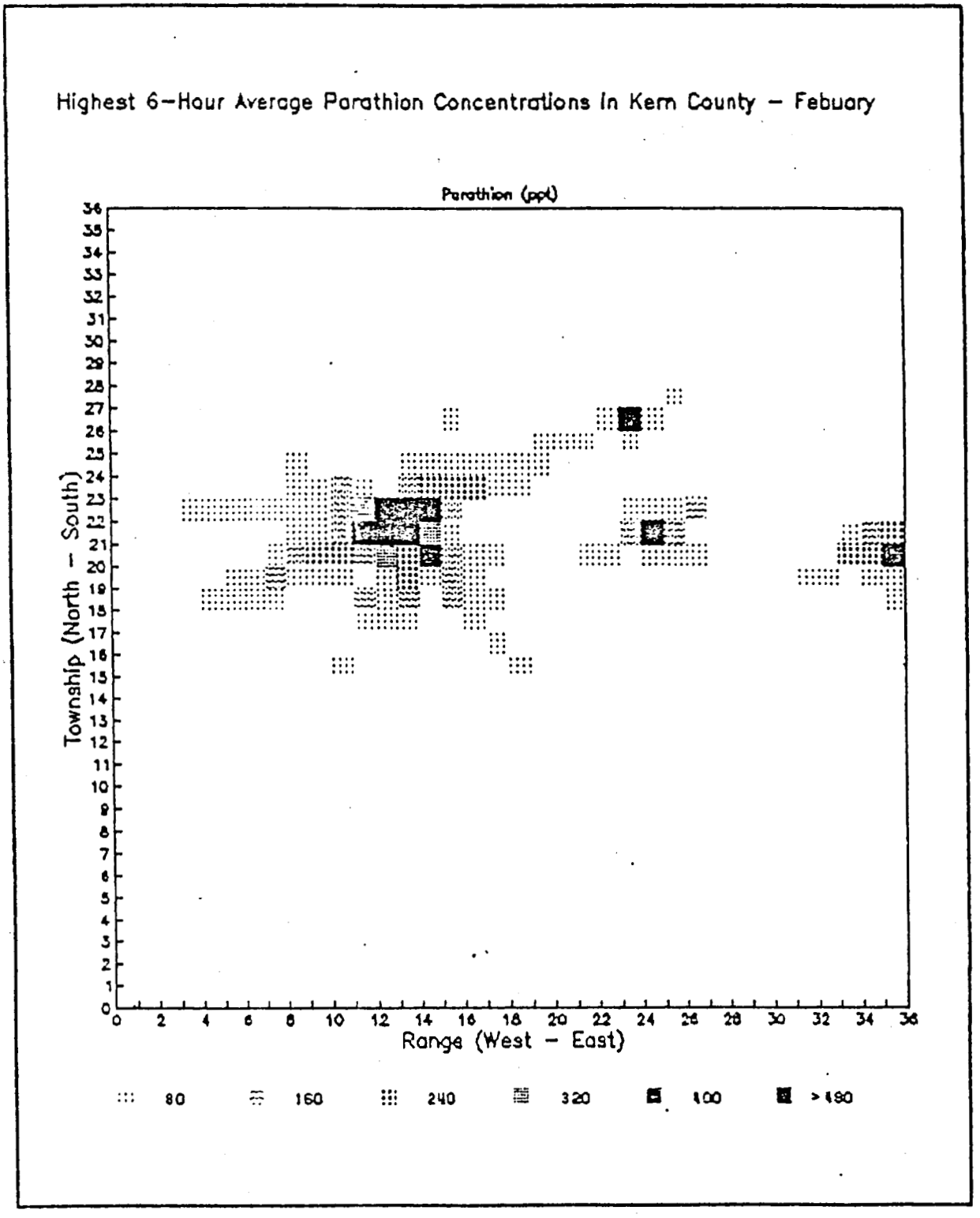

Highest 6-Hour Average Parathion Concentrations In Kern County - Febuary
Parathion (ppt)
Township (North - South)
Range (West - East)
80
160
240
320
400
> 480

Figure 5

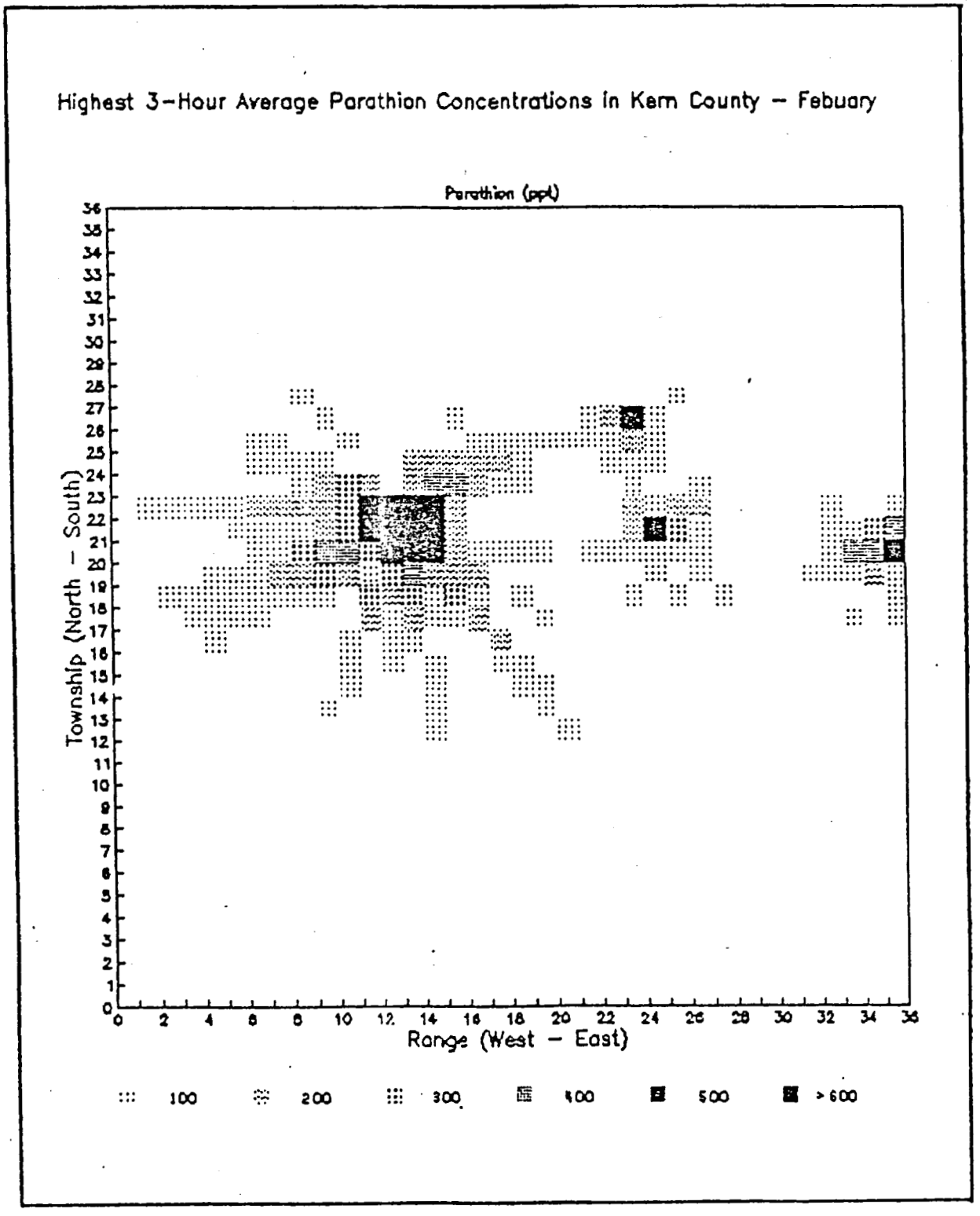

Highest 3-Hour Average Parathion Concentrations In Kern County – Febuary
Parathion (ppt)
Township (North – South)
Range (West – East)
100
200
300
400
500
> 600

Figure 7

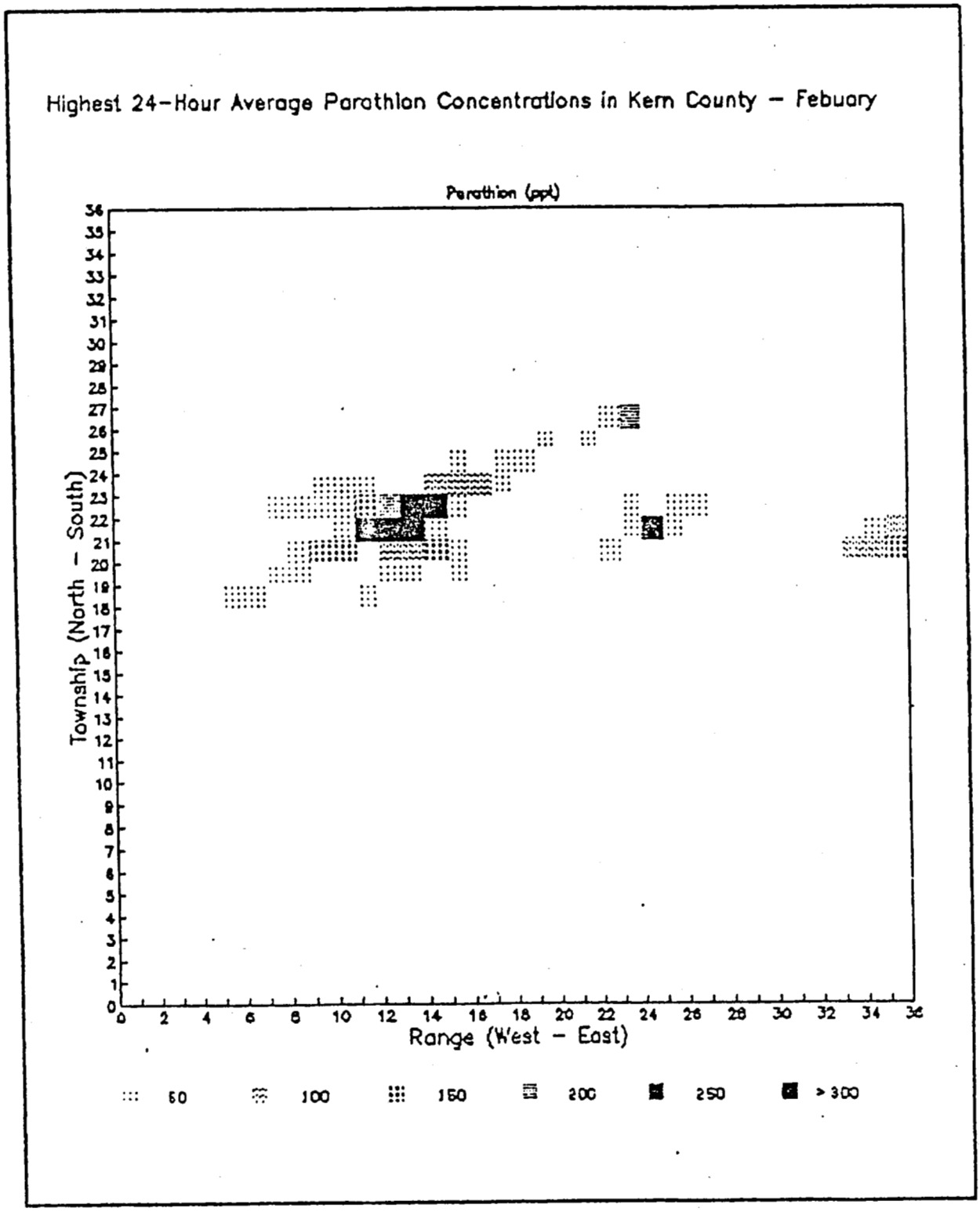
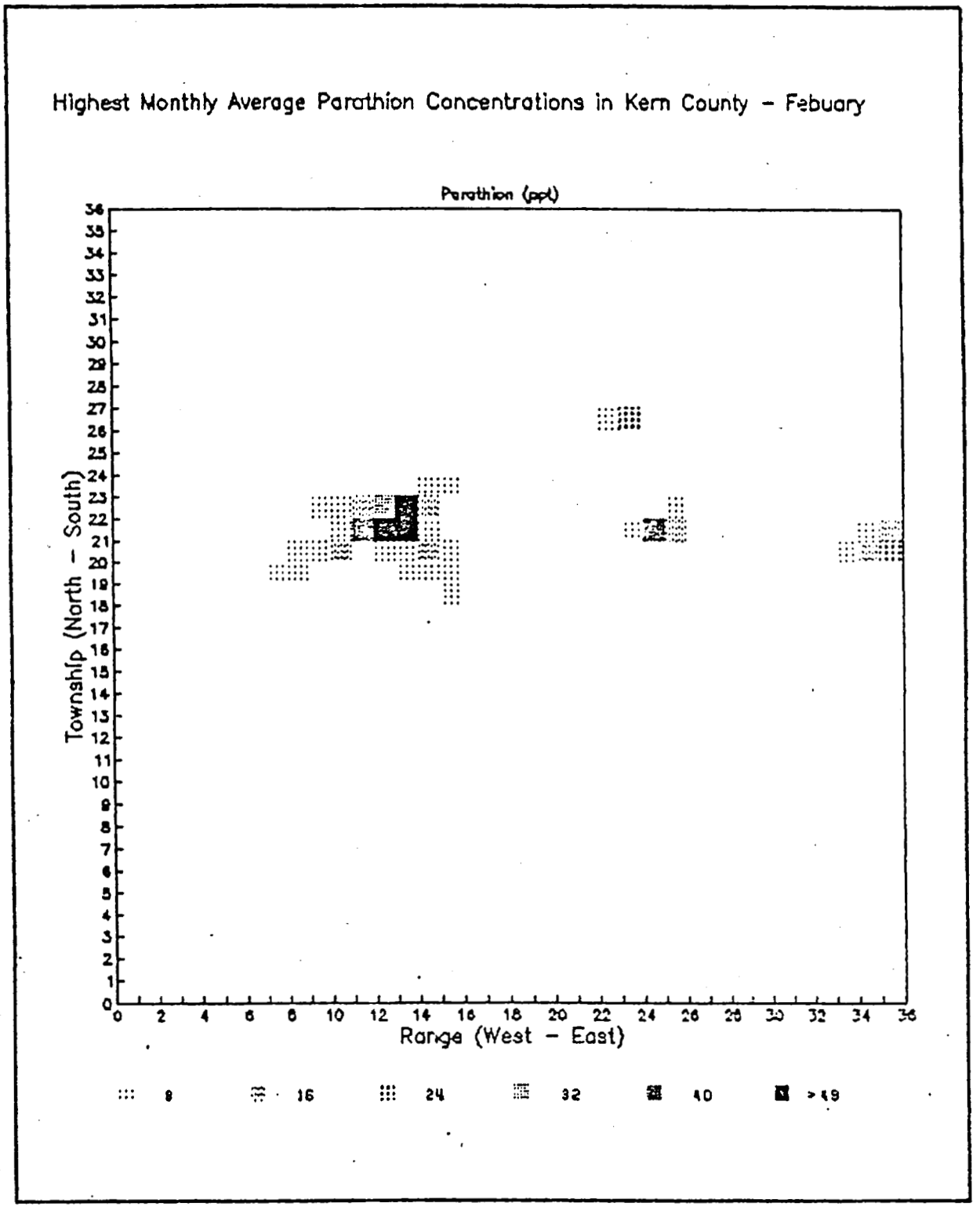

Highest 24-Hour Average Parathion Concentrations in Kern County – Febuary
Parathion (ppt)
Township (North – South)
Range (West – East)
50
100
150
200
250
> 300

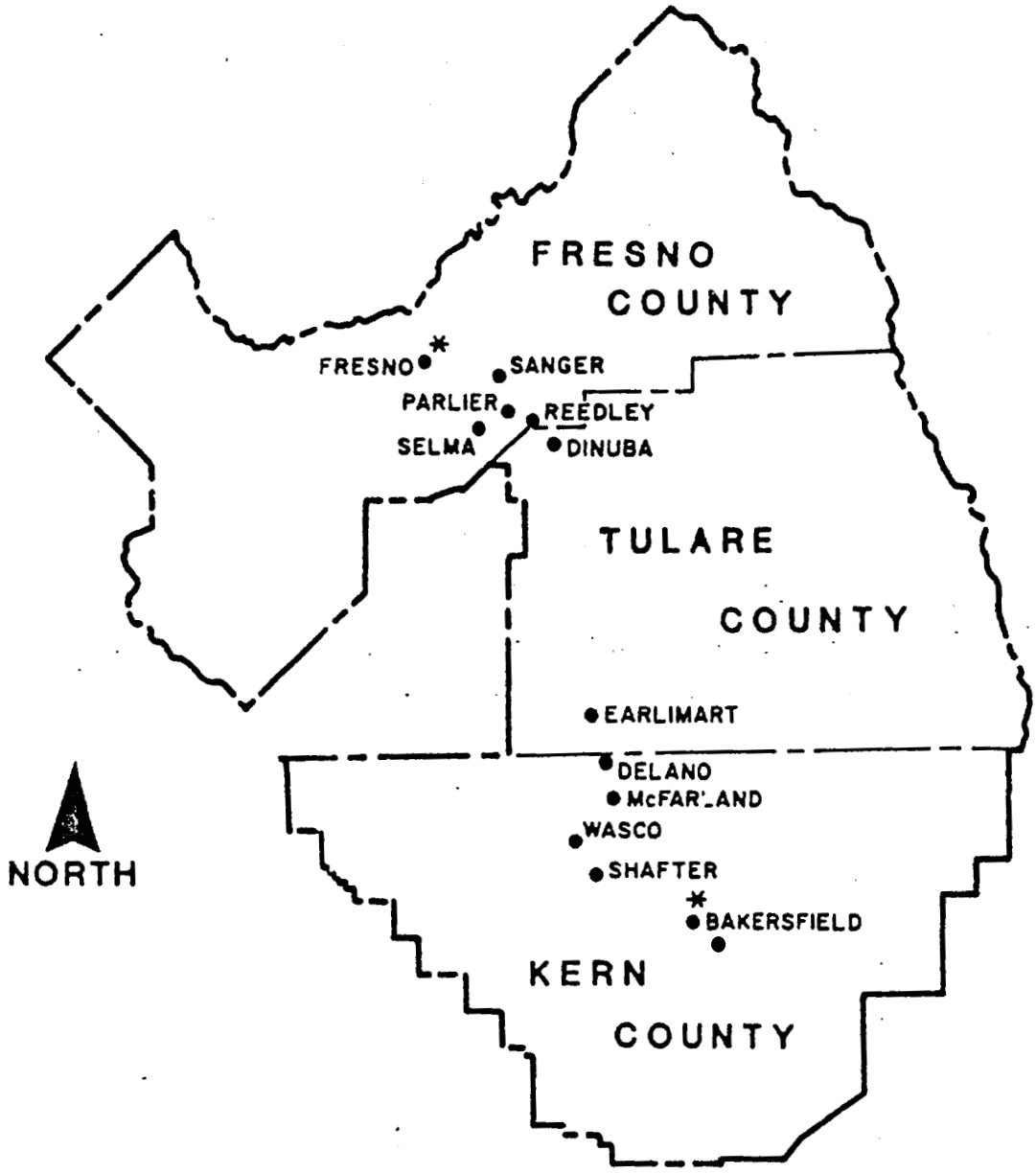
Figure 8


Highest Monthly Average Parathion Concentrations in Kern County - Febuary
Parathion (ppt)
Township (North - South)
Range (West - East)
8
16
24
32
40
> 49

ATTACHMENT III

Site Descriptions

San Joaquin Valley
Sampling Sites



* Denotes background sampling site. Sacramento was also included as a background site, but is not included on this map.

Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 6 - 31, 1986

Site address: Sanger (Fresno County)
Jefferson School
Tucker Ave. & Annadale Ave.

Contact at site: Dallon Ragland
(209) 875-4591

Direction from site to fields which may be sprayed: N & E

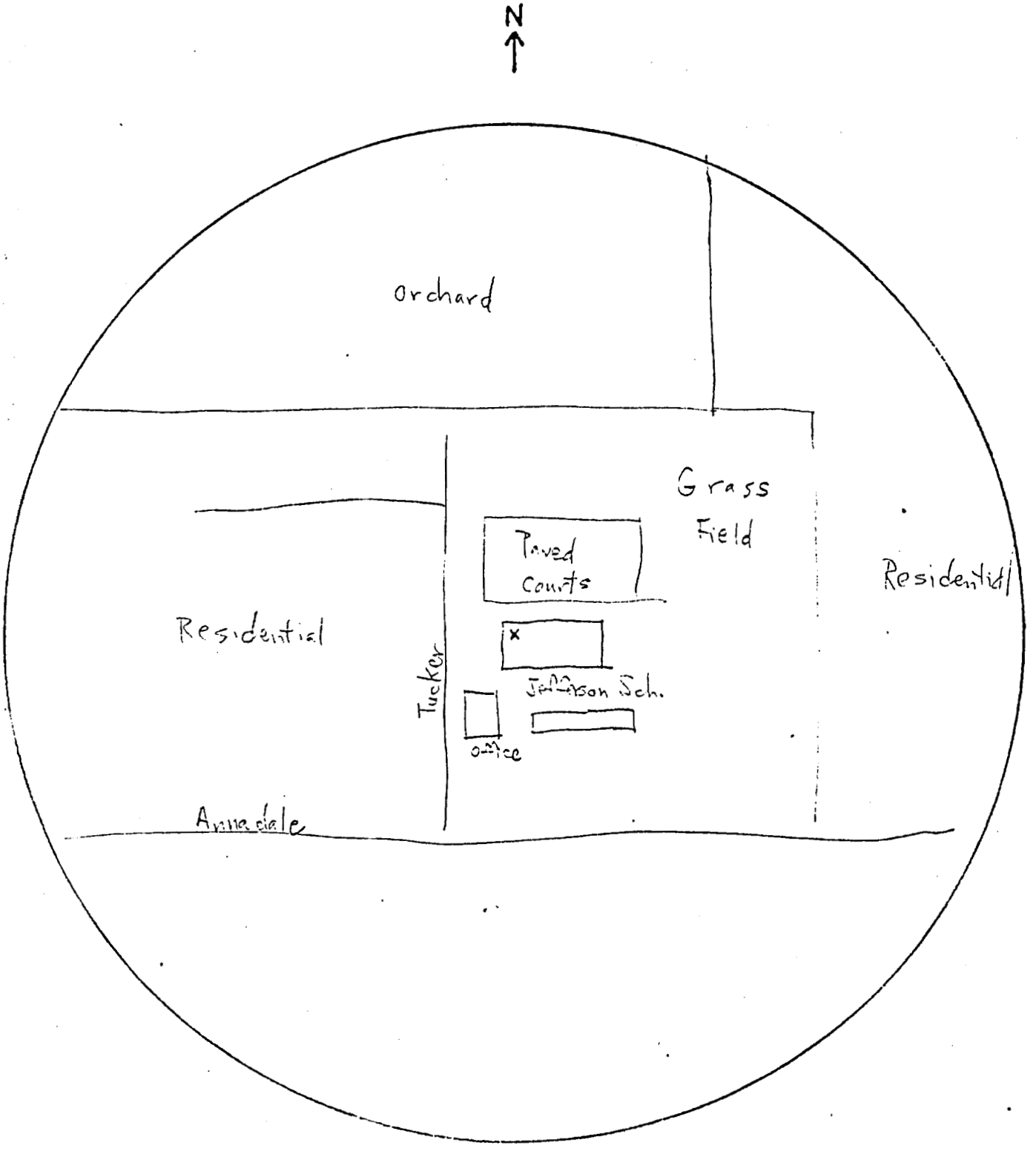
Distance from site to fields which may be sprayed: N (150 yd)
E (~ 1 mile)

Sampling method (power source AC or DC): AC

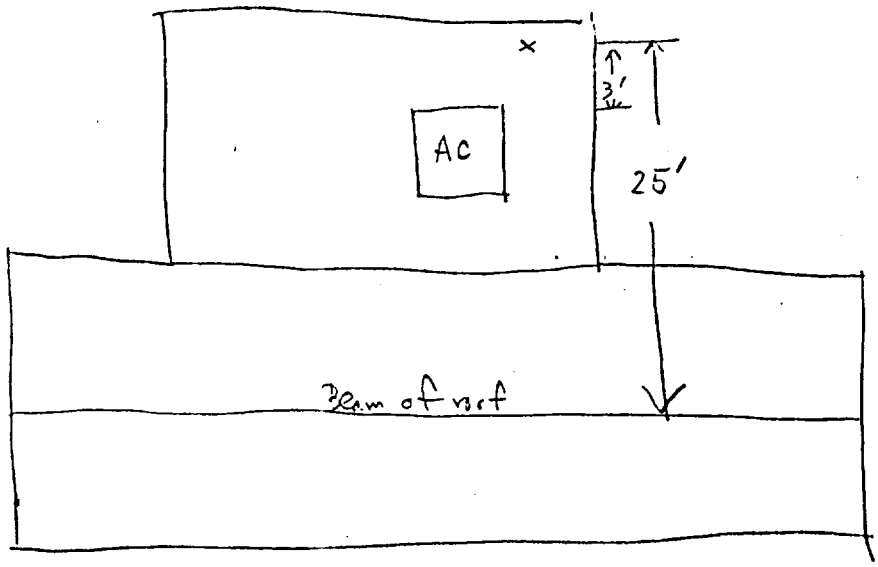
Height of monitoring probe: 16.5 ft.

Distance to obstructions: 25 ft. (beam of roof is 5 ft. above sampler inlet)

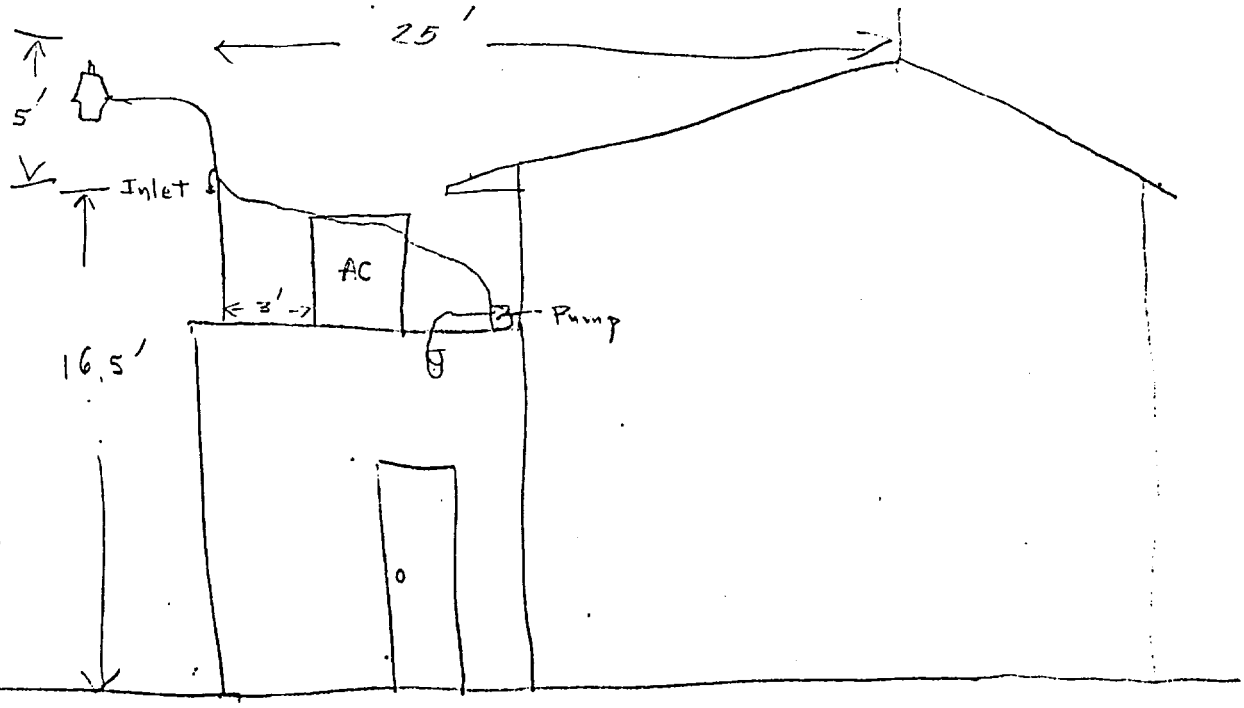
Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)



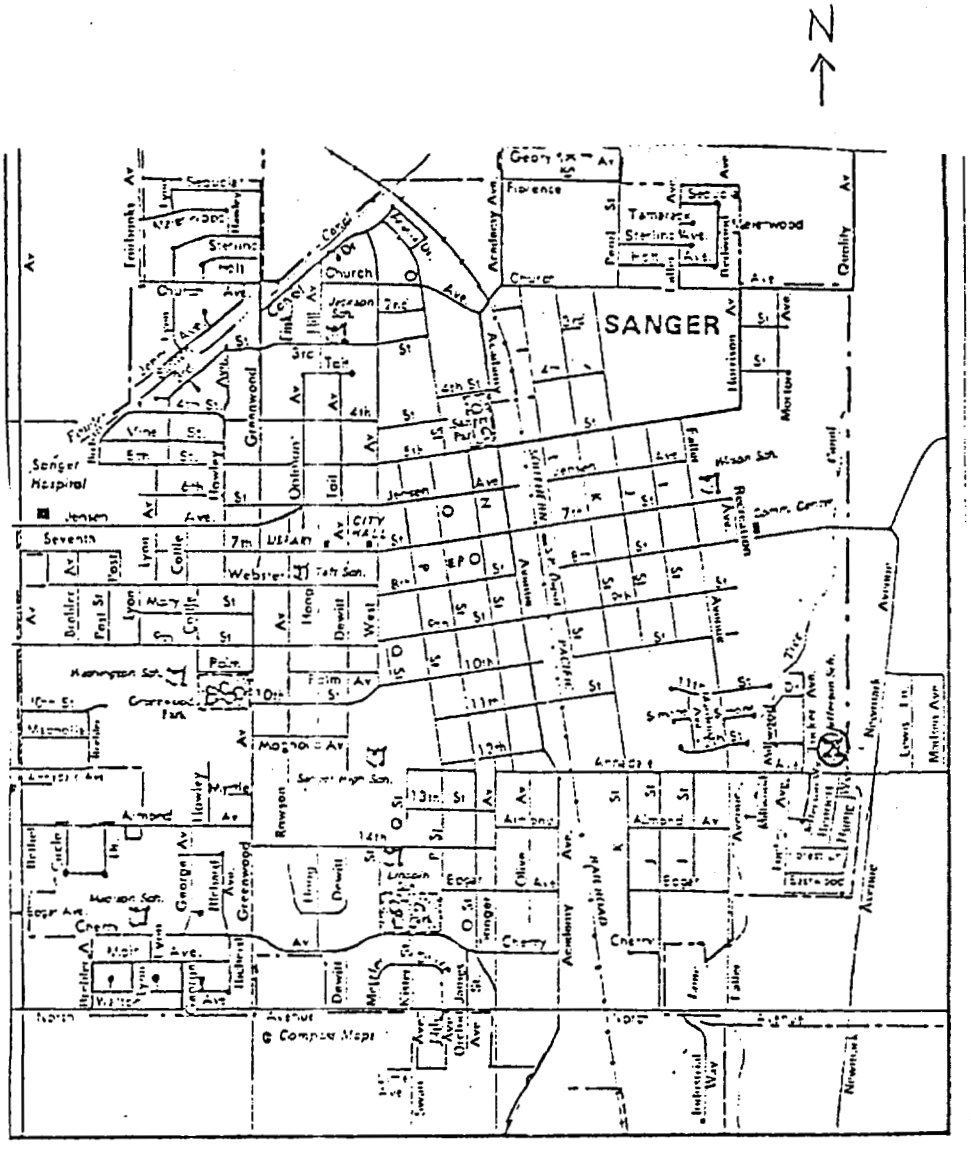
Site Sketch - Top View (distance to bldgs., obstructions, trees)



Site Sketch - Side View (Height of probe, distance to obstructions)



Town Map Showing Monitoring Site



Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 6-31, 1986

Site address: Parlier (Fresno County)
Kearney Agri. Research Field Station
Manning Road & Riverbend

Contact at site: Bill House, Fresno APCD (209)445-3239
John Chevalier (Kearney), 888-2537

Direction from site to fields which may be sprayed: All directions

Distance from site to fields which may be sprayed: 1/4 mile

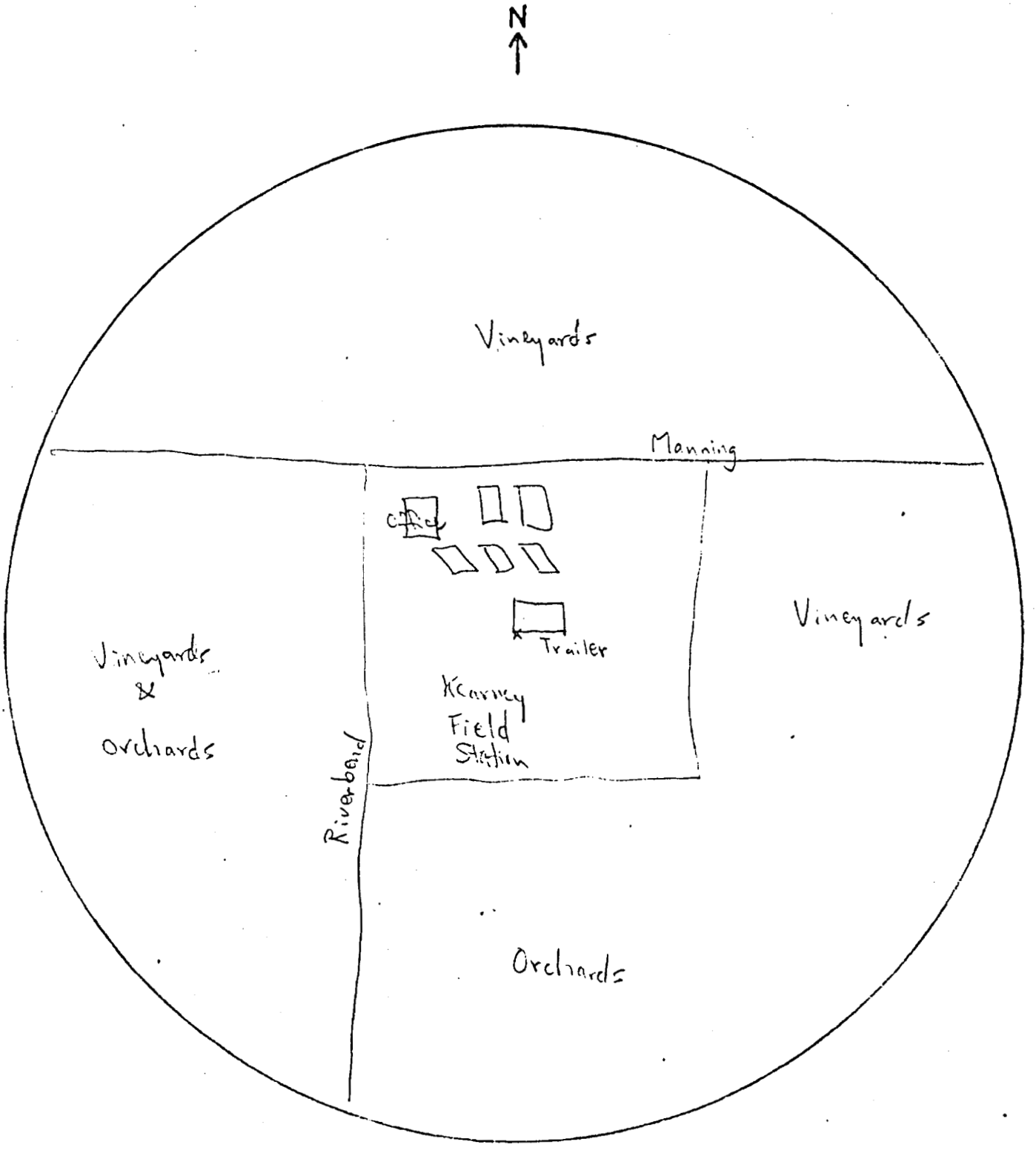
Sampling method (power source AC or DC): AC

Height of monitoring probe: Primary 12'
Duplicate 12'
3-hr 14'

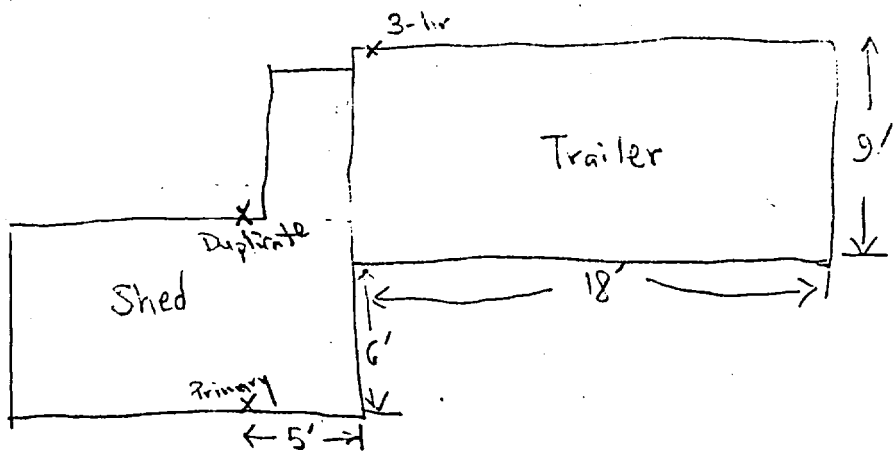
Distance to obstructions:

None

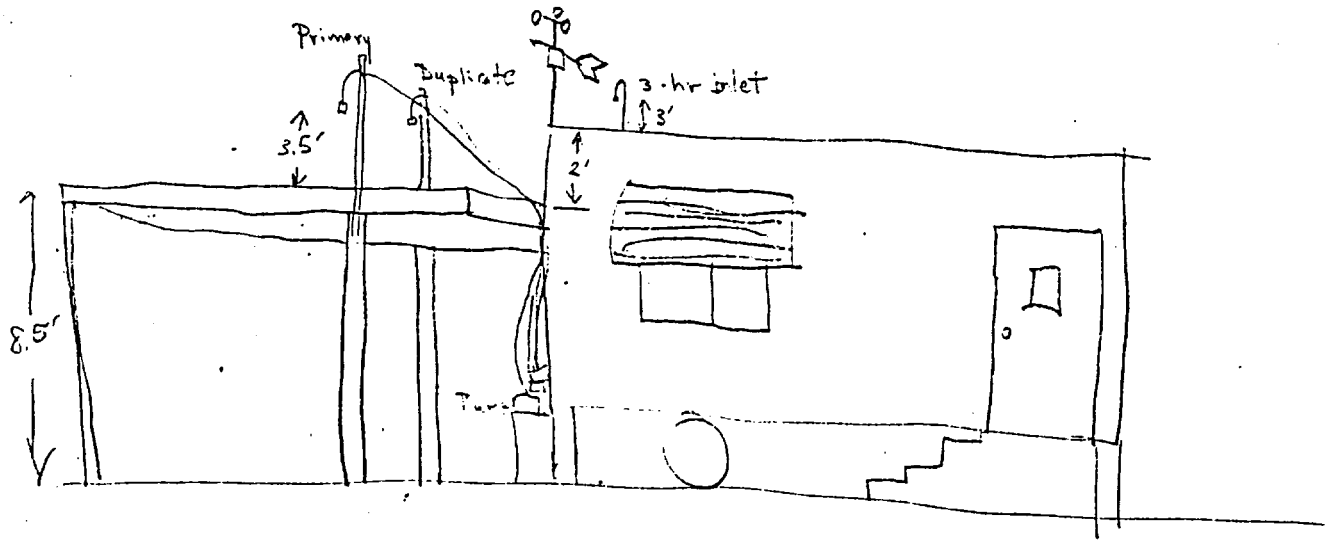
Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)



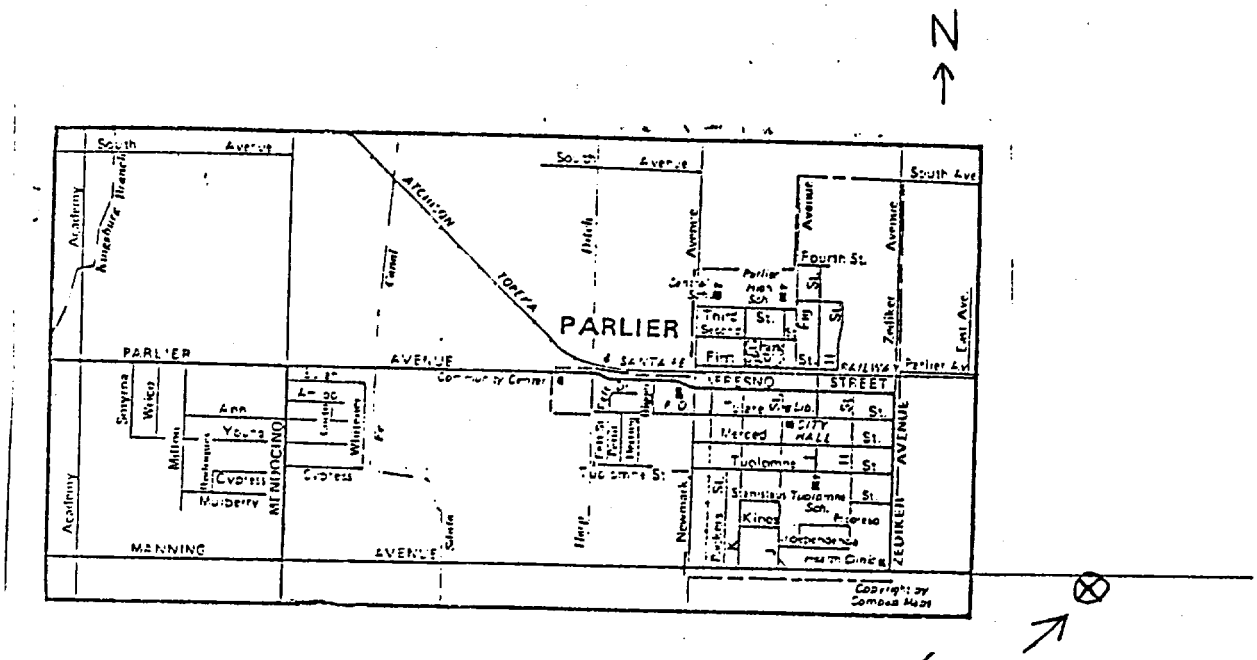
Site Sketch - Top View (distance to bldgs., obstructions, trees)



Site Sketch - Side View (Height of probe, distance to obstructions)



Town Map showing Monitoring Site



South side of Manning Road (cross street is Riverbend)

Scale ⅛ ½ ¾ 1 mile

Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 6 - 31, 1986

Site address: Reedley (Fresno County)
Monte Vista School
1221 E. Duff Ave.

Contact at site: Kent Tanaka, Principal, (209) 888-2840

Direction from site to fields which may be sprayed: E & S

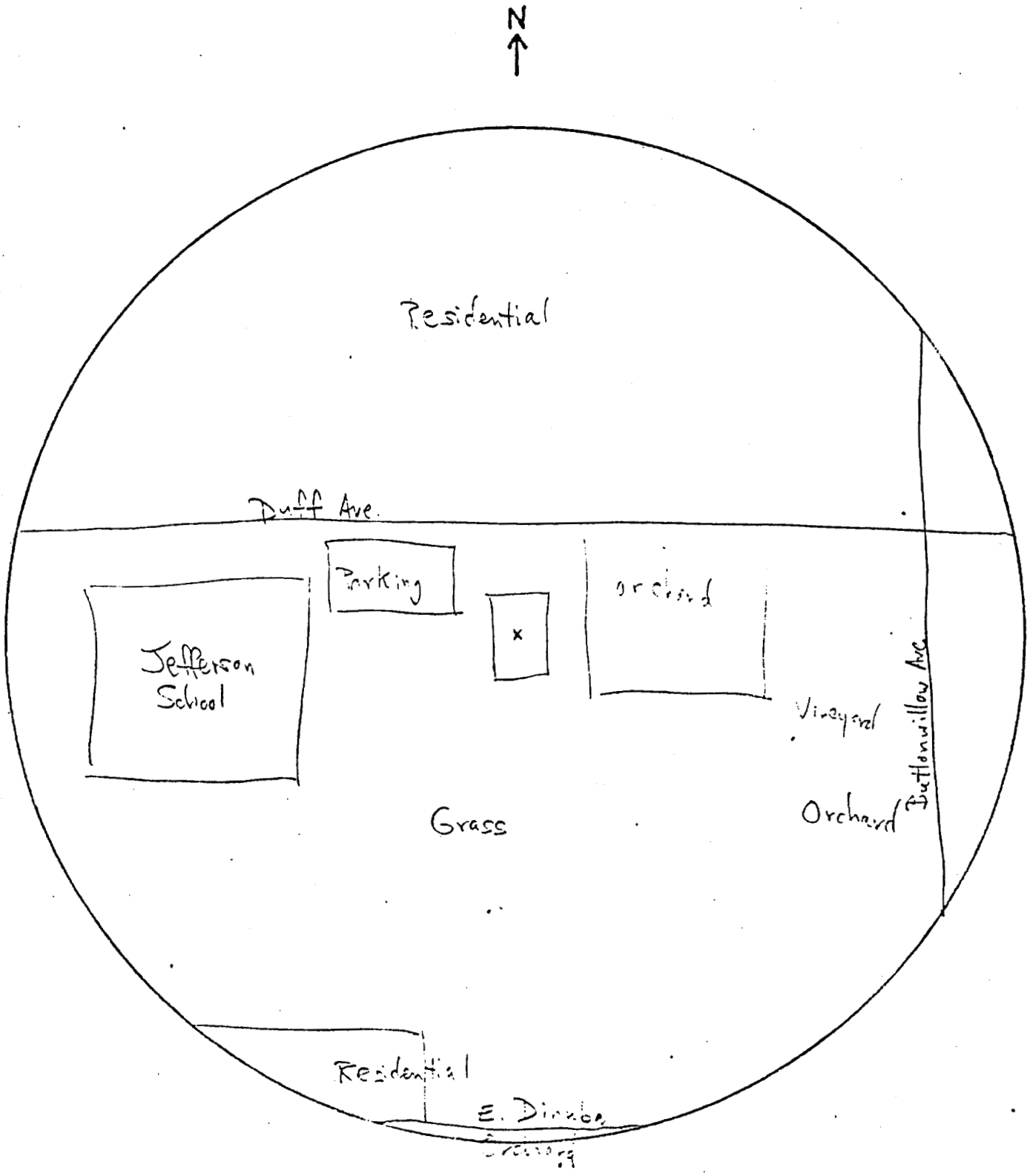
Distance from site to fields which may be sprayed: E (50 yd)
S (1/4 mile)

Sampling method (power source AC or DC): AC

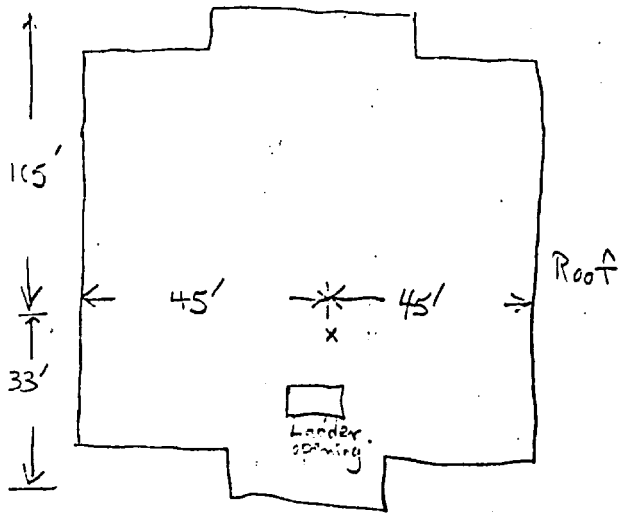
Height of monitoring probe: 5' above roof
19' above ground

Distance to obstructions: None

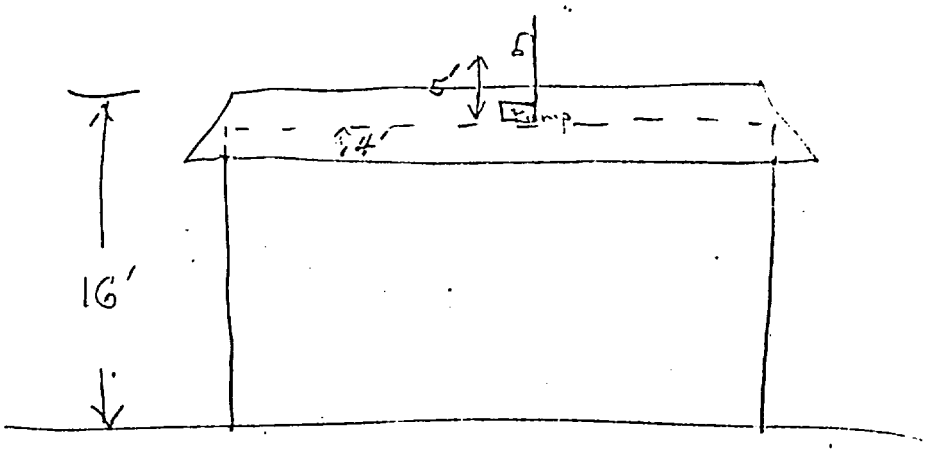
Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)



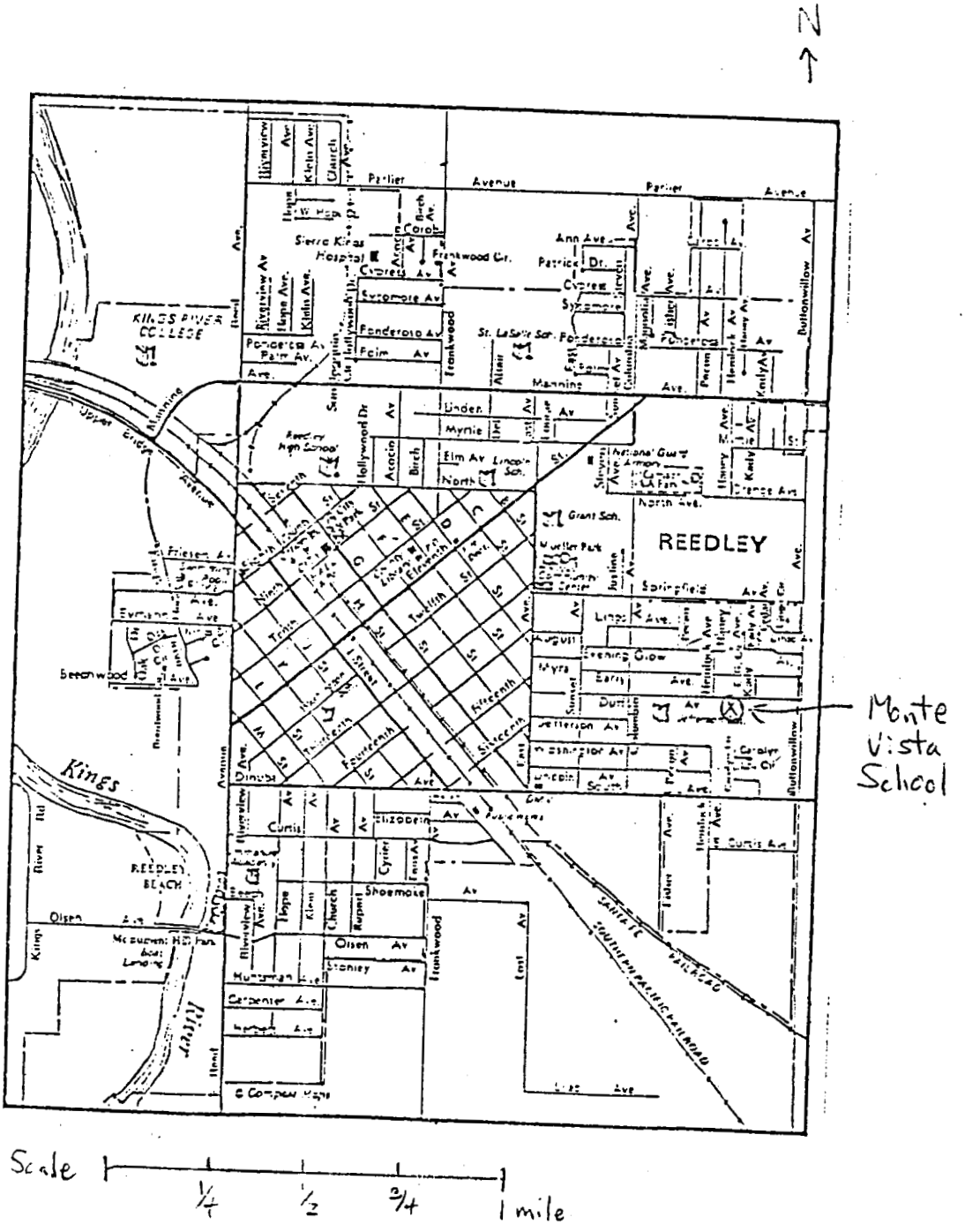
Site Sketch - Top View (distance to bldgs., obstructions, trees)



Site Sketch - Side View (Height of probe, distance to obstructions)



Town Map showing Monitoring Site



Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 6-31, 1986.

Site address: Selma (Fresno County)
Community Health Center
1041 Rose Ave.

Contact at site: Maxine Helman, Manager

Direction from site to fields which may be sprayed: N, E, S

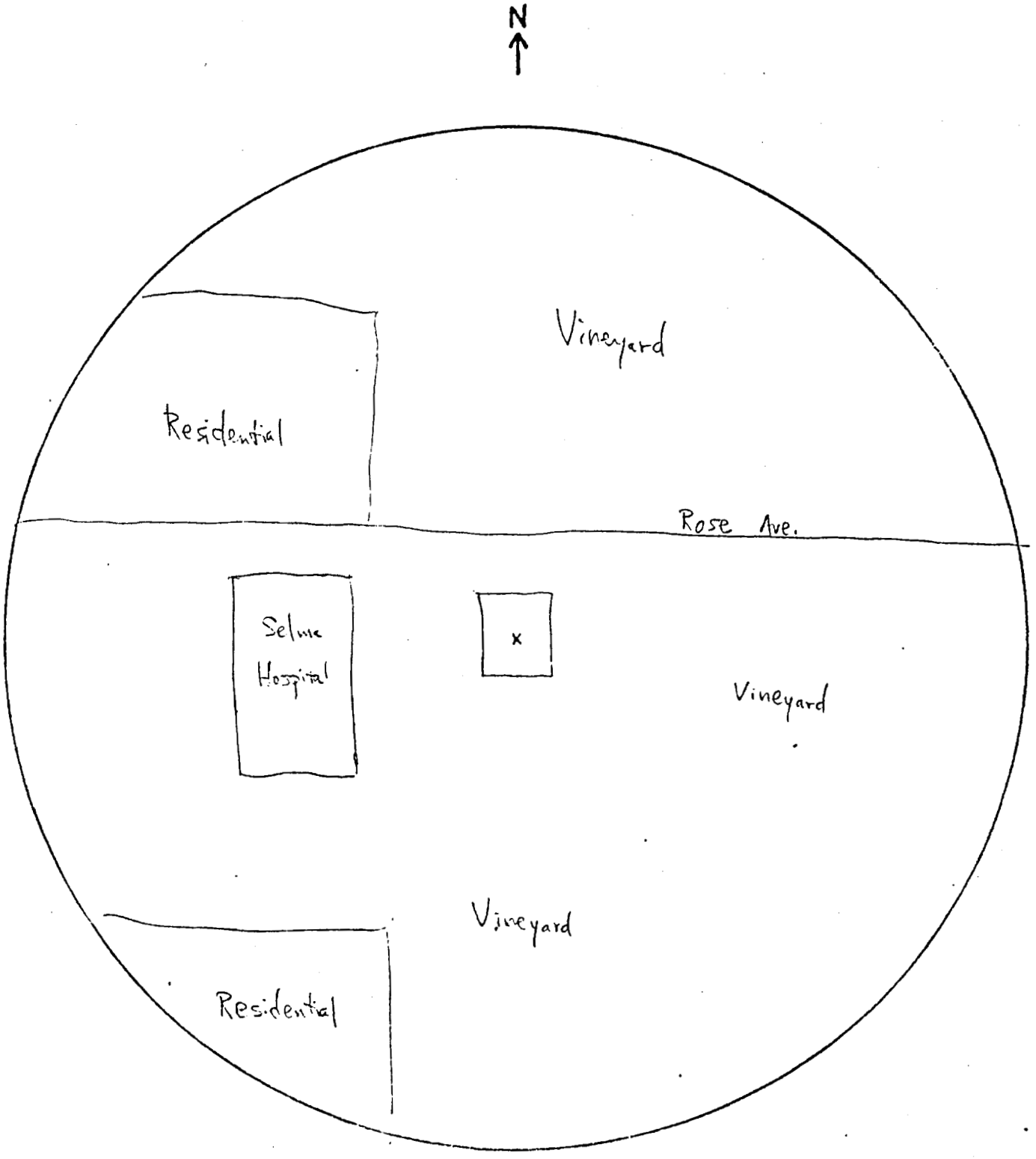
Distance from site to fields which may be sprayed: 50 yd N, E, S

Sampling method (power source AC or DC): AC

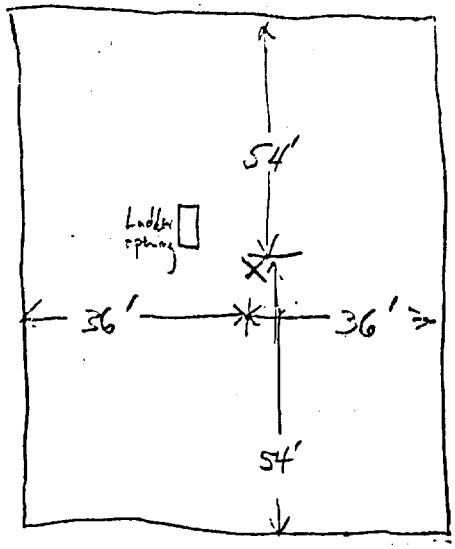
Height of monitoring probe: 17'

Distance to obstructions: None

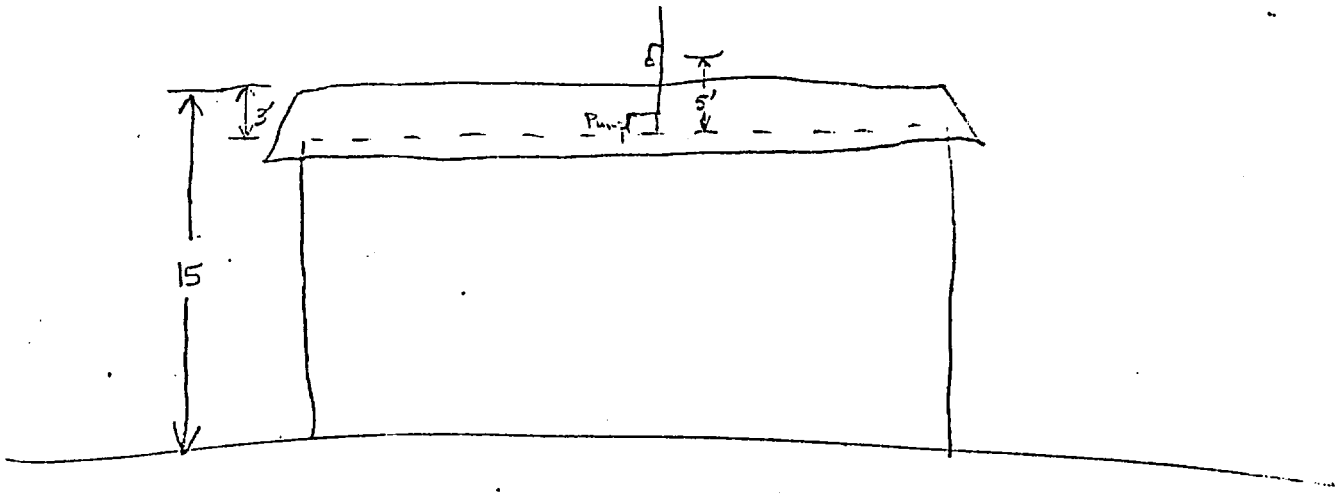
Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)



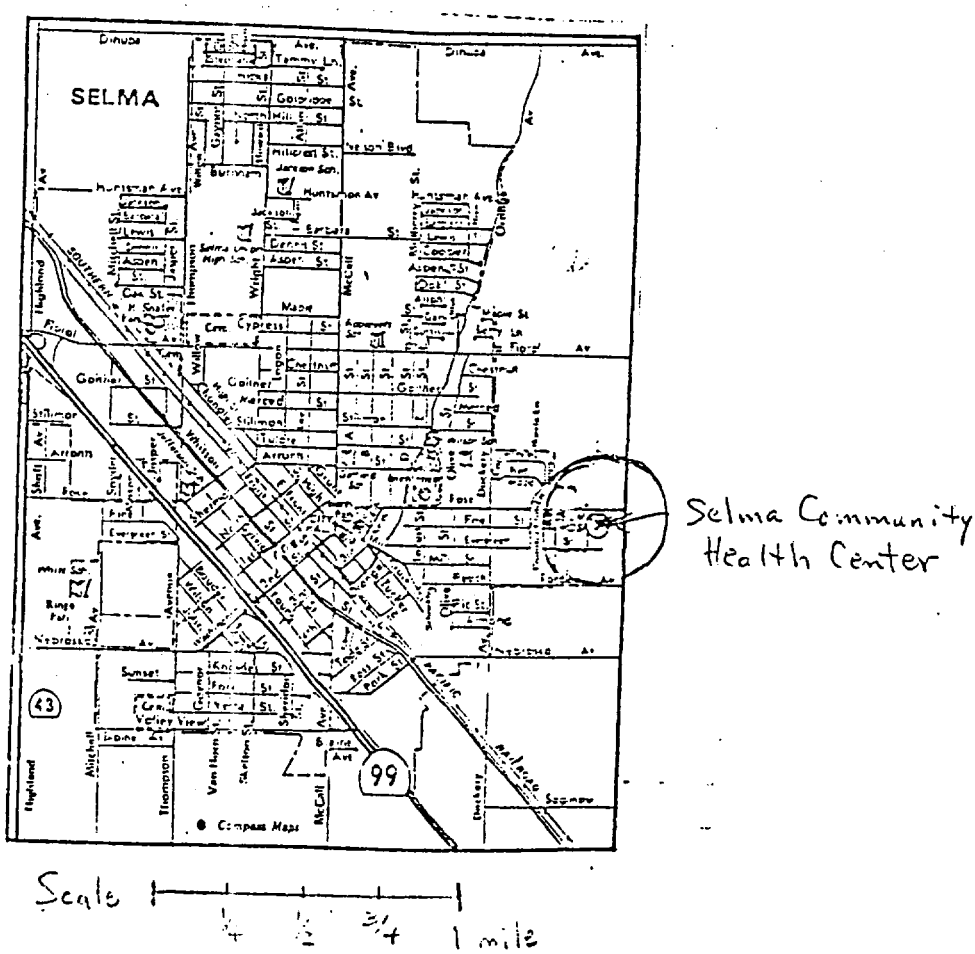
Site Sketch - Top View (distance to bldgs., obstructions, trees)



Site Sketch - Side View (Height of probe, distance to obstructions)



Town Map showing Monitoring Site



Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 6 -31, 1986

Site address: Dinuba (Tulare County)
Water Pump Station
E. Kamm Ave. near Greene (near Wilson School)

Contact at site: Robert Koster, Tulare APCD, (209) 733-6438
Stan Moore, City Public Works

Direction from site to fields which may be sprayed: W & S

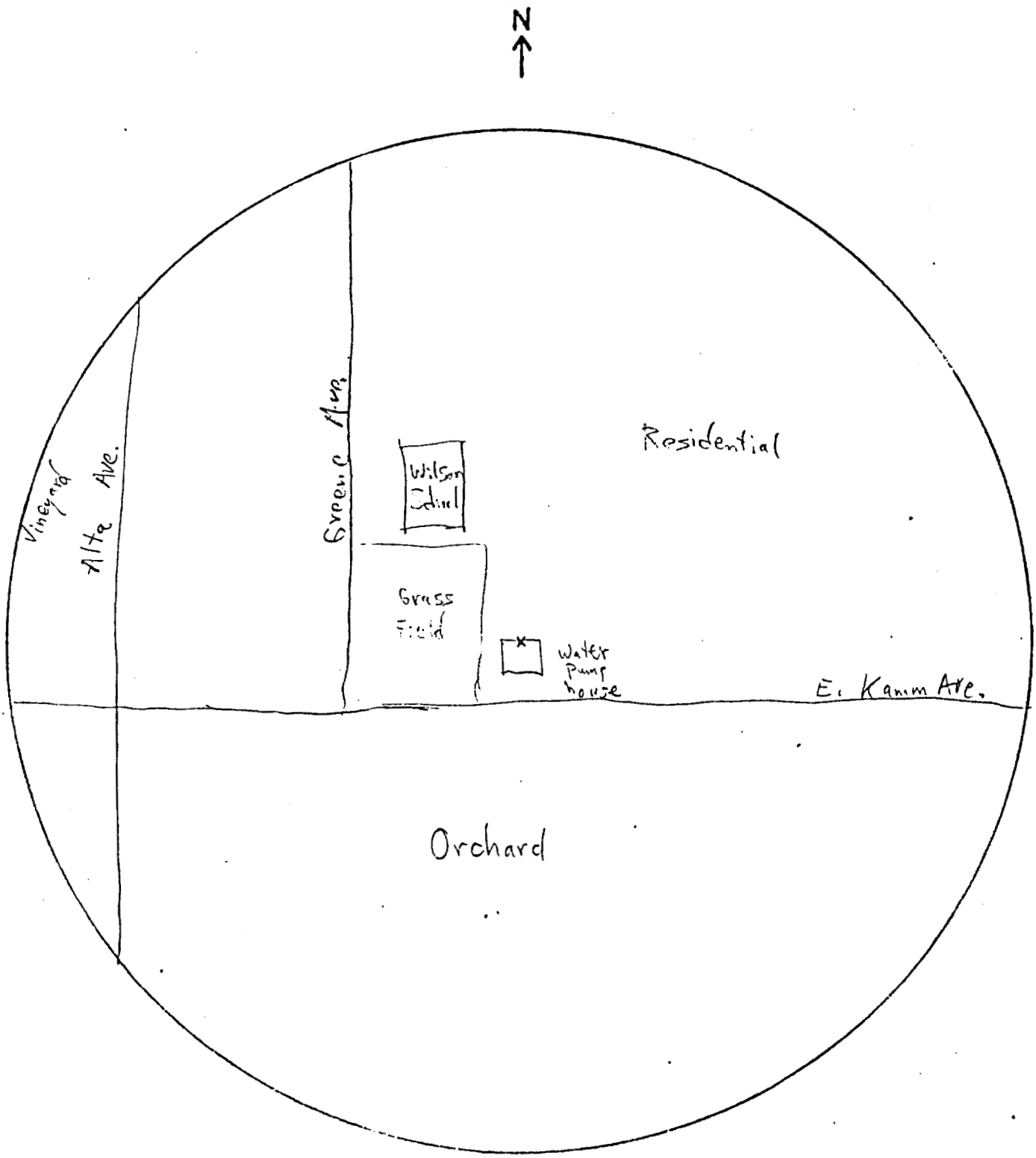
Distance from site to fields which may be sprayed: W (1/3 mile)
S (50 yd)

Sampling method (power source AC or DC): AC

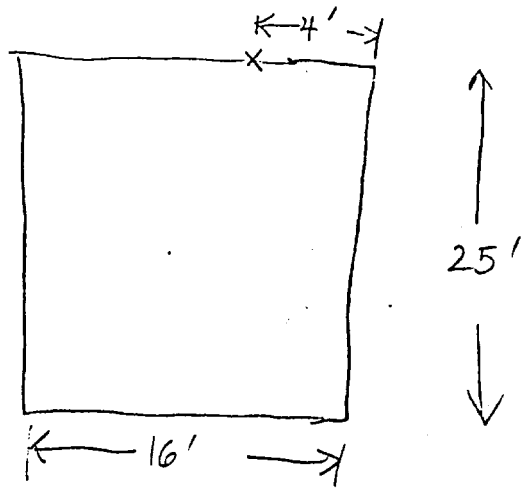
Height of monitoring probe: 14.5'

Distance to obstructions: None

Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)

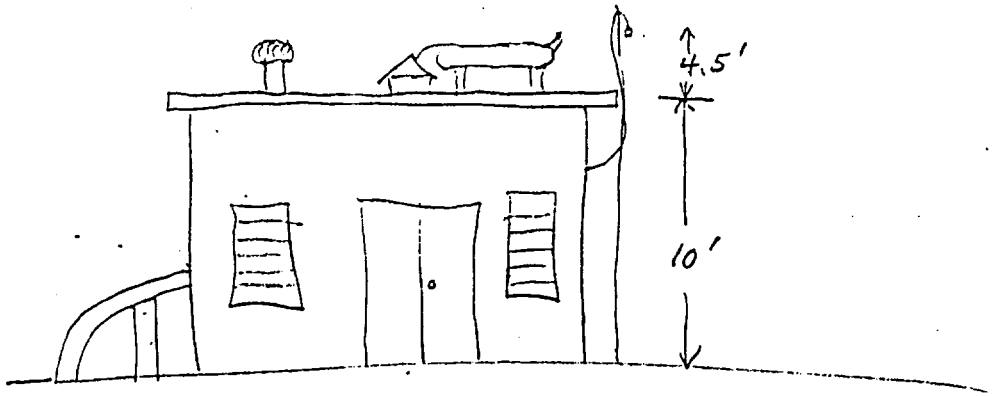


Site Sketch - Top View (distance to bldgs., obstructions, trees)



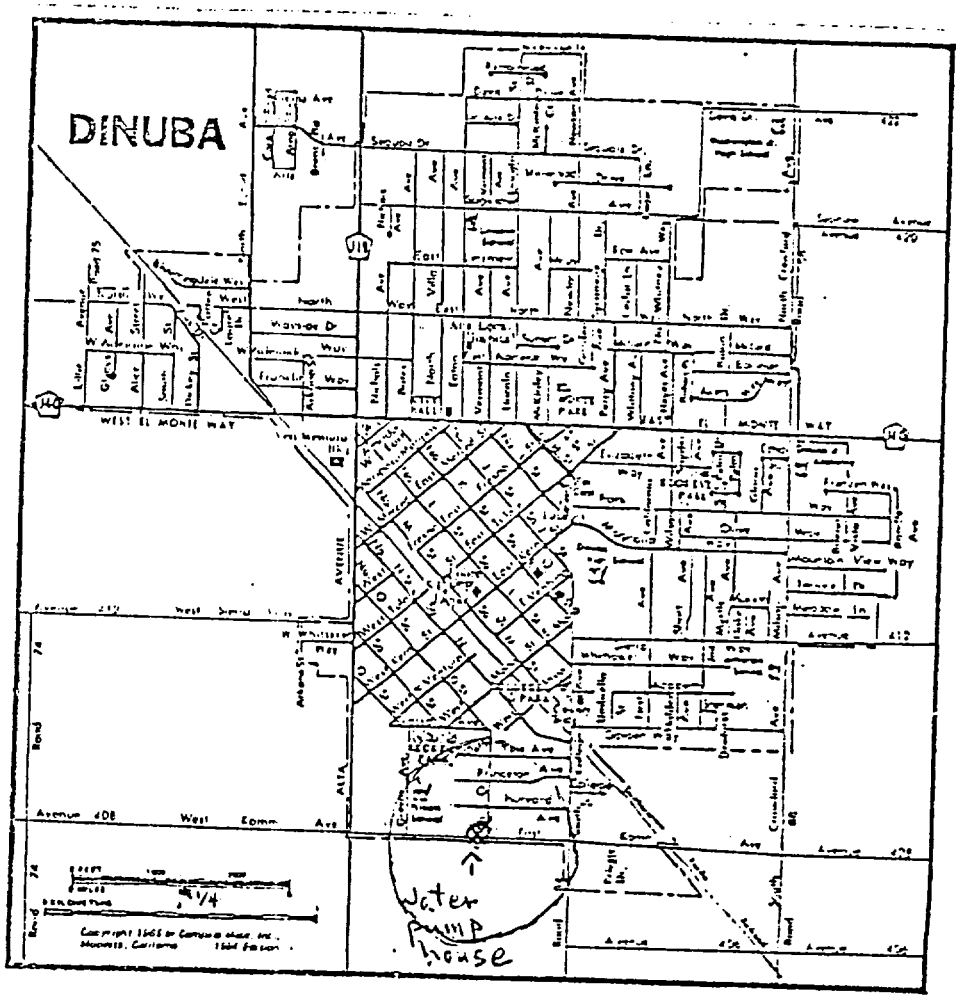
Site Sketch - Side View (Height of probe, distance to obstructions)

Looking W



Town Map showing Monitoring Site

N



Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 21 – Feb. 14, 1986

Site address: Earlimart
Intermediate School
State Road

Contact at site: Vic Sylvester (805) 849-2621
or Victor Love

Direction from site to fields which may be sprayed: E

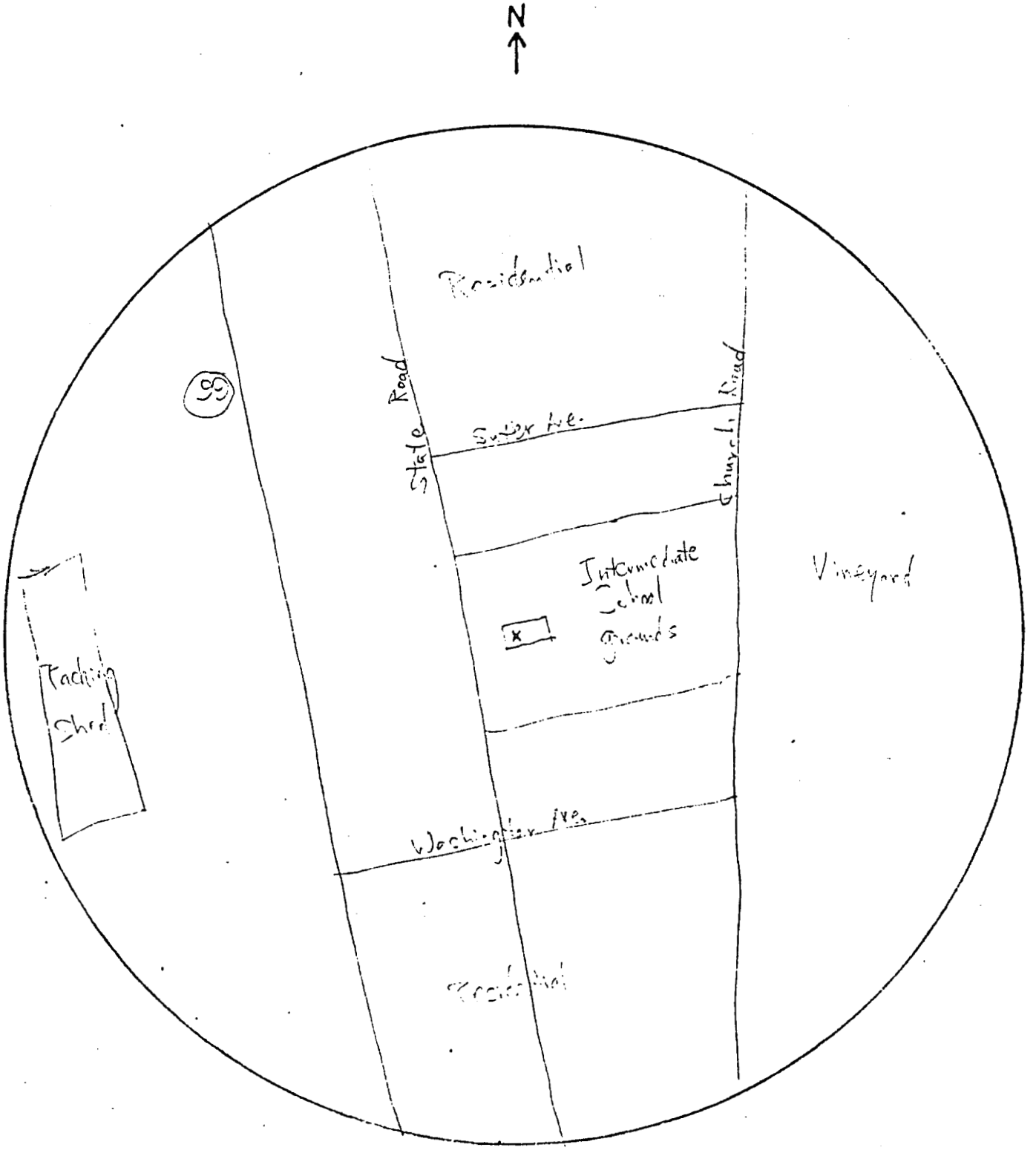
Distance from site to fields which may be sprayed: 1/8 mile

Sampling method (power source AC or DC): AC

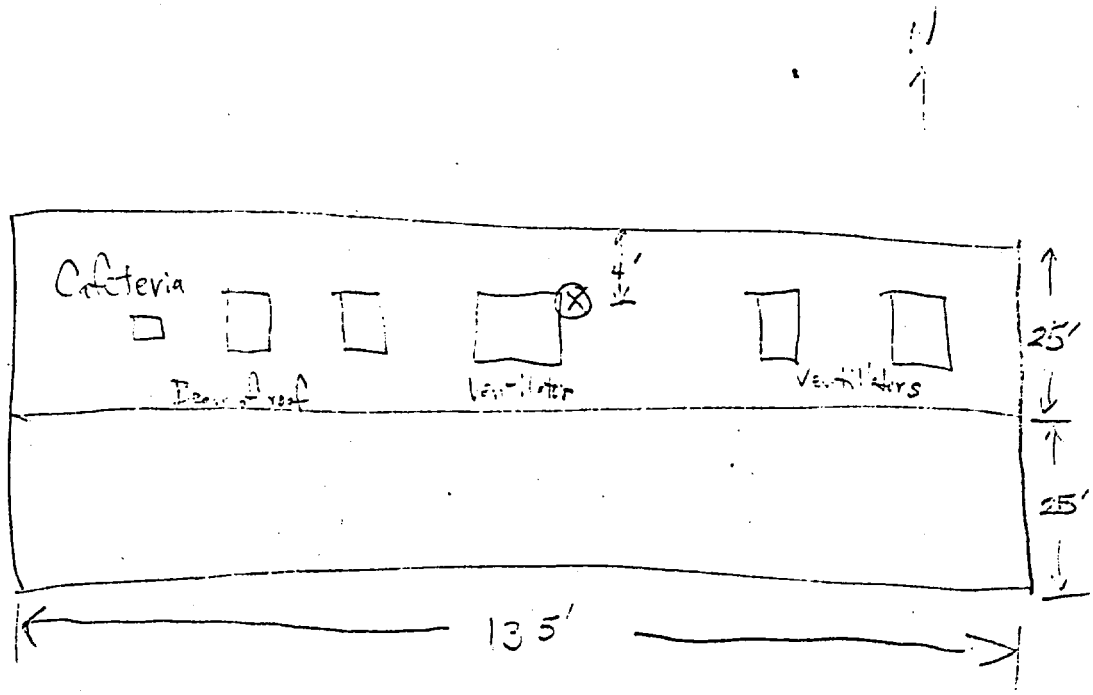
Height of monitoring probe: 16'

Distance to obstructions: [illegible] 2' above sampler unit 20' away

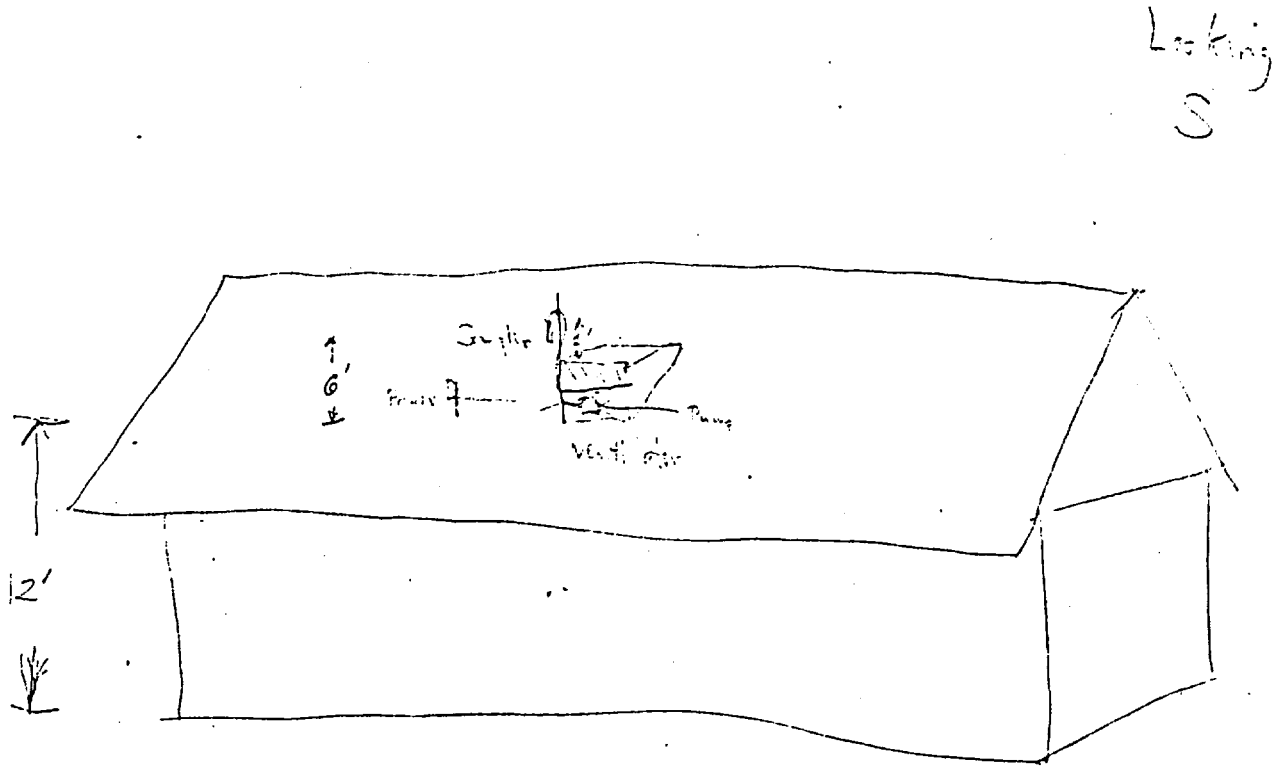
Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)



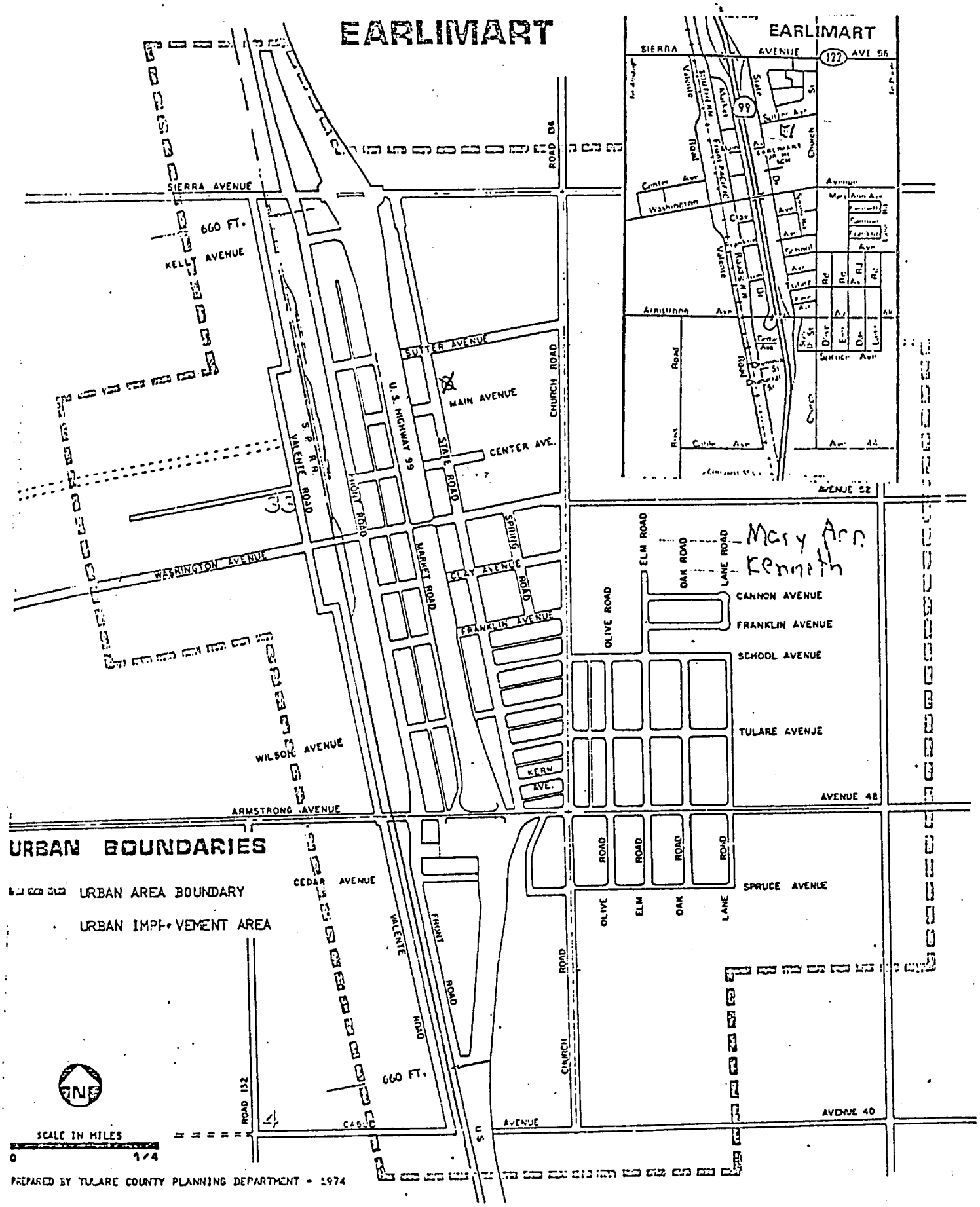
Site Sketch - Top View (distance to bldgs., obstructions, trees)



Site Sketch - Side View (height of probe, distance to obstructions)



Town Map showing Monitoring Site



Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 21 - Feb. 14, 1986

Site address: Delano
City Works Bldg.
725 S. Lexington St.

Contact at site: Eddie Ahumada, Superintendent (805) 725-2147

Direction from site to fields which may be sprayed: W & E

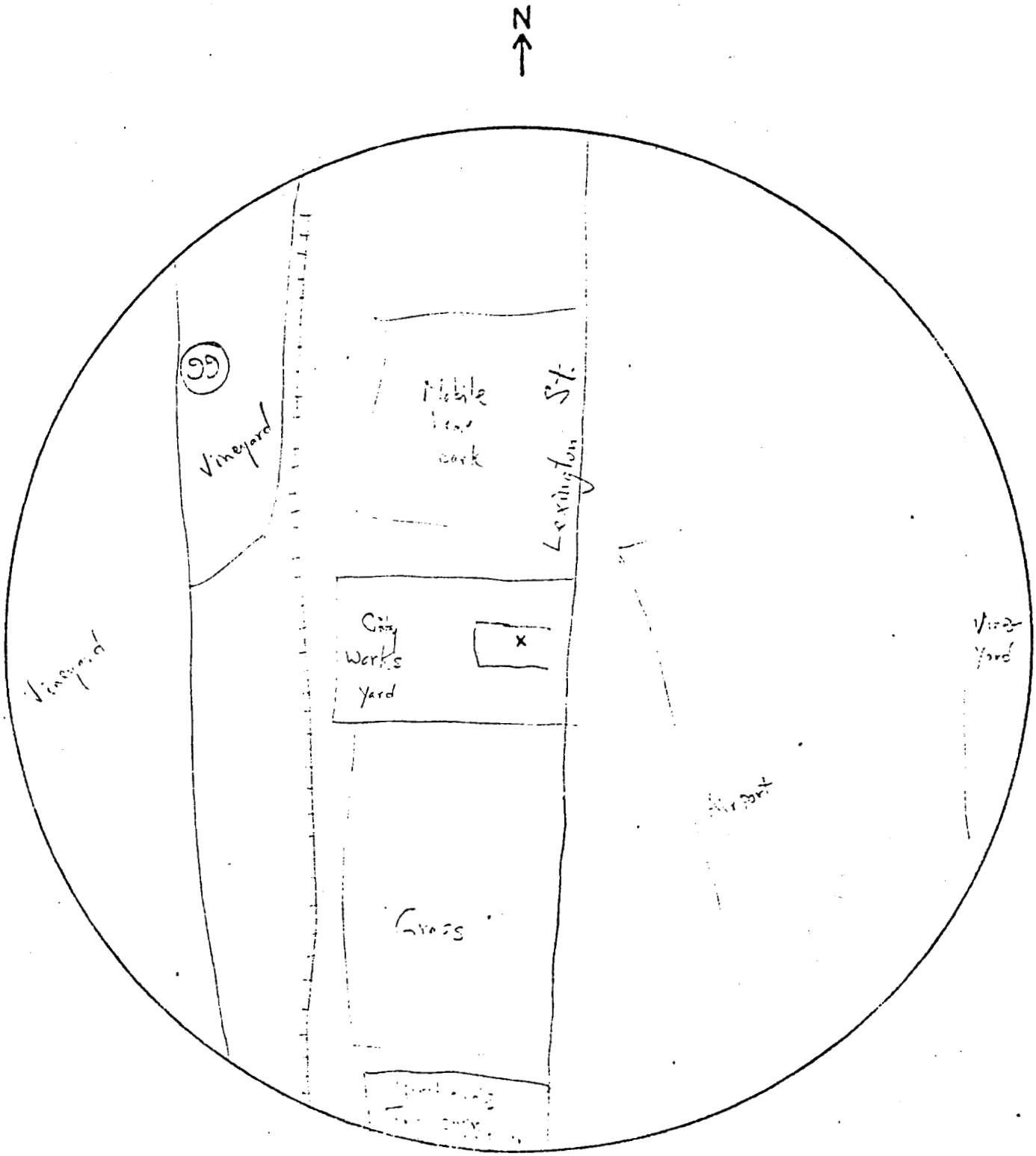
Distance from site to fields which may be sprayed: W (1/8 mile) vineyards
E (1/4 mile)

Sampling method (power source AC or DC): AC

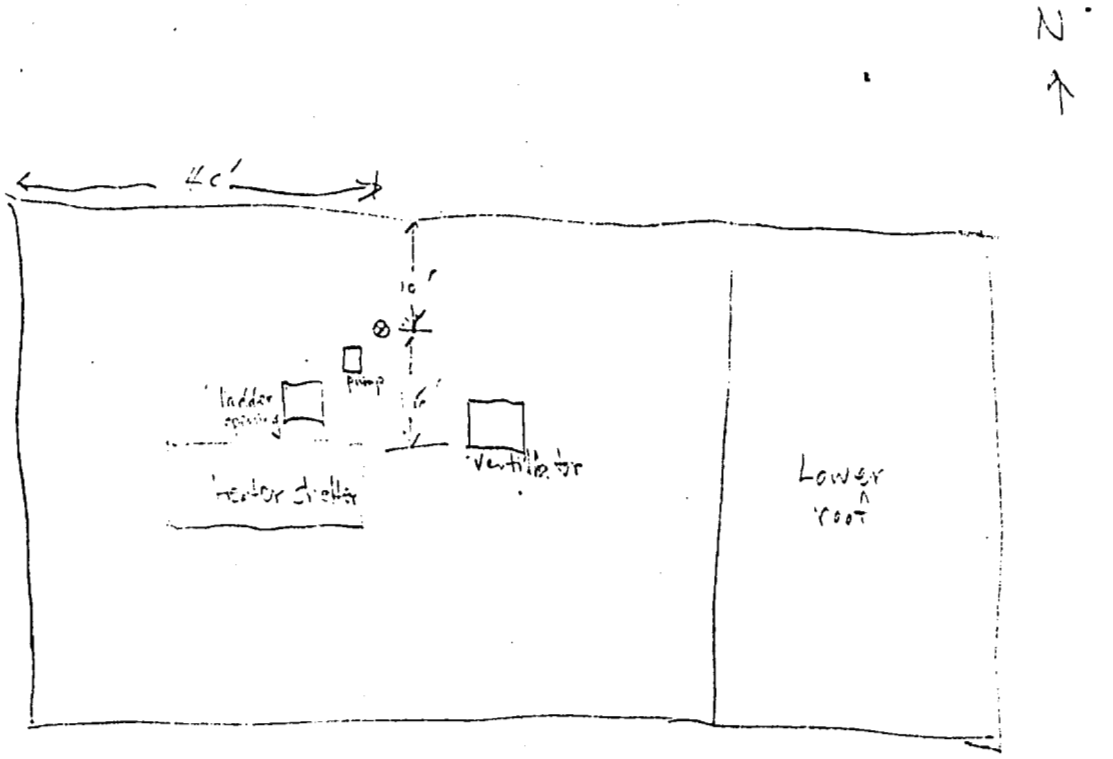
Height of monitoring probe: 23'

Distance to obstructions: None

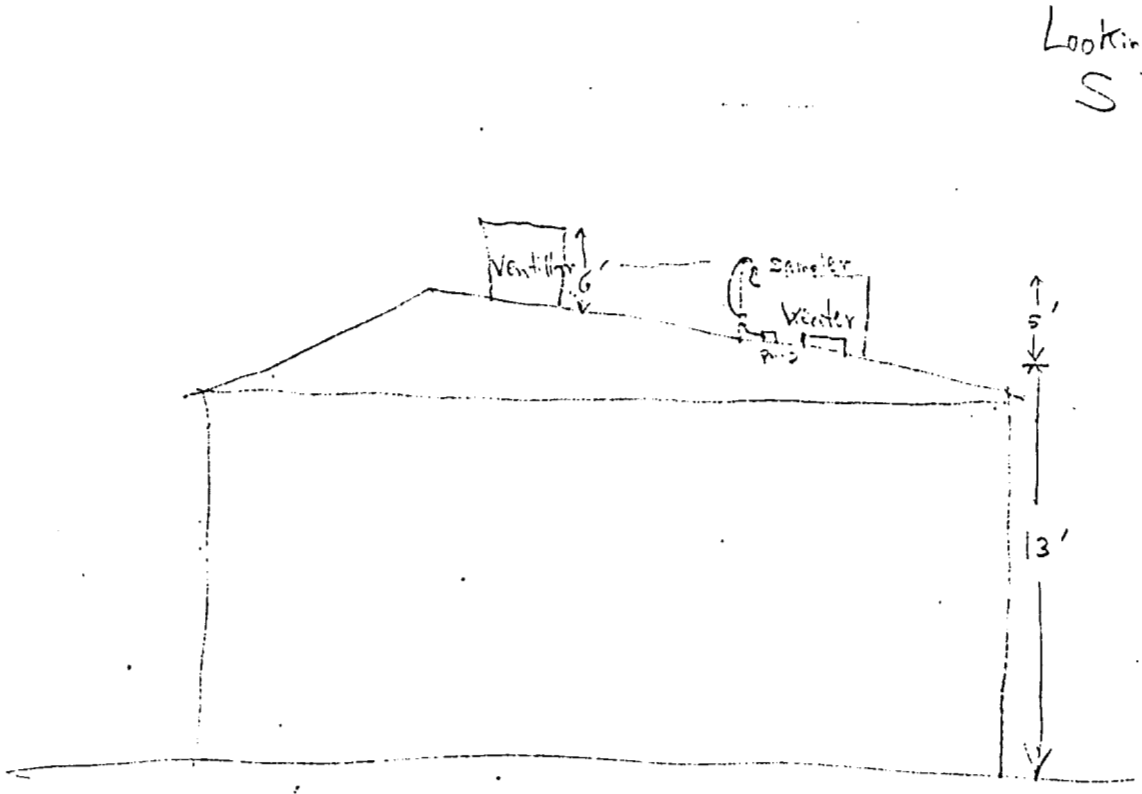
Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)



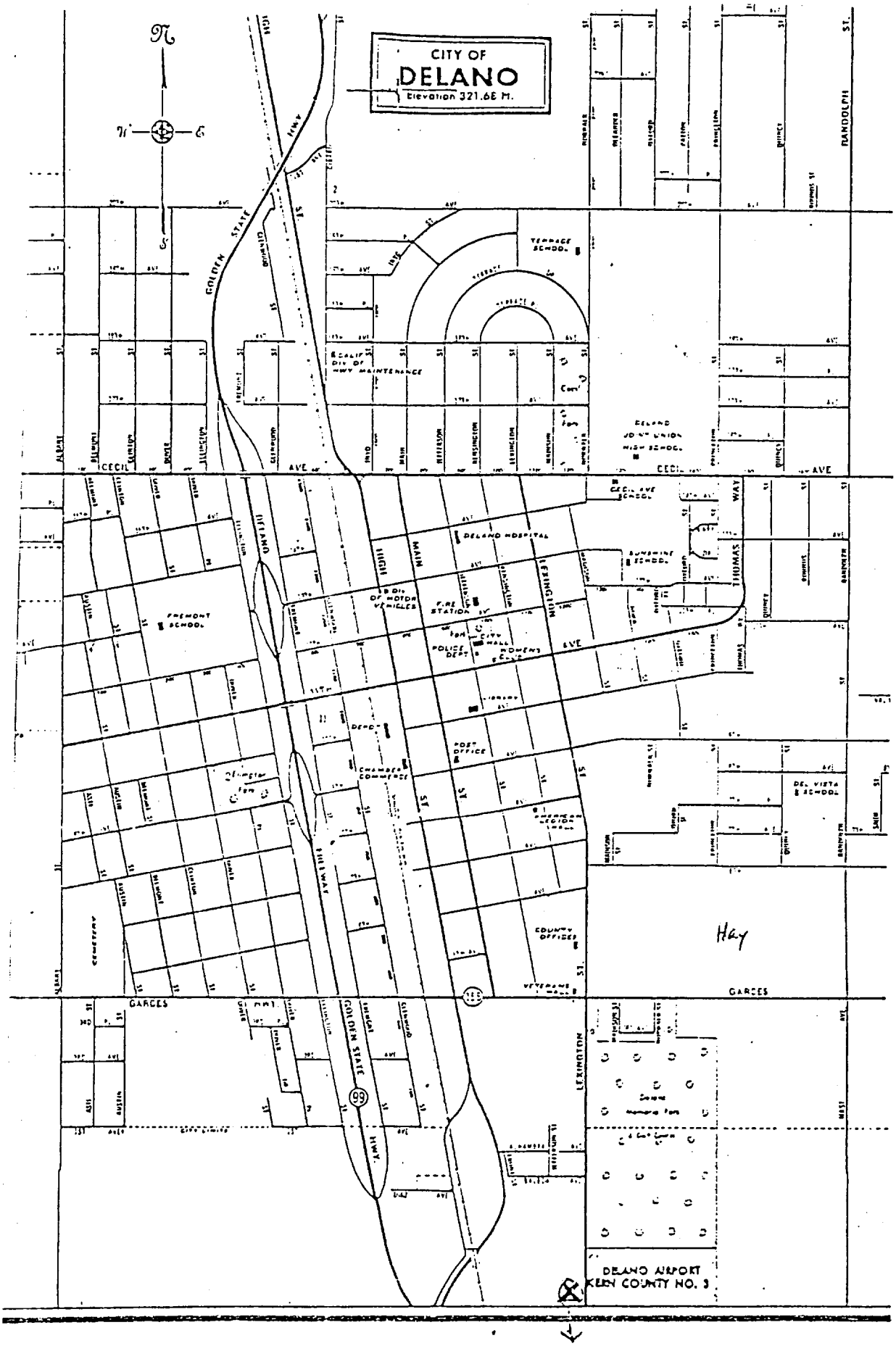
Site Sketch - Top View (Distance to bldgs., obstructions, trees)



Site Sketch - Side View (Height of probe, distance to obstructions)



Town Map showing Monitoring Site



Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 21 - Feb. 14, 1986

Site address: McFarland
City Hall
Kern Ave. & 4th

Contact at site: Mike O'Haver, City Planner (805) 792-3091

Direction from site to fields which may be sprayed: W

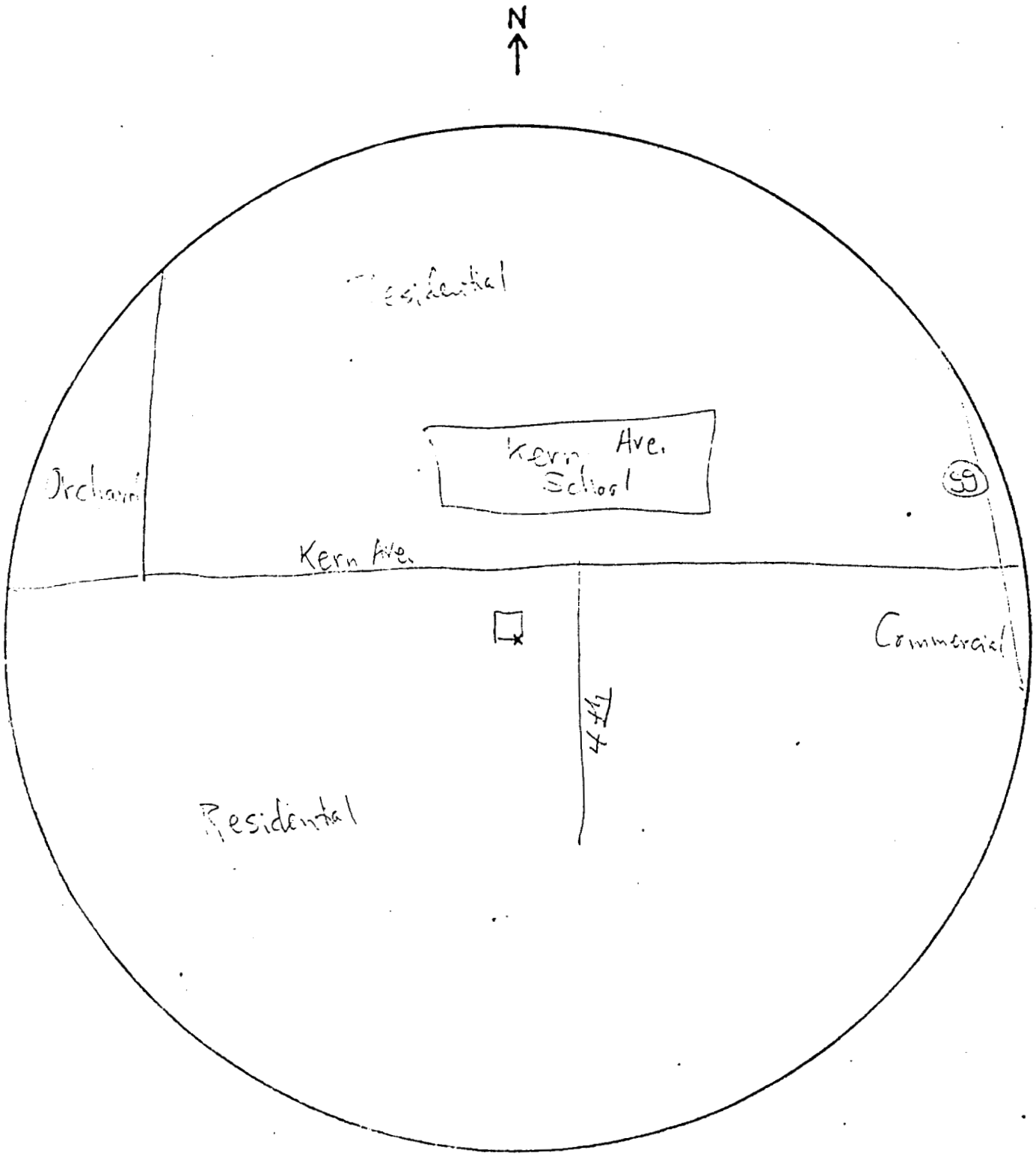
Distance from site to fields which may be sprayed: 1/4 mile

Sampling method (power source AC or DC): AC

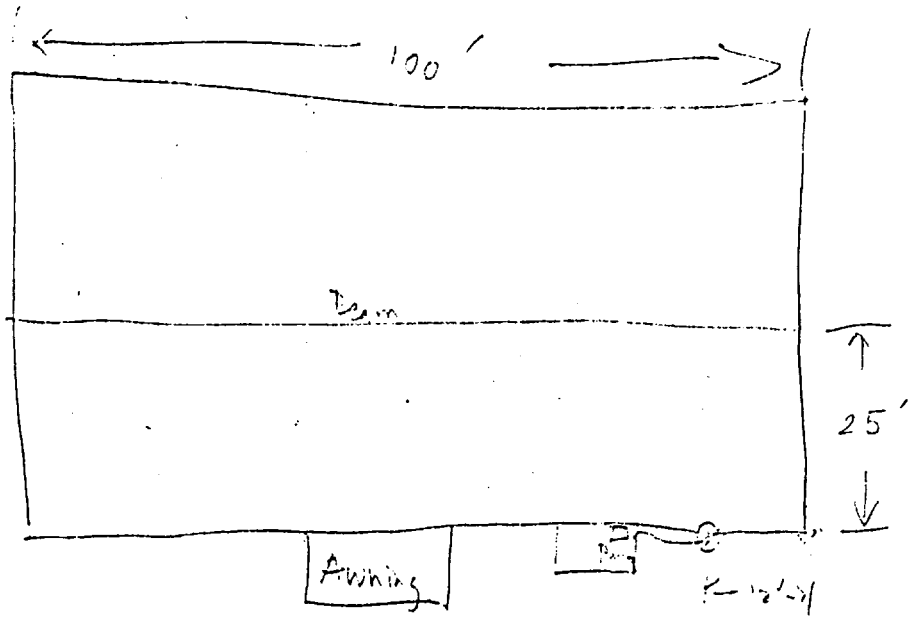
Height of monitoring probe: 13'

Distance to obstructions: None

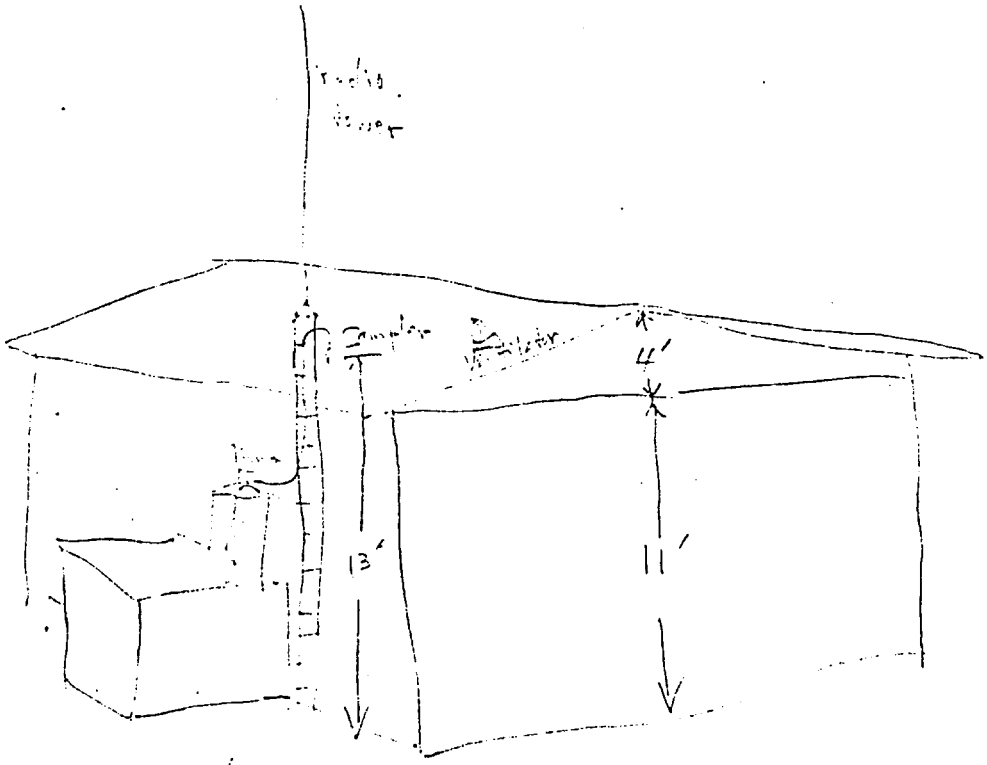
Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)



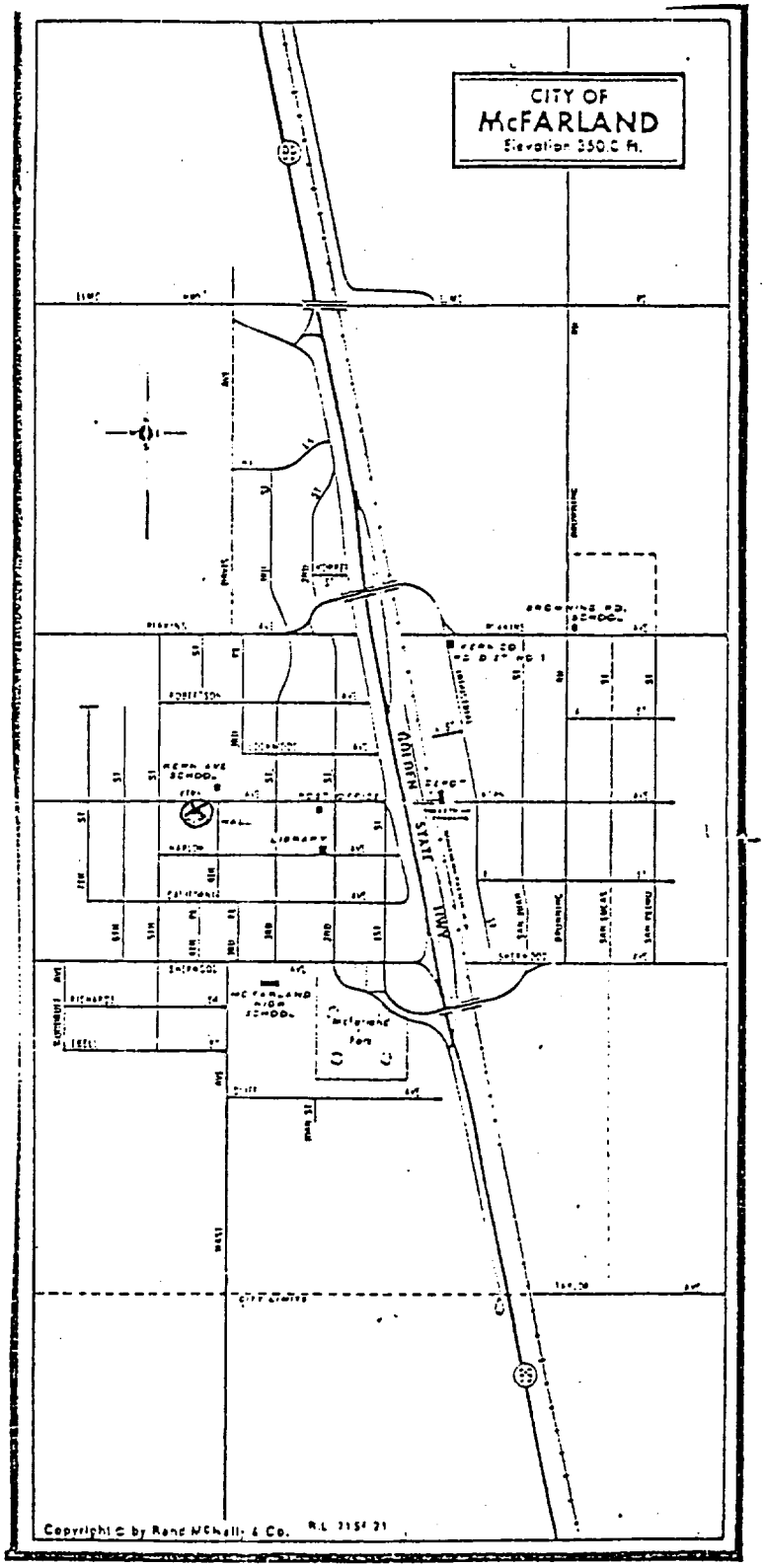
Site Sketch - Top View (distance to bldgs., obstructions, trees)



Site Sketch - Side View (Height of probe, distance to obstructions)



Town Map showing Monitoring Site



Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 21 - Feb. 14, 1986

Site adress: Wasco
2101 7th St. at Palm

Contact at site: Scott Blakley, administrator (805) 758-5123
or Becky, Secretary

Direction from site to fields which may be sprayed: NW

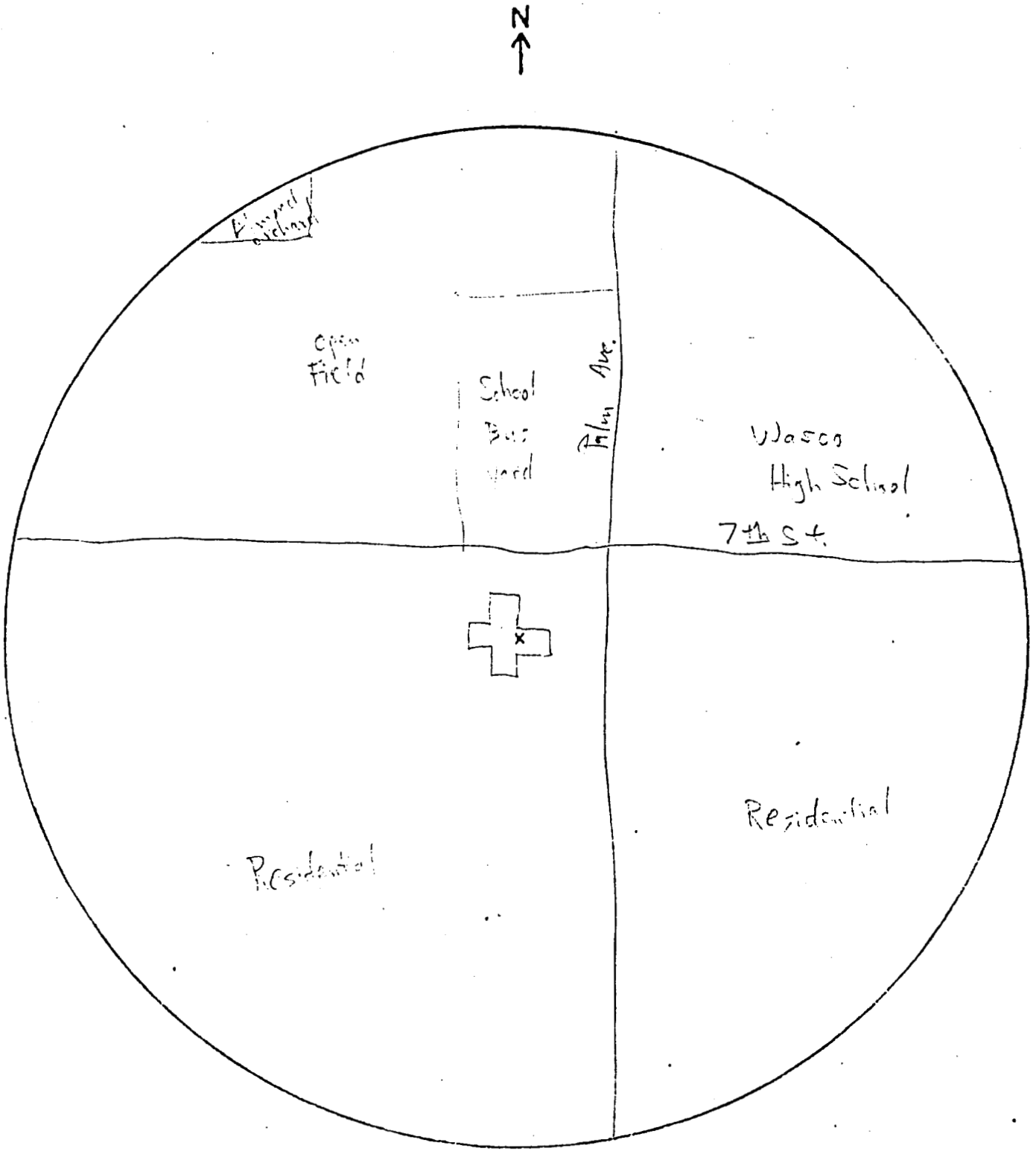
Distance from site to fields which may be sprayed: 1/4 mile

Sampling method (power source AC or DC): AC

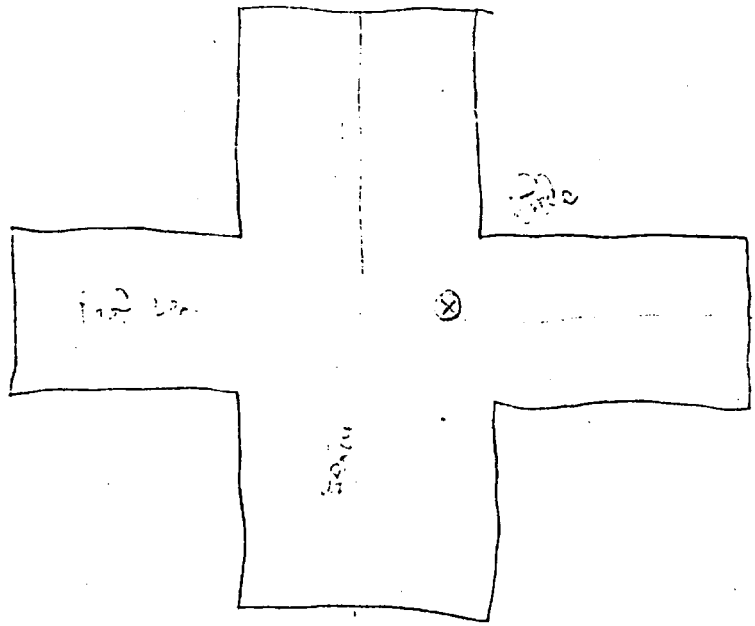
Height of monitoring probe: 18'

Distance to obstructions: None

Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)

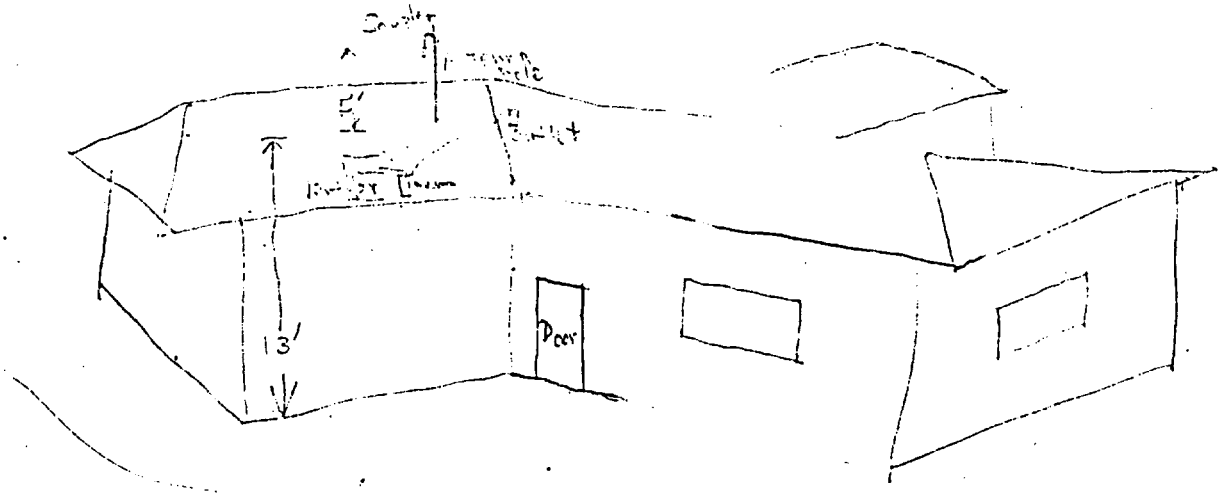


Site Sketch - Top View (distance to bldgs., obstructions, trees)

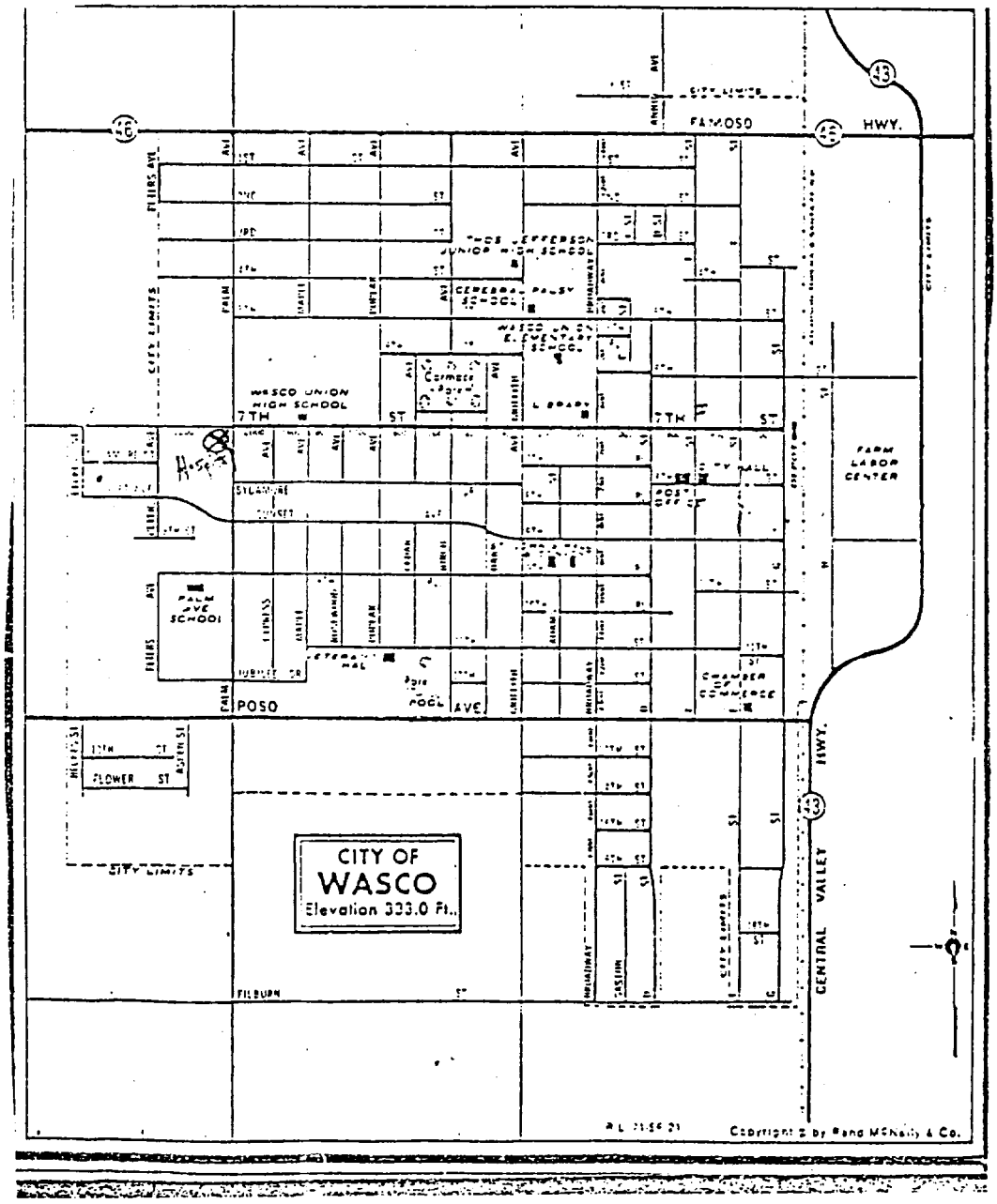


Site Sketch - Side View (Height of probe, distance to obstructions)

Looking



Town Map Showing Monitoring Site



Pesticide Monitoring Site Description

Pesticide: Ethyl Parathion

Monitoring period: Jan. 21 - Feb. 14, 1986

Site address: Shafter, CA 93263
Richland School District office.
331 N. Shafter Ave. at Richland Dr.

Contact at site: Vera Stone, Superintendent (805) 746-3904
or Evelyn Little, Sec.

Direction from site to fields which may be sprayed: W

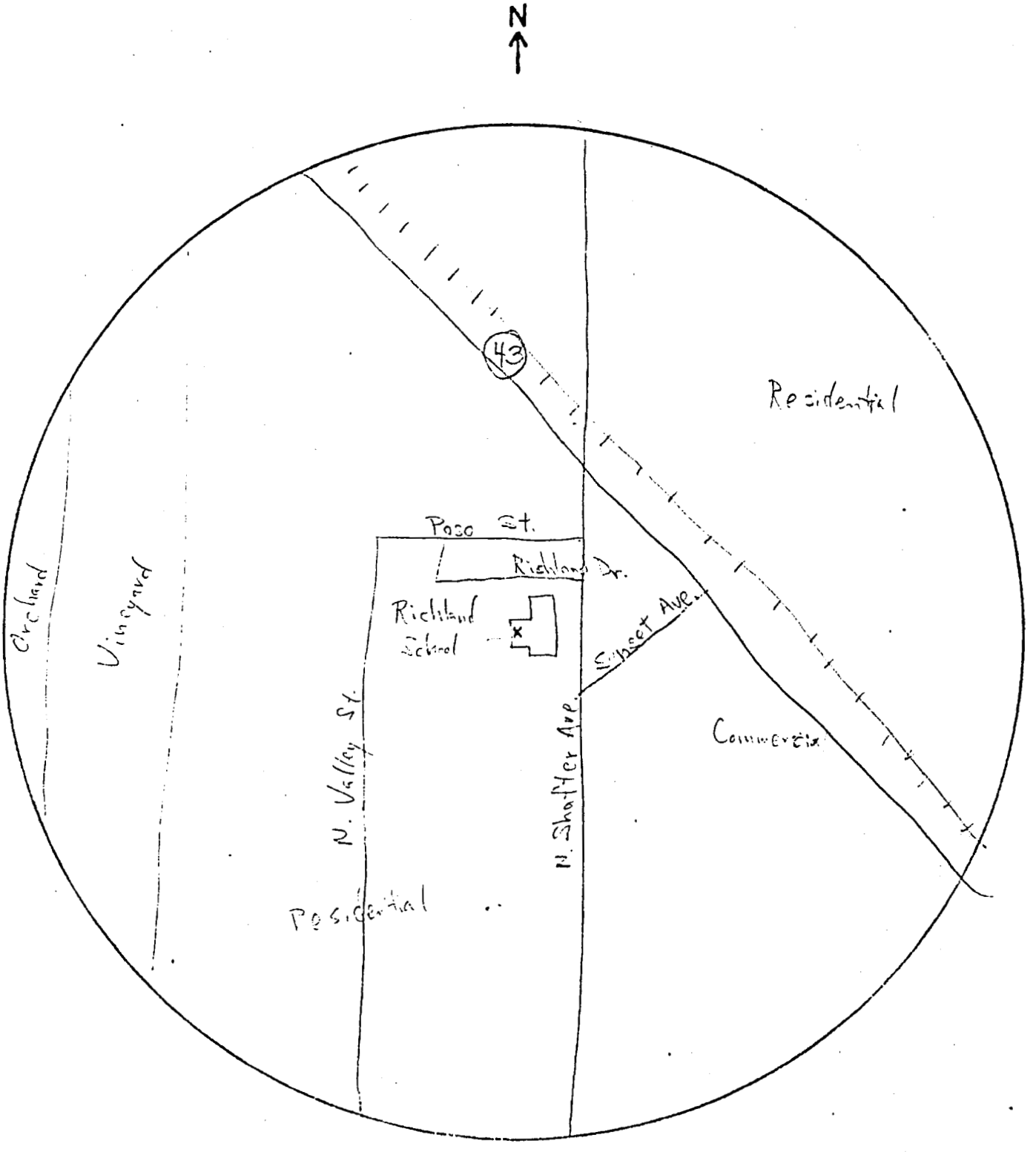
Distance from site to fields which may be sprayed: 1/4 mile

Sampling method (power source AC or DC): AC

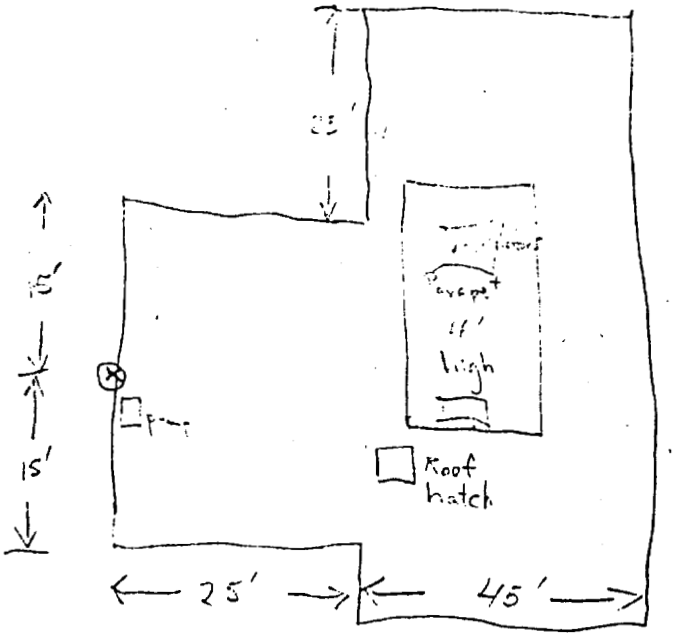
Height of monitoring probe: 18'

Distance to obstructions: None

Site Map - (1/4 mile radius showing roads, fields, orchards, water, multi-story structures, etc.)

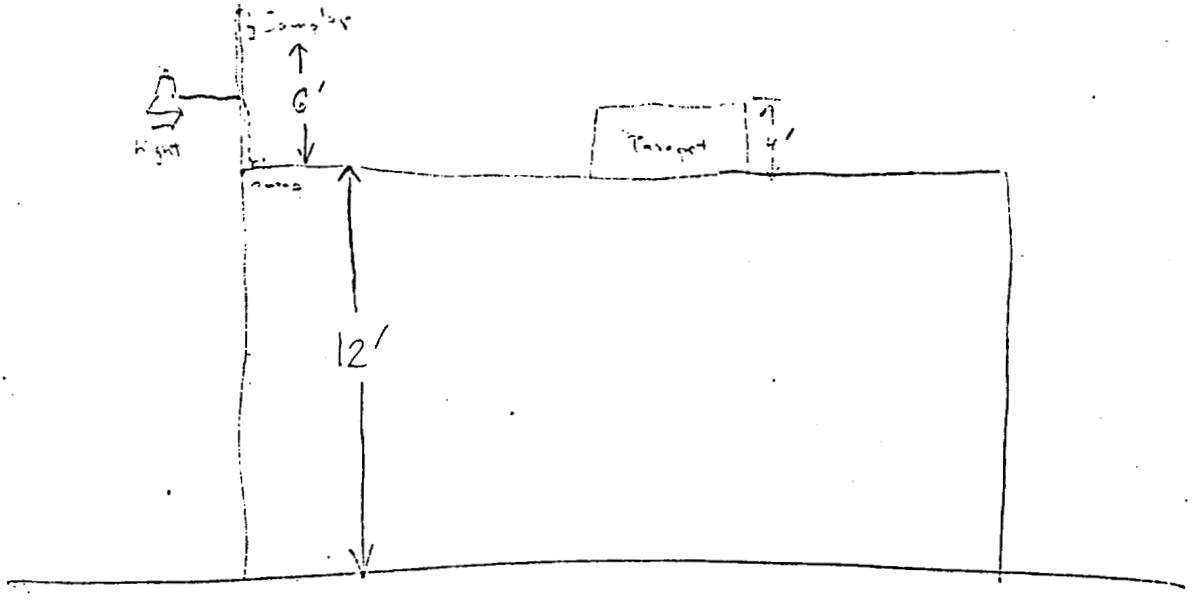


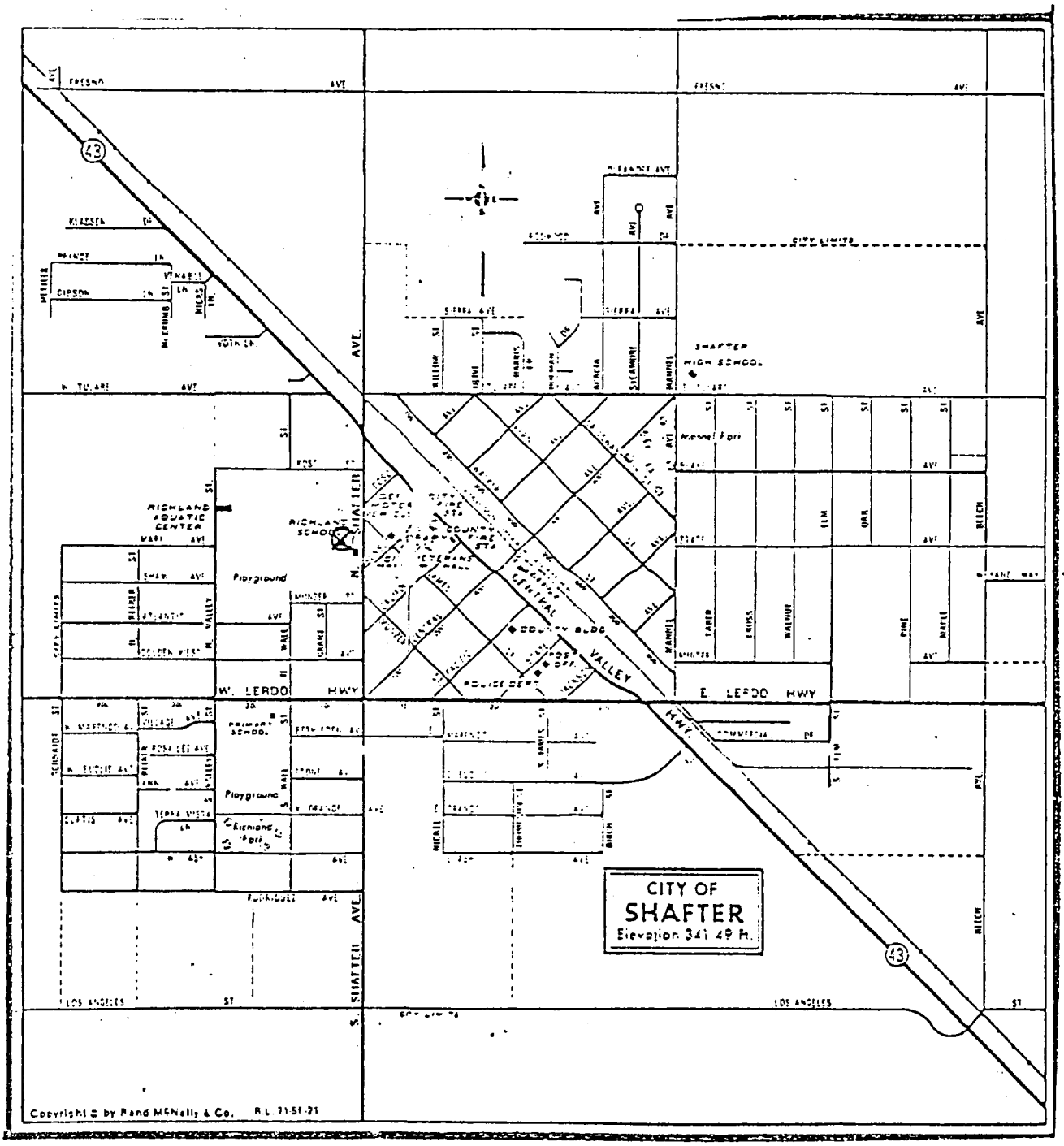
Site Sketch - Top View (distance to bldgs., obstructions, trees)



Site Sketch - Side View (Height of probe, distance to obstructions)

Looking N




CITY OF
SHAFTER
Elevation 341.49 ft.
SHAFTER HIGH SCHOOL
RICHLAND AQUATIC CENTER
RICHLAND SCHOOL
Playground
Richland Park
PRIMARY SCHOOL
Playground
Richland Park
Michael Park
CENTRAL VALLEY
COUNTY BLDG
POLICE DEPT
W. LERDO HWY
E. LERDO HWY
SHAFTER AVE.
S. SHAFTER AVE.
FRESNO AVE
W. TULARE AVE
LOS ANGELES ST
CITY LIMITS
43
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ATTACHMENT IV

Complete Data Set

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: SANGER

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-7	1/2	23/1	2.75	—		
1-8	15/16	23/33	3.0	—		
1-9	29/30	NA		—		
1-13	41/42	20/11	3.1	—		
1-14	56/57	23/01	NA	—		
1-15	70/71	24/38	2.75	0.05	1.02	1.85
1-16	84/85	23/02	3.05	0.23	4.53	8.24
1-21	101	20/32	2.9	0.38	8.83	16.05
1-22	109	23/16	2.95	0.06	1.21	2.2
1-23	115/116	24/24	3.0	0.04	0.76	1.38
1-27	129/130	25/30	2.95	0.18	3.31	6.02
1-28	147/148	22/10	3.0	—		
1-29	157/158	25/57	3.0	0.20	3.55	6.45

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

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PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: PARLIER

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-7	3/4	23/02	2.88	0.15	3.13	5.69
1-7	5/6	23/02	3.2	0.16	3.0	5.45
1-8	17/18	23/25	3.0	0.06	1.18	2.14
1-8	19/20	23/28	3.0	0.06	1.18	2.14
1-9	31/32	24/01	3.0	—		
1-9	33/34	23/58	3.05	0.04	0.76	1.38
1-13	43/44	20/37	2.95	0.16	3.64	6.62
1-13	45/46	20/33	3.05	0.12	2.65	4.82
1-13	47	3/05	2.95	—		
1-14	58/59	23/09	3.0	0.32	6.37	11.58
1-14	60/61	23/09	3.0	0.15	2.99	5.44
1-14	62	3/07	2.85	—		
1-14	63	3/06	≈3.0	—		
1-15	72/73	24/30	3.0	0.17	3.2	5.82

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Corrected for Pressure

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: PARLIER

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-15	74/75	24/30	3.05	0.28	5.18	9.42
1-15	76	3/10	3.0	—		
1-15	77	3/05	≈3.0	—		
1-16	86/87	22/55	2.95	0.18	3.68	6.69
1-16	88/89	22/55	3.0	0.25	5.03	9.14
1-16	90	3/04	3.0	—		
1-16	91	3/04	3.0	—		
1-17	100	3/00	3.0	—		
1-21	102	20/35	3.1	0.25	5.42	9.85
1-21	103	20/38	3.0	0.32	7.15	13.0
1-22	110	23/10	3.0	0.22	4.38	7.96
1-22	111	23/10	3.0	0.36	7.16	13.02
1-23	117/118	24/15	2.95	0.53	10.2	18.54
1-23	119/120	24/19	3.05	0.40	7.46	13.56

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (65°F) and 760 mm Hg (1 atm)

** Corrected for Pressure

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: PARLIER

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-27	131/132	24/43	3.15	2.14	38.0	69.09
1-28	145/146	22/16	2.95	1.50	31.6	57.45
1-29	155/156	25/52	3.0	0.52	9.27	16.85

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Corrected for Pressure

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: REEDLEY

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (PPt)*	Sample Conc. (ppt)**
1-7	7/8	22/17	3.25	0.12	2.29	4.16
1-8	21/22	23/28	2.9	0.09	1.83	3.33
1-9	35/36	23/28	3.0	0.08	1.57	2.85
1-13	48/49	20/28	3.25	0.31	6.45	11.73
1-14	64/65	24/05	3.25	0.32	5.66	10.29
1-15	78/79	23/40	2.9	0.42	8.46	15.38
1-16	92/93	23/36	3.05	0.38	7.30	13.27
1-21	104	20/45	3.35	0.94	18.7	34.0
1-22	112	23/09	2.95	0.62	12.6	22.91
1-23	121/122	24/44	2.95	0.42	7.96	14.47
1-27	133/134	23/58	3.5	0.99	16.3	29.64
1-28	143/144	22/22	2.9	0.59	12.6	22.91
1-29	153/154	25/43	2.9	0.56	10.4	18.91

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

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PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: DINUBA

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-7	9/10	21/43	2.75	0.07	1.62	2.94
1-8	23/24	23/23	3.1	0.17	3.24	5.89
1-9	37/38	23/28	3.05	0.08	1.55	2.82
1-13	50/51	20/30	3.0	0.14	3.15	5.73
1-14	66/67	24/10	3.05	0.91	17.1	31.09
1-15	80/81	24/18	3.1	0.72	13.2	24.0
1-16	94/95	23/33	3.05	0.26	4.36	7.93
1-21	105	20/45	2.95	0.17	3.84	6.98
1-22	113	23/10	3.0	0.16	3.18	5.78
1-23	123/124	24/43	3.0	0.18	3.36	6.11
1-27	135/136	23/11	3.25	0.29	5.32	9.67
1-28	141/142	22/32	3.1	0.36	7.13	12.96
1-29	151/152	25/36	3.05	0.28	4.96	9.02

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Corrected for Pressure

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: SELMA

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-7	11/12	21/19	2.65	—		
1-8	25/26	23/25	3.1	—		
1-9	39/40	23/21	3.0	—		
1-13	52/53	20/34	3.0	—		
1-14	68/69	24/09	3.0	0.66	12.6	22.91
1-15	82/83	23/39	3.1	0.11	2.08	3.78
1-16	96/97	23/00	≈3.0	—		
1-21	106	20/42	3.4	0.36	7.08	12.87
1-22	114	23/02	2.9	0.23	4.76	8.65
1-23	125/126	24/41	3.05	0.17	3.12	5.67
1-27	137/138	20/00	3.2	0.37	8.0	14.54
1-28	139/140	22/33	3.0	0.58	11.9	21.64
1-29	149/150	25/27	2.9	0.32	6.0	10.91

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Computed from P

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: SHAFTER

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-28	201/202	23/22	3.1	—		
1-29	211/212	24/39	3.45	—		
2-3	229/230	19/55	3.25	—		
2-5	259/260	23/28	2.85	—		
2-6	275/276	21/52	3.0	—		
2-10	281/282	22/08	3.0	—		
2-11	293/294	24/24	3.4	—		
2-12	305/306	22/44	3.0	—		

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Corrected for Pressure

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: WASCO

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-28	203/204	22/51	2.9	0.15	3.13	5.69
1-29	213/214	24/52	2.95	0.05	0.94	1.71
2-4	241/242	24/12	2.9	—		
2-5	257/258	23/47	2.95	—		
2-6	273/274	22/47	3.1	—		
2-10	283/284	22/50	2.85	—		
2-11	295/296	24/37	3.1	0.06	1.09	1.98
2-12	307/308	22/56	2.9	0.04	0.83	1.51

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Corrected for Pressure

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: McFARLAND

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-28	205/206	22/48	3.0	0.20	4.04	7.34
1-29	215/216	24/58	3.0	0.18	3.32	6.04
2-4	239/240	24/20	3.15	0.02	0.36	0.65
2-5	255/256	23/46	2.8	—		
2-6	271/272	23/46	2.95	—		
2-10	285/286	22/22	3.0	0.04	0.82	1.49
2-11	297/298	27/39	3.0	0.07	1.17	2.13

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Corrected for Pressure

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: DELANO

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-28	207/208	22/35	3.25	—		
1-29	217/218	25/00	3.1	0.04	0.71	1.29
2-3	223/224	19/42	2.9	—		
2-3	225/226	19/40	3.15	—		
2-3	227/228	2/40	2.9	—		
2-4	231/232	24/29	3.1	—		
2-4	233/234	24/29	3.0	—		
2-4	235/236	3/00	2.9	—		
2-4	245/246	3/00	3.0	—		
2-5	247/248	23/43	3.0	—		
2-5	249/250	23/44	2.95	—		
2-5	251/252	3/03	2.9	—		
2-5	261/262	3/07	3.0	—		
2-6	263/264	25/13	3.1	—		

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

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PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: DELANO

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
2-6	265/266	25/10	2.95	—		
2-6	267/268	3/01	3.0	—		
2-6	277/278	3/00	3.0	—		
2-10	287/288	22/07	3.25	—		
2-10	289/290	22/07	2.9	—		
2-11	299/300	26/06	3.1	0.04	0.68	1.24
2-11	301/302	26/06	3.0	—		

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Corrected for Pressure

PESTICIDE MONITORING DATA SHEET

Summary of Results

Monitoring Site: EARLIMART

Date	Log No.	Elapsed Time (Hrs/min)	Average Flow, (lpm)	Sample Wt. (ug)	Sample Conc. (ppt)*	Sample Conc. (ppt)**
1-28	209/210	22/33	2.95	0.11	2.29	4.16
1-29	219/220	25/00	3.0	0.15	2.77	5.04
2-4	237/238	24/23	3.1	—		
2-5	253/254	23/46	3.1	—		
2-6	269/270	25/16	3.1	—		
2-11	303/304	24/53	3.0	—		

* ppm = $\frac{24.05 \times ug/l}{\text{Compound Mole. Wt.}}$ @ 294° K (68°F) and 760 mm Hg (1 atm)

** Corrected for Recovery

ATTACHMENT V

Laboratory Results

State of California

Memorandum

To : Bob Barham, Manager
Source Evaluation Section

Thru: Don Crowe, Chief
Aerometric Projects & Laboratory Branch

From : Air Resources Board
Robert Kuhlman, Manager
Laboratory Services Section
Aerometric Data Division

Date : March 5, 1986

Subject : Laboratory Results from the San Joaquin Valley Pesticide Study

RECEIVED

MAR 6 1986

Engineering Section
Air Resources Board

Attached are the results of the analysis of San Joaquin Valley samples submitted in January and February 1986, for organo-phosphate pesticides. The samples were submitted as XAD-2 solid sorbant tubes and were analyzed by gas chromatography/Thermionic Specific Detection according to Method ADDL003. The results have been tabulated in total micrograms (ug) per sample as no sample volumes were submitted.

Background monitoring concentrations at the ARB sampling sites in Fresno and Bakersfield during this period are currently being processed into the TEALE Toxics data base and will be transmitted to you under separate cover. If you have any questions concerning the data, please contact Michael Poore of our staff at 4-1970.

Attachment

cc: Dean Simeroth
Ralph Propper
Michael Poore
Lynn Baker
Gary Murchison

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: January 9, 1986

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
1S-F	*	*	*	*	*
1S-B	*	*	*	*	*
3	0.20	*	*	*	0.15
4	*	*	*	*	*
5	0.23	*	*	*	0.16
6	*	*	*	*	*
7	*	*	*	*	0.12
8	*	*	*	*	*
9	*	*	*	*	0.07
10	*	*	*	*	*
11	*	*	*	*	*
12	*	*	*	*	*
13	*	*	*	*	*
14	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: January 13, 1986

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
15	*	*	*	*	*
16	*	*	*	*	*
17	*	*	*	*	0.06
18	*	*	*	*	*
19	*	*	*	*	0.06
20	*	*	*	*	*
21	*	*	*	*	0.09
22	*	*	*	*	*
23	*	*	*	*	0.17
24	*	*	*	*	*
25	*	*	*	*	*
26	*	*	*	*	*
27	*	*	*	*	*
28	*	*	*	*	*
29	*	*	*	*	*
30	*	*	*	*	*
31	*	*	*	*	*
32	*	*	*	*	*
33	*	*	*	*	0.04
34	*	*	*	*	*
35	*	*	*	*	0.08
36	*	*	*	*	*
37	*	*	*	*	0.08
38	*	*	*	*	*
39	*	*	*	*	*
40	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: January 21, 1986

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
41	*	*	*	*	*
42	*	*	*	*	*
43	*	*	*	*	0.16
44	*	*	*	*	*
45	*	*	*	*	0.12
46	*	*	*	*	*
47	*	*	*	*	*
48	*	*	*	*	0.31
49	*	*	*	*	*
50	*	*	*	*	0.14
51	*	*	*	*	*
52	*	*	*	*	*
53	*	*	*	*	*
54	*	*	*	*	*
55	*	*	*	*	*
56	*	*	*	*	*
57	*	*	*	*	*
58	*	*	*	*	0.32
59	*	*	*	*	*
60	*	*	*	*	0.15
61	*	*	*	*	*
62	*	*	*	*	*
63	*	*	*	*	*
64	*	*	*	*	0.32
65	*	*	*	*	*
66	*	*	*	*	0.91
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: January 21, 1986 (Page 2)

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
67	*	*	*	*	*
68	*	*	*	*	0.66
69	*	*	*	*	*
70	*	*	*	*	0.05
71	*	*	*	*	*
72	*	*	*	*	0.17
73	*	*	*	*	*
74	*	*	*	*	0.28
75	*	*	*	*	*
76	*	*	*	*	*
77	*	*	*	*	*
78	*	*	*	*	0.42
79	*	*	*	*	*
80	*	*	*	*	0.72
81	*	*	*	*	*
82	*	*	*	*	0.11
83	*	*	*	*	*
84	*	*	*	*	0.23
85	*	*	*	*	*
86	*	*	*	*	0.18
87	*	*	*	*	*
88	*	*	*	*	0.25
89	*	*	*	*	*
90	*	*	*	*	*
91	*	*	*	*	*
92	*	*	*	*	0.38
Detection Limit	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: January 21, 1986 (Page 3)

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
93	*	*	*	*	*
94	*	*	*	*	0.26
95	*	*	*	*	*
96	*	*	*	*	*
97	*	*	*	*	*
98	*	*	*	*	*
99	*	*	*	*	*
100	*	*	*	*	*
Detection Limit	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: January 29, 1986

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
101	*	*	*	*	0.38
102	*	*	*	*	.25
103	.05	*	*	*	.32
104	.08	*	*	*	.94
105	*	*	*	*	.17
106	*	*	*	*	.36
107	*	*	*	*	*
108	*	*	*	*	*
109	*	*	*	*	.06
110	.25	*	*	*	.22
111	.46	*	*	*	.36
112	.08	*	*	*	.62
113	*	*	*	*	.16
114	*	*	*	*	.23
115	.06	*	*	*	.04
116	*	*	*	*	*
117	.34	*	*	*	.53
118	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: January 29, 1986 (Page 2)

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
119	0.28	*	*	*	0.40
120	*	*	*	*	*
121	0.05	*	*	*	0.42
122	*	*	*	*	*
123	*	*	*	*	0.18
124	*	*	*	*	*
125	0.06	*	*	*	0.17
126	*	*	*	*	*
127	*	*	*	*	*
128	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: February 3, 1986

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
129	0.07	*	*	*	0.18
130	*	*	*	*	*
131	0.15	*	0.09	*	2.14
132	*	*	*	*	*
133	0.08	*	0.04	*	0.99
134	*	*	*	*	*
135	*	*	*	*	*
136	*	*	*	*	0.29
137	*	*	*	*	0.37
138	*	*	*	*	*
139	0.04	*	*	*	0.58
140	*	*	*	*	*
141	*	*	0.04	*	0.36
142	*	*	*	*	*
143	0.08	*	0.09	*	0.59
144	*	*	*	*	*
145	3.58	0.02	0.09	*	1.12
146	0.06	*	0.06	*	0.38
147	*	*	*	*	*
148	*	*	*	*	*
149	*	*	*	*	0.32
150	*	*	*	*	*
151	0.06	*	*	*	0.28
152	*	*	*	*	*
153	0.05	*	0.06	*	0.56
154	*	*	*	*	*
155	2.15	*	*	*	0.52
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: February 3, 1986 (Page 2)

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
156	*	*	*	*	*
157	0.09	*	*	*	0.20
158	*	*	*	*	*
159	*	*	*	*	*
160	*	*	*	*	*
201	*	*	*	*	*
202	*	*	*	*	*
203	*	*	*	*	0.15
204	*	*	*	*	*
205	*	*	*	*	0.20
206	*	*	*	*	*
207	*	*	*	*	*
208	*	*	*	*	*
209	*	*	*	*	0.11
210	*	*	*	*	*
211	*	*	*	*	*
212	*	*	*	*	*
213	*	*	*	*	0.05
214	*	*	*	*	*
215	*	*	*	*	0.18
216	*	*	*	*	*
217	*	*	*	*	0.04
218	*	*	*	*	*
219	*	*	*	*	0.15
220	*	*	*	*	*
221	*	*	*	*	*
222	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: February 10, 1986

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
223	*	*	*	*	*
224	*	*	*	*	*
225	*	*	*	*	*
226	*	*	*	*	*
227	*	*	*	*	*
228	*	*	*	*	*
229	*	*	*	*	*
230	*	*	*	*	*
231	No results reported, sample not available.				
232	*	*	*	*	*
233	*	*	*	*	*
234	*	*	*	*	*
235	*	*	*	*	*
236	*	*	*	*	*
237	*	*	*	*	*
238	*	*	*	*	*
239	*	*	*	*	0.02
240	*	*	*	*	*
241	*	*	*	*	*
242	*	*	*	*	*
243	*	*	*	*	*
244	*	*	*	*	*
245	*	*	*	*	*
246	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: February 10, 1986 (Page 2)

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
247	*	*	*	*	*
248	*	*	*	*	*
249	*	*	*	*	*
250	*	*	*	*	*
251	*	*	*	*	*
252	*	*	*	*	*
253	*	*	*	*	*
254	*	*	*	*	*
255	*	*	*	*	*
256	*	*	*	*	*
257	*	*	*	*	*
258	*	*	*	*	*
259	*	*	*	*	*
260	*	*	*	*	*
261	*	*	*	*	*
262	*	*	*	*	*
263	*	*	*	*	*
264	*	*	*	*	*
265	*	*	*	*	*
266	*	*	*	*	*
267	*	*	*	*	*
268	*	*	*	*	*
269	*	*	*	*	*
270	*	*	*	*	*
271	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: February 10, 1986 (Page 3)

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
272	*	*	*	*	*
273	*	*	*	*	*
274	*	*	*	*	*
275	*	*	*	*	*
276	*	*	*	*	*
277	*	*	*	*	*
278	*	*	*	*	*
279	*	*	*	*	*
280	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: February 18, 1986

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
281	*	*	*	*	*
282	*	*	*	*	*
283	*	*	*	*	*
284	*	*	*	*	*
285	*	*	*	*	0.04
286	*	*	*	*	*
287	*	*	*	*	*
288	*	*	*	*	*
289	*	*	*	*	*
290	*	*	*	*	*
291	*	*	*	*	*
292	*	*	*	*	*
293	*	*	*	*	*
294	*	*	*	*	*
295	*	*	*	*	0.06
296	*	*	*	*	*
297	*	*	*	*	0.07
298	*	*	*	*	*
299	*	*	*	*	0.04
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

Results of Stationary Source Pesticide Monitoring, 1986

Date Received at Laboratory: February 18, 1986 (Page 2)

SSD Sample No.	Analysis, Micrograms				
	Diazinon	Meth. Parathion	Paraoxon	Malathion	Parathion
300	*	*	*	*	*
301	*	*	*	*	*
302	*	*	*	*	*
303	*	*	*	*	*
304	*	*	*	*	*
305	*	*	*	*	*
306	*	*	*	*	*
307	*	*	*	*	0.04
308	*	*	*	*	*
309	*	*	*	*	*
310	*	*	*	*	*
Detection Limits	0.04	0.02	0.04	0.04	0.02

* - Not detected.

ATTACHMENT VI

Fog Study

Memorandum

To : Ralph Propper
Stationary Source Division

Thru: Bob Kuhlman, Manager
Lab Services Section
Aerometric Data Division

From : Air Resources Board
Michael Poore, Spectroscopist
Lab Services Section
Aerometric Data Division

Date : December 27, 1985

Subject : Organo-Phosphate Pesticide Sampling During Periods of Heavy Fog

RECEIVED
DEC 30 1985
Stationary Source Division
Air Resources Board

As requested, the ADD laboratory has conducted a study to determine the effectiveness of XAD-2 resins in sampling the ambient atmosphere for organo-phosphate pesticides during periods of heavy fog.

Two sampling systems identical with those to be used in field studies were placed at the ADD laboratory parking area at 1309 T Street during a period of heavy fog. A XAD-2 sampling tube (SKC, Inc #226-30-06) was spiked with 1.0 micrograms each of diazinon, malathion, methyl parathion, parathion, and paraoxon. A second tube was spiked with 0.06 micrograms of parathion and paraoxon. The tubes were placed in the sampling systems and the atmosphere sampled for 24 hours (12/20/85, 0845 to 12/21/85, 0900; total time: 1455 minutes) at a rate of 3.0 liters per minute (total volume: 4.4 m^3). The average Relative Humidity measured during the sampling period was 98% with 17 of the 24 hourly average readings at 100%. At the end of the sampling period, the exposed tubes were removed, taken to the laboratory, and stored under refrigeration.

On 12/23/85, each tube section (primary and secondary) was desorbed with solvent and analyzed separately to determine the recoveries of the spiked materials as well as the possibility of breakthrough. The results of those analyses are shown in Table I. As can be seen in Table I, there was no detectable breakthrough into the secondary section of the XAD-2 tubes and the recoveries of the spikes were within acceptable limits.

The conclusion of this study is that there is no indication that the presence of fog significantly affects the collection efficiency of the XAD-2 resin for the five organo-phosphate pesticides studied.

Attachment IV

Background Information Regarding Quality Assurance

Quality Assurance Plan for Pesticide Monitoring

Prepared by the

Air Resources Board

Toxic Pollutants Branch
Stationary Source Division

and

Quality Assurance Section
Aerometric Data Division

Updated as of October, 1983

1) Introduction

At the request of the Dept. of Food and Agriculture, the ARB will document the "level of airborne emissions" of specified pesticides. Short-term ambient monitoring will be conducted in the area and during the season of peak pesticide application. The purpose of this plan is to specify quality assurance procedures for field sampling and lab analysis.

2) Quality Assurance Policy Statement

Pesticide air sampling will be conducted by staff of either the U C Davis Environmental Toxicology Department or the Engineering Evaluation Branch of SSD, in cooperation with the Toxic Pollutants Branch. Samples will be analyzed by either the UCD group or by the Laboratory Services Section of ADD. Sampling will be conducted following the ambient monitoring guidelines of 40 CFR 58 for siting, calibration, field and lab precision and accuracy, and data validation. The Quality Assurance Section of ADD will review all quality assurance and quality control procedures.

3) QA Objectives for Measurement Data

The following QA objectives should be followed throughout all monitoring:

a) Sampling precision will be calculated from at least two samplers collocated at a site of expected maximum concentrations. The samplers should be located between 2 and 4 meters apart. Collocated samples will be collected at least once per week. One sampler will be designated as the primary sampler and others will be designated as duplicate or duplicates #1 & 2 with triplicate sampling.

b) Sampling accuracy will be determined by checking the sampler flow against a referenced flow meter. Analytical accuracy will be determined by analyzing blank lab samples as well as field and lab samples spiked with referenced standards.

c) Completeness of data will be calculated by subtracting the number of invalidated samples from the total number of samples and be reported as a percentage of valid data.

d) Siting criteria outlined in 40 CFR 58 Appendix E will be followed. Site description forms will be completed for each site. The monitoring objective for primary sites is to measure population exposure near the perimeter of towns, in the area of the town where high concentrations are expected, based on prevailing winds and proximity to applications. Background sites should be sited away from any applications. The probe siting criteria which apply to pesticide monitoring are listed in Table 1.

Table I. Pesticide Monitor Siting Criteria

The following probe siting criteria apply to pesticide monitoring and are summarized from the EPA ambient monitoring criteria (40 CFR 58 Appendix E) which are used by the ARB.

Height above ground, meters	Distance from supporting structure, m		Other spacing criteria
	Vert.	Horiz.	
2-15	>1	>1	1. Should be >20 m from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. No furnace or incineration flues should be within 10 m.

4) Sampling and Analysis Methods

The sampling and analysis methods will differ for many of the pesticides. Analytical recoveries will vary from pesticide to pesticide and may influence uniform analytical precision and accuracy. Prior to monitoring, specific sampling methods will be prepared in a separate monitoring plan for each pesticide. The methods will include equipment specifications, acceptance testing, field spiking procedures, conversion studies and analysis of breakdown products, sample handling and chain of custody procedures such as length of time before analysis, temperature control on samples, and shipping procedures to prevent sample loss. The monitoring plan will outline measures to protect the sampling apparatus and media from interference or damage due to rain. Use of chain of custody forms is recommended. An ARB chain of custody record is attached as an example. Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, analysis and data reduction, sample number, initial and final time and flow, malfunctions, leak checks, and weather conditions (e.g., rain) which could influence sample results. The initial and final flow will be averaged for the 24-hour sampling period.

5) Calibration Procedures

The monitoring plan will specify calibration procedures including calibration intervals for recalibration, calibration standards, environmental conditions for calibrations, and a calibration record keeping system.

If elapsed-time meters are used, rather than noting beginning and ending times, the meters must be checked and calibrated to within ±5 minutes for a 24-hour period. Samplers operated with an automatic on-off timer should be calibrated so that the sampling period is 24 hours ±15 minutes.

Flow meters or flow controllers with critical orifices should be calibrated against a referenced flow meter at the initiation of a monitoring period.

Indicated flows should be checked in the field and noted at least once per week. Before flows are checked, the sampling system should be leak checked. The initial flow should be within ±10% if a calibrated pressure transducer is used to check flows or within ±15% if a calibrated rotameter is used. Flow meters should be recalibrated if flows are found to be outside of these control limits.

6) Data Validation, Reduction, and Reporting

Data will be invalidated if the power is out at a site and the length of a sample cannot be verified, or if the sampling medium breaks during sampling or shipment for analysis. Data will be corrected to reflect verified discrepancies in the sampling flow.

Data reduction will be done by determining the mass of pesticide (ug) found in each sampling medium and then using the field data sheet information to calculate the mass/volume for each sample. For each sampling date and site, concentrations will be reported in ug/m^3 as well as ppm and/or ppt, along with the atmospheric pressure and temperature at the time of sampling.

7) Internal Quality Control Checks

The monitoring plan will specify the frequency for control sample analyses. Analysis of control samples is recommended before each day of lab analysis, after every tenth sample, and as the last analysis of the day. Control samples should be analyzed to be within previously established control limits of ±3 standard deviations. If results are outside control limits, the method should be reviewed, recalibrated, and the control standard reanalyzed. Blank sampling media will be included with each week's batch of samples. Only the field operator will know the sample number of these blank tubes.

8) Performance Audits

A referenced flow measuring device with a standard limiting orifice will be used to verify the indicated flows on the samplers. Flow audits will be conducted with a frequency of between once per month and once every three months, depending on the length of a particular pesticide monitoring period. Analytical audits will be conducted by spiking field and lab samples with referenced standards or by having another lab analyze split samples for comparison of results. Siting of each sampler will also be verified against the siting criteria.

9) Preventative Maintenance

To prevent loss of data, spare pumps and sampling materials will be kept available in the field by the operator. A schedule should be prepared for regularly checking sampling pumps, meteorological instruments, extension cords, crimps in sampling tubing, and leaks.

10) Calculation of Precision, Accuracy, and Completeness

Procedures outlined in 40 CFR 58 will be followed to calculate data precision from the collocated sites. Accuracy will be calculated from the flow verification and from the results of the spiked samples. Data completeness will be calculated as a percentage of valid data compared to the total possible amount of data if no invalidations had occurred.

11) Quality Assurance Reports

Quality assurance activities and data will be summarized by the staff conducting the sampling and included as an attachment to the final ambient data summary.

CALIFORNIA AIR RESOURCES BOARD

CHAIN OF CUSTODY RECORD

REPORTING AGENCY: _____

STATION ADDRESS: _____

STATION NAME: _____

STATION OPERATOR:*

Relinquished By:*	Received By:*	Date/Time
Relinquished By:*	Received By:*	Date/Time
Received for Laboratory By:*		Date/Time

Method of Shipment:

TO BE COMPLETED BY LABORATORY

SAMPLE NO.	LABORATORY NO.

DISPOSITION:

IMMEDIATE ANALYSIS [ ] STORAGE [ ] REFRIGERATOR [ ] ID_____ FREEZER [ ] ID_____

SECURED YES [ ] NO [ ]

* Print name after signature.

Air Resources Board
Laboratory Services Section
1309 T Street
Sacramento, CA 95814

State of California

Memorandum

To : Lynn Baker
Associate Air Pollution Specialist
Stationary Source Division

Date : April 9, 1986

Subject : Pesticide Monitoring Site & Sampler Evaluation

RECEIVED

APR 10 1986

Stationary Source Division Air Resources Board

Dick Lindquist
Associate Air Pollution Specialist
Aerometric Data Division

From : Air Resources Board

On August 26, 1985 the Stationary Source Division (SSD) requested assistance from Aerometric Data Division (ADD) in the analysis and collection of samples for parathion. A copy of the memorandum in which the request was made is attached. The sampling program described in the memorandum can be summarized as follows:

Phase One - Early short term monitoring in Imperial County for purposes of evaluating the more extensive San Joaquin Valley plan;

Phase Two - Extensive monitoring in and around small towns near Fresno and Bakersfield; and

Phase Three - Monitoring at existing urban ARB sites in Sacramento, Fresno and Bakersfield to provide background data.

In December 1985, after Phase One had been completed, you requested that ADD's Quality Assurance Section (QA) evaluate the pesticide monitoring sites operated by SSD's Testing Section and ADD's Air Monitoring Sections. The following is a summary of our findings including a brief statement on the sites and a general discussion on the sampling apparatus. As a part of the evaluation QA staff measured true flow through the tube(s) with a standard limiting orifice. Results are shown in the attached table. Flow measurements could not be conducted at three of the ten sites. The samplers at Dinuba, Wasco, and Earlimart were inaccessible or not operating at the time of our visit.

Sites

In general, the sites were properly sited in accordance with EPA guidelines summarized in "Network Design and Site Exposure Criteria for Selected Non-criteria Air Pollutants," EPA-450/4-84-022, pp. 38, 41 (attached) and in the manual sampling method requirements found in Title 40 of the Code of Federal Regulations, Part 58, Appendix E. Exceptions were:

1. The sample intake probe did not extend the required one meter minimum from a supporting structure at any of the sites.

   Note 1: The supporting structure as assembled was not likely to interfere with air flow. Any future design of the sampling system, however, should maximize the distance between support and probe.

2. The Sacramento Phase Three sampler was initially operated in the parking lot east of ARB's 13th and T Streets facility in conflict with EPA and ARB siting criteria. The unit was relocated to the roof of a trailer behind ARB's 12th and S Streets building.

   Note 2: The sampler was not operated in the parking lot while collecting samples for background assessment. The sampler was there to provide samples for quality control spikes and analytical method development.

Sampling Apparatus

Phases One and Two were conducted by SSD's Testing Section using a prototype sampling apparatus with pump, flow meter and tube holder, whereas the Phase Three operation conducted by ADD staff utilized a modified dichotomous sampler. Both samplers used four inch glass tubes packed with XAD-2 resin adsorbent.

In SSD's prototype sampling system, two XAD-2 tubes were connected in series and oriented in a downward position. The tubes were connected to the flow-meter and pump with a combination of Teflon and surgical tubing. The modified dichotomous sampler used one XAD-2 tube oriented in the upward position and held in place by 5/16" Jayco plastic fittings. Photographs of each type are on file in the QA office.

The flow rate of the sampler at the Sacramento site was low. The connecting air lines downstream from the tube appeared wet from air condensate. The sampler was returned to ADD's Support Section for maintenance and repair and shortly thereafter reinstalled. A second flow measurement was made with satisfactory results.

Note 3: There was no way to determine if downstream moisture affects the analytical results. To minimize a potential problem the outlet lines should be elevated in as much as possible to prevent the pooling of water.

During our evaluation we discovered a few possible problems:

1. The XAD-2 tubes at Sacramento and Fresno background sites were not protected from sunlight which is known to cause parathion degradation;

2. The control module at the Bakersfield site was installed so low that adjustments were difficult and could cause improper settings, although none were observed. Additionally, the operator at the Bakersfield site noted that the control module sampling pump assembly caused vibrations that had infrequently dislodged the XAD-2 tube. These conditions will be corrected before the upcoming Fall phase of the monitoring project by elevating and stabilizing the control module.

Recommendations

1. Future sampling should be conducted using established procedures and if at all possible identical sampling equipment.

2. Standardize XAD-2 tube openings, although this is less important if constant flow can be achieved with mass flow controllers.

3. Improve the sampling system with a critical orifice and rotameter which will ensure that the flow is consistent and operate within the range of the particular sampling media.

4. Perform daily flow checks with a Vol-o-Flo or similar device to assure the system is operating properly.

If you have any questions concerning the pesticide monitoring evaluation, please call me at 2-6049.

Attachments

Flow Data Summary

San Joaquin Valley Pesticide Monitoring Project

	Indicated Flow Meter, l/m	As Found True Flow, l/m
Background Sites, ADD		
Sacramento*	6.7, 6.9	5.5, 6.0
Fresno	6.0	5.8
Bakersfield**	8.4	10.2
Monitoring Sites, SSD		
Sanger	3.0	1.6
Parlier	3.2	1.6
Reedley	4.0	2.3
Selma	3.4	1.6
Delano	3.0	1.3
McFarland	3.0	2.1
Shafter	3.0	1.0

* Modified dichot returned to shop for calibration and repair; flow re-measured.

** Unit vibrates excessively causing tube to dislodge from holder.

State of California

Memorandum

: Spencer Duckworth, Chief
Aerometric Data Division

Date : August 26, 1985

Subject: Parathion Analysis Requirements

Peter D. Venturini, Chief
Stationary Source Division

From : Air Resources Board

As a result of the request of the Department of Food and Agriculture to monitor parathion, the ARB will conduct field sampling this winter at six locations in the region of Fresno eastward, and at six locations in the region of Bakersfield northward. This memo is to formally request your division's assistance in the analysis and collection of samples for parathion. I understand our respective staffs have discussed this.

Engineering Evaluation Branch (SSD) will collect 24-hour samples using XAD resin for adsorbent. Samples will be taken five days per week for a period not to exceed three months, and will be brought to your lab for elution and analysis. Sampling will commence shortly after January 1, 1986. In addition, three-hour samples will be taken at one site per region for one week (ten days total) at a time of high use, with two samples taken per day. We expect this sampling will take place in January, 1986. ADD will conduct monitoring at Sacramento, Bakersfield, and Fresno, from September 3, 1985 to March 28, 1986. The 24-hour samples will be taken at ADD's permanent monitoring stations in these cities, with the use of autotimers. The 1985 monitoring will serve to provide background data during periods of low usage, and the 1986 data will be used to determine urban exposure levels.

We also plan to conduct monitoring during a period from mid-September to mid-October in Imperial County in order to identify any possible problems with the monitoring plan. These samples will be collected by Engineering Evaluation Branch and analyzed by ADD. A summary and schedule of this monitoring effort is presented in Attachment I.

A final report, documenting levels of airborne emissions of parathion, must be transmitted to the Department of Food and Agriculture in early May 1986. Therefore, we will need the results of this monitoring no later than April 15, 1986.

ATTACHMENT I

Schedule and Summary of Parathion Monitoring

1. ADD sampling and analysis at Sacramento, Bakersfield, and Fresno, September 3, 1985 to March 28, 1986; 15 samples/week.

2. SSD sampling at monitoring sites in Fresno and Bakersfield regions, with ADD analyses, January 2 - March 28, 1986 (non-peak); 6 samples/day, 5 days/week; or 30 samples/week. In addition, for one month of this period (peak), 30 samples/week additional may be sampled by SSD and analyzed by ADD.

3. SSD sampling at monitoring sites in Fresno and Bakersfield regions, with ADD analyses; two 3-hour samples per day, for one week per region during winter; 10 days, or 20 samples total.

4. SSD sampling and ADD analyses, one week during September 23 - October 11*, Imperial County - three sites; 3 samples/day, or 15 samples total.

* These dates to be confirmed.

EPA-450/4-84-022
September 1984

Network Design and Site Exposure Criteria For Selected Noncriteria Air Pollutants

by

R. C. Koch, M. B. Charlton,
D. J. Pelton, and H. R. Stern
GEOMET Technologies, Inc.
1801 Research Boulevard
Rockville, Maryland 20850

Contract Number 68-02-3584
Assignment No. 4

Project Officer

David Lutz
U.S. Environmental Protection Agency
Research Triangle Park
North Carolina 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

etc. The objectives of the sampling activity must be clearly stated so the sampling strategy and locations can be selected to collect the most relevant information.

The first step in the site selection procedure is to determine source. The logic that this step requires is depicted in Figure 2. The type of sources that will be encountered and their locations are combined with meteorological information in the next step of the procedure. A representative climatological wind summary is needed. A wind rose (see Figure 3) readily shows the prevalent wind directions and most frequent wind speed. From the wind data, the logical sectors for downwind (impact) or upwind (background) sites can be determined.

Dispersion modeling is a good way to analyze the available source and meteorological data in an objective manner to identify areas of relatively good and poor air quality. Model results may be used to define distances from sources to find maximum concentrations or the most frequently impacted areas, which is the next step in the procedure. Site selection can be narrowed down to zones within the sectors favored by wind direction and to zones within those sectors that will be impacted by emissions as indicated by modeling. A preliminary prioritization of candidate sites can be made based on the modeling information. However, the candidate areas should be viewed before final evaluation. A semifinal ranking of all locations can be finalized after preliminary or screening sampling has been performed.

The site selection procedure described above is appropriate to all sources in a general way but is most appropriate to sources that may be defined as point sources or small area sources. Depending on the spatial scale of the monitoring problem, an area source can be considered as a point source if the monitoring location is far enough downwind (e.g., on the order of 5 to 10 times the diameter of the area source). Monitoring area source may require sampling sites along the perimeter of a well-defined small area source or sampling within the perimeter of a large area source.

The following criteria are recommended guidelines in the final site selection step.

- Locate the sampler in an area that has unobstructed air flow, especially in the direction of any recognized sources of the materials being sampled. Turbulence and eddys from obstructions will cause nonrepresentative results. The distance between the obstruction and the sampler should not be closer than two times the height of the obstruction.

- Avoid locations that will be unduly influenced by nearby sources or activities.

- Avoid locations where reactive surfaces may cause chemical changes in the air sampled.

- Be aware of micrometeorological influences due to nearby hills, bodies of water, valley drainage flow patterns, etc.

- Place the intake probe at a representative height. The guidance given for criteria pollutants is for probe height to be 3 to 15 m above ground level, as near to building height as possible but not where a building is an obstruction or the equipment is easily vandalized.

- The probe should extend at least 2 m from a supporting structure; if located on a building, it must be mounted on the windward side.

Monitoring site selection criteria should be the same in most regards whether the site will be used for a fixed station or for the nonfixed (mobile) site. Uniformity among the sites should be achieved to the greatest degree possible. Descriptions should be prepared for all sampling sites. The description, at a minimum, should include the type of ground surface; the direction, distance, and approximate height to any obstruction to airflow; and the direction and distance to any local pollutant sources (actual or potential). Photographs of the site are valuable for analysts who will not have firsthand knowledge of the site.

Monitoring Point and Isolated Area Sources

Once an isolated source of interest is identified, the preferred sampling locations are selected based on climatological data and perhaps dispersion modeling information. Representative wind data for an isolated area is especially important for plants that are built in a coastal area. Many of the chemical plants that are of concern for noncriteria air pollutants are built along the Gulf Coast where sea-breeze effects will be an important factor in sample site selection. An experienced meteorologist's advice will be necessary to interpret available data and to select the most suitable locations for downwind sampling. Accessibility to the desired locations may be a determining factor for final site selection; therefore, site visits will be necessary in order to ensure that monitoring is practical in the selected area.

Memorandum

To : Ralph Propper
Stationary Source Division

Thru: Bob Kuhlman, Manager
Lab Services Section
Aerometric Data Division

From : Air Resources Board
Michael Poore, Spectroscopist
Lab Services Section
Aerometric Data Division

Date : December 27, 1985

Subject : Organo-Phosphate Pesticide Sampling During Periods of Heavy Fog

RECEIVED
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As requested, the ADD laboratory has conducted a study to determine the effectiveness of XAD-2 resins in sampling the ambient atmosphere for organo-phosphate pesticides during periods of heavy fog.

Two sampling systems identical with those to be used in field studies were placed at the ADD laboratory parking area at 1309 T Street during a period of heavy fog. A XAD-2 sampling tube (SKC, Inc #226-30-06) was spiked with 1.0 micrograms each of diazinon, malathion, methyl parathion, parathion, and paraoxon. A second tube was spiked with 0.06 micrograms of parathion and paraoxon. The tubes were placed in the sampling systems and the atmosphere sampled for 24 hours (12/20/85, 0845 to 12/21/85, 0900; total time: 1455 minutes) at a rate of 3.0 liters per minute (total volume: 4.4 m^3). The average Relative Humidity measured during the sampling period was 98% with 17 of the 24 hourly average readings at 100%. At the end of the sampling period, the exposed tubes were removed, taken to the laboratory, and stored under refrigeration.

On 12/23/85, each tube section (primary and secondary) was desorbed with solvent and analyzed separately to determine the recoveries of the spiked materials as well as the possibility of breakthrough. The results of those analyses are shown in Table I. As can be seen in Table I, there was no detectable breakthrough into the secondary section of the XAD-2 tubes and the recoveries of the spikes were within acceptable limits.

The conclusion of this study is that there is no indication that the presence of fog significantly affects the collection efficiency of the XAD-2 resin for the five organo-phosphate pesticides studied.

TABLE I

PESTICIDE SAMPLING DURING PERIOD OF
HIGH RELATIVE HUMIDITY

DATE SAMPLED: 12/20/85 08:45 - 12/21/85 09:00

VOLUME SAMPLED: 4.4 m^3

Compound	1.0 Microgram Spike Amount Recovered, ug		0.06 Microgram Spike Amount Recovered, ug	
	Primary	Secondary	Primary	Secondary
Diazinon	1.0	< 0.04	-	-
Methyl Parathion	1.0	< 0.02	-	-
Paraoxon	0.8	< 0.04	0.06	< 0.04
Malathion	0.8	< 0.04	-	-
Parathion	0.8	< 0.02	0.06	< 0.02

Memorandum

To : Spencer Duckworth, Chief
Aerometric Data Division

Thru: Bob Effa, Manager
Quality Assurance Section

From : Peggy Vanicek
Associate Air Pollution Specialist
Air Resources Board

Date : October 16, 1986

Subject: Imperial County
Parathion Study
Field Audit Results

Attached for your information is a report summarizing the results of the Quality Assurance Section's October 1 field audit of the parathion study being conducted in Imperial County by ARB-SSD.

In addition to the field audit we will be conducting a performance audit of the ADD laboratory. The ADD laboratory is responsible for the parathion analysis for this study. We have arranged with Bob Kuhlman to conduct the performance audit at their convenience after they have begun the analyses.

Attachment

cc: Kevin Kalthoff

Field Audit Report of
Parathion Air Monitoring Project

Imperial County, California

Summary

On Wednesday, October 1, 1986 the Quality Assurance Section (QA) of the California Air Resources Board (ARB) performed a field audit of the parathion monitoring project being conducted in Imperial County by the ARB's Stationary Source Division (SSD). Performing the audit were Kevin Kalthoff and Peggy Vanicek. The ARB-SSD field representatives present were Bud Thoma and Dwight Warner.

Six sites were visited that had a total of seven samplers operating. Collocated samplers were operated at Calipateria. The field audit consisted of verifying conformance with siting criteria listed in the June 1986 SSD "Quality Assurance Plan for Pesticide Monitoring", an inspection of each site for overall maintenance, a review of site activity documentation, and the taking of site photographs. All the samplers were properly sited except for the sampler at Brawley School which did not meet the distance from supporting structure criteria (> 1 meter). Documentation of site activities, sampling conditions and chain of custody were current and adequate for the monitoring study.

Included in the site audit was a flow audit of each sampling apparatus against a certified NBS traceable mass flowmeter. To insure a meaningful representation of actual field flows, the flow audits were conducted under actual field operating conditions with the sample tubes installed. The flow audit compared the sampling flows as measured by the field operator to true flows. The flow audit procedure used is attached (Attachment I). The flow audits demonstrated that all the sampling flows were within 4 percent of the true flows.

Following is a description of the audit activities along with copies of the field audit data sheets.

Field Operations

The six sampling sites visited were Brawley A (APCD), Calipatria Fire Station (collocated), Holtville School, Brawley School, Heber and El Centro. Each sampling site except for Brawley school met the siting criteria as outlined in SSD's "Quality Assurance Plan for Pesticide Monitoring". At Brawley School the sample tube inlet was located less than 1 meter vertically from the supporting structure. In addition, it was noted that the sampling tube at Holtville School was approximately 7 meters from the air conditioner/heat exchanger unit which may affect the sampling depending on wind conditions.

The documentation for the site activities was sufficient and current. Chain of custody forms were being maintained to record sample handling history.

Flow Audits

The sampling apparatus consisted of a Gast Model 211 vacuum pump housed in an enclosed box to prevent water damage. A 0-5 liter Dwyer rotameter with valve was in line to provide flow measurement and control. Each rotameter was calibrated by ARB-QA in conjunction with SSD-shop on September 16, 1986. The calibration data was not available in the field, but is recorded at the SSD-shop. The sample tubes were mounted as close to vertical as possible with a black rubber tube to protect the XAD-2 resin from light.

The flow accuracy audits were conducted with a Matheson Mass Flowmeter Model 8143 according to the procedures described in Attachment I. The mass flowmeter is certified against ARB's primary standard Brooks flow calibrator. The results of the flow audit are summarized in Table I.

Table I

Flow Accuracy Audit Results
Parathion Air Monitoring Study

Site	Measured Flow, L/min	True Flow, L/min	Percent Difference*
Brawley A	3.0	3.05	-1.6
Calipatria Fire Station, 3N	3.0	2.94	+2.0
Calipatria Fire Station, 8S	3.0	2.96	+1.4
Holtville School	3.0	2.92	+2.7
Brawley School	3.0	3.01	-0.3
Heber	3.0	2.90	+3.4
El Centro	3.0	2.96	+1.4

* Percent Difference = $\frac{\text{Measured Flow - True Flow}}{\text{True Flow}} \times 100$

Flow Audit Procedure for Pesticide Samplers

Introduction: The pesticide sampler is audited using a Matheson Mass Flow Meter, Model 8143, that is standardized against a NBS traceable Brooks flow calibrator corrected to 25°C and 760 mm Hg.

The mass flow meter (MFM) is placed in series with the sample probe and the flows checked while the sampler is operating at the normal sampling flow rate. The standard (true) flow rates are obtained from the calibrative curve of the MFM and the indicated flow rates are applied to the sampler's calibration curbe to determine the reported flow rates which are then compared to true flow rates.

Equipment: The basic equipment required for the pesticide sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. Matheson Mass Flow Meter, Model 8143, Transfer Standard with a 10 SLPM transducer.

2. Tygon tubing, 1/8" and 1/4" I.D., for connections to sampler.

3. Teflon tubing, 1/4" I.D.

4. Stainless steel Swaglok fittings, cleaned with methanol and heated overnight at 100°C.

5. Plastic caps to cover flow meter ports.

6. Audit log book and data sheets.

Audit Procedures:

1. Plug the Matheson MFM into a 110 VAC outlet. Allow 10 minutes for the MFM to warm up.

2. Connect the MFM to the sample tube using the 1/4" teflon tubing and tygon tubing. If it is desired not to use the sample tube a dummy tube may be used in its place.

3. Allow the flow to stabilize for 1-2 minutes and record the indicated flows on the data sheet.

4. Apply the indicated flows to the calibration curve of the Matheson MFM standard to obtain the true flow and record in the blanks provided on the field data sheet. Obtain the sampler measured flow from the field operator. Calculate the difference between the true flow and measured flow and report as percent difference on the field data sheet.

Audit Checksheet - Pesticides

Site Name: Heber

Audit Date: October 1, 1986

Site Number:

Field Representative: Bud Thoma & Dwight Warner

Auditor(s): Kalthoff- Vanicek

Field Operations Supervisor: Al Jenkins

Targeted Pesticide(s): Parathion

Site Inspection

Does the siting meet the criteria listed below and outlined in the "Quality Assurance Plan for Pesticide Monitoring?"

	Yes	No
Height above ground, 2-15 meters:	X	
Distance from supporting structure: Vertical > 1 meter	X	
Horizontal > 1 meter	X	
Spacing from trees > 20 meters:	X	
Distance from obstacles at least two times the height the obstacle* protrubes above the sampler:	X	
Unrestricted air flow 270° around the sampler:	X	
No furnace or incineration flues within 10 meters:	X	

Type of sampler used: Gast vacuum pump w/D

Date last calibrated: Sept. 16, 1986

By Whom? ARB-QA

Is the calibration data available for review? No - available at SSD shop

Sampling Media: XAD-2

Is the sampling media protected from sunlight if necessary?	black tube	X	
If a sorbant tube, is it vertically mounted?		X	
Is the sampler operative?-		X	

If no, state reason:

) all applicable tubing and wiring free of cracks, cramps or breaks? X

* 6M from airconditioner heat exchanger (air going both in & out) (to the Southwest)

	Yes	No
Is the site clean and well maintained?	X	
Are field measurements recorded in a log book or on data forms?	X	
Are they up-to-date?	X	
Operator's initials? Not in log sheets-are on chain of custody & on sample tube		
Initial and Final Flows?	X	
Are records maintained regarding maintenance, site visits, problems, etc.	X	
Are the inlet and outlet ports of the sampler capped when not in use?	NA	

Field Audit

Mass Flow Meter ARB # 6853

Date Last Certified: 10-2-86

Certification Equation: Std Airflow = 0.10120 (Display) -0.01

Sampler ID # _____ Collocated ( )

Audit int	Mass Flowmeter Flow, L/min Run 1	2	3	Indicated Flow Run 1	2	3	Measured Flow	True Flow	Percent Difference
/	28.8			3.5			3.0	2.90	+3.4%

Sampler ID # _____ Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run 1	2	3	Indicated Flow Run 1	2	3	Measured Flow	True Flow	Percent Difference
-									

Comments Barometric Pressure & Weather #12-18 1st Roll Film

conditions recorded on chain of custody form.

.te Name El Centro

Audit Date October 1, 1986

ite Number

Field Representative Bud Thoma & Dwight Warner

d. r(s) Kalthoff & Vanicek

Field Operations Supervisor Al Jenkins

argeted Pesticide(s) Parathion

ite Inspection

oes the siting meet the criteria listed below and outlined in the Quality Assurance Plan for Pesticide Monitoring?*

	Yes	No
Height above ground, 2-15 meters:	X	
Distance from supporting structure: Vertical > 1 meter	X	
Horizontal > 1 meter	X	
Spacing from trees > 20 meters:	X	
Distance from obstacles at least two times the height the obstacle protrubes above the sampler: 4 ft. from high vol-level w/tube	X	
Unrestricted air flow 270° around the sampler:	X	
No furnace or incineration flues within 10 meters:	X	

Type of sampler used: Gast vacuum pump Rot #1

Date last calibrated: Sept. 16, 1986

By Whom? ARB-QA

Is the calibration data available for review? available at SSD laboratory

Sampling Media XAD-2

Is the sampling media protected from sunlight if necessary?	X	
If a sorbant tube, is it vertically mounted?	X	
Is the sampler operative?-	X	

If no, state reason:

Are all applicable tubing and wiring free of cracks, cramps or breaks?	X	

	Yes	No
Is the site clean and well maintained?	X	
Are field measurements recorded in a log book or on data forms?	X	
Are they up-to-date?	X	
Operator's initials?	X	
Initial and Final Flows?	X	
Are records maintained regarding maintenance, site visits, problems, etc.	X	
Are the inlet and outlet ports of the sampler capped when not in use?	N/A	

Field Audit

Mass Flow Meter ARB # 6853

Date Last Certified: 10-2-86

Certification Equation: Std. Airflow = 0.10120 (Display) - 0.01

Sampler ID # Rotameter # 1 Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run			Indicated Flow Run			Measured Flow	True Flow	Percent Difference
	1	2	3	1	2	3			
1	29.3			3.5			3.0	2.96	+1.4%

Sampler ID # _____ Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run			Indicated Flow Run			Measured Flow	True Flow	Percent Difference
	1	2	3	1	2	3			

Comments _____

Site Name Calipatria Firestation Audit Date 10-1-86

Site Number Colocated Samplers Field Representative Bud Thoma & Dwight Warner

Auditor(s) Kalthoff & Vanicek Field Operations Supervisor Al Jenkins

Targeted Pesticide(s) Parathion

Site Inspection

Does the siting meet the criteria listed below and outlined in the "Quality Assurance Plan for Pesticide Monitoring?"

	Yes	No
Height above ground, 2-15 meters:	X X	
Distance from supporting structure: Vertical > 1 meter	X X	
Horizontal > 1 meter	X X	
Spacing from trees > 20 meters:	X X	
Distance from obstacles at least two times the height the obstacle protrubes above the sampler:	X X	
Unrestricted air flow 270° around the sampler:	X X	
No furnace or incineration flues within 10 meters:	X X	

Type of sampler used: Gast Vacuum pump w/0-5L rotameter in line

Date last calibrated: Sept. 16, 1986

By Whom? ARB - QA

Is the calibration data available for review? No, available at SSD lab

Sampling Media XAD - 2

Is the sampling media protected from sunlight if necessary?	X X	
If a sorbant tube, is it vertically mounted?	X X	
Is the sampler operative?-	X X	

If no, state reason: _____

Are all applicable tubing and wiring free of cracks, cramps or breaks?	X X	

Pictures take N-W-S-E

	Yes	No
Is the site clean and well maintained?	X	
Are field measurements recorded in a log book or on data forms?	X	
Are they up-to-date?	X	
Operator's initials?	X	
Initial and Final Flows?	X	
Are records maintained regarding maintenance, site visits, problems, etc.	X	
Are the inlet and outlet ports of the sampler capped when not in use?	N/A	

Field Audit

Mass Flow Meter ARB # 6853

Date Last Certified: 10-2-86

Certification Equation: Std. Airflow = 0.10120 Display - 0.01

Sampler ID # Rotameter #3 Collocated ( ) #3 North

Audit Point	Mass Flowmeter Flow, L/min Run 1	2	3	Indicated Flow Run 1	2	3	Measured Flow	True Flow	Percent Difference
1	29.2			3.5			3.0	2.94	+2.0%

Sampler ID # Rotameter #8 Collocated (X) #8 South

Audit Point	Mass Flowmeter Flow, L/min Run 1	2	3	Indicated Flow Run 1	2	3	Measured Flow	True Flow	Percent Difference
1	29.4			3.5			3.0	2.96	+1.4

Comments

Audit Checklist - Pesticides

te Name Brawley A (APCD) Audit Date 10-1-86

.te Number Field Representative Bud Thoma & Dwight Warner

ıditor(s) Kalthoff & Vanicek Field Operations Supervisor Al Jenkins

ırgeted Pesticide(s) Parathion

ite Inspection

oes the siting meet the criteria listed below and outlined in the Quality Assurance Plan for Pesticide Monitoring?*

	Yes	No
Height above ground, 2-15 meters:	X	
Distance from supporting structure: *. Vertical > 1 meter	X	
Horizontal > 1 meter	X	
Spacing from trees > 20 meters:	X	
Distance from obstacles at least two times the height the obstacle protrubes above the sampler:	X	
Unrestricted air flow 270° around the sampler:	X	
o furnace or incineration flues within 10 meters:	X	

Type of sampler used: Gast Vacuum Pump with 0-5 L rotameter in line - Rot #6

Date last calibrated: Sept. 16, 1986

By Whom? ARB-QA

Is the calibration data available for review? No, available at SSD lab

Sampling Media XAD - 2

Is the sampling media protected from sunlight if necessary?	X	
If a sorbant tube, is it vertically mounted?	X	
Is the sampler operative?-	X	

If no, state reason:

Are all applicable tubing and wiring free of cracks, cramps or breaks?	X	

* High Vol- located 4-5' away - not operating (equal height w/tube)

Pictures taken S-EW-N (road to the West) golf course to the North

	Yes	No
Is the site clean and well maintained?	X	
Are field measurements recorded in a log book or on data forms?	X	
Are they up-to-date?	X	
Operator's initials?	X	
Initial and Final Flows?	X	
Are records maintained regarding maintenance, site visits, problems, etc.	X	
Are the inlet and outlet ports of the sampler capped when not in use?	N/A	

Field Audit

Mass Flow Meter ARB # 6853 (10L Transducer)

Date Last Certified: 10-2-86

Certification Equation: Std. Airflow = 0.10120 (Display) -0.01

Sampler ID # Rotameter #6 Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run			Indicated Flow Run			Measured Flow	True Flow	Percent Difference
	1	2	3	1	2	3			
1	30.2			3.5			3.0	3.05	-1.5%

Sampler ID # _____ Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run			Indicated Flow Run			Measured Flow	True Flow	Percent Difference
	1	2	3	1	2	3			

Comments _____

Site Name Brawley School Audit Date 10-1-86

Site Number _____ Field Representative Bud Thoma & Dwight Warner

Auditor(s): Kalthoff & Vanicek Field Operations Supervisor Al Jenkins

Targeted Pesticide(s) Parathion

Site Inspection

Does the siting meet the criteria listed below and outlined in the "Quality Assurance Plan for Pesticide Monitoring?"

	Yes	No
Height above ground, 2-15 meters:	X	
Distance from supporting structure: Vertical > 1 meter *		X
Horizontal > 1 meter	X	
Spacing from trees > 20 meters:	X	
Distance from obstacles at least two times the height the obstacle protrubes above the sampler: **	X	
Unrestricted air flow 270° around the sampler:	X	
No furnace or incineration flues within 10 meters: *	X	

Type of sampler used: Gast Vacuum Pump Model #211 w/0-5L Dyer # 7

Date last calibrated: Sept. 16, 1986

By Whom? ARB-QA

Is the calibration data available for review? No, available at SSD shop

Sampling Media XAD - 2

Is the sampling media protected from sunlight if necessary?	X	
If a sorbant tube, is it vertically mounted? ≈ 5-10° from vertical	X	
Is the sampler operative?	X	

If no, state reason: _____

Are all applicable tubing and wiring free of cracks, cramps or breaks?	X	

* Tube < 1 meter from vertical support.
** Heat pump exchange ≈7 feet.

	Yes	No
Is the site clean and well maintained?	X	
Are field measurements recorded in a log book or on data forms?	X	
Are they up-to-date?	X	
Operator's initials?	X	
Initial and Final Flows?	X	
Are records maintained regarding maintenance, site visits, problems, etc.	X	
Are the inlet and outlet ports of the sampler capped when not in use?	N/A	

Field Audit

Mass Flow Meter ARB # 6853

Date Last Certified: 10-2-86

Certification Equation: Std Airflow = 0.10120 (Display) -0.01

Sampler ID # Rotometer # Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run 1	2	3	Indicated Flow Run 1	2	3	Measured Flow	True Flow	Percent Difference
1	29.8			3.5			3.0	3.01	-0.3

Sampler ID # _____ Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run 1	2	3	Indicated Flow Run 1	2	3	Measured Flow	True Flow	Percent Difference

Comments _____

ite Name Holtville School Audit Date 10-1-86

ite Number _____ Field Representative Bud Thoma & Dwight Warner

udi.or(s) Kalthoff & Vanicek Field Operations Supervisor Al Jenkins

argeted Pesticide(s) Parathion

ite Inspection

oes the siting meet the criteria listed below and outlined in the Quality Assurance Plan for Pesticide Monitoring?*

	Yes	No
Height above ground, 2-15 meters:	X	
Distance from supporting structure: Vertical > 1 meter	X	
Horizontal > 1 meter	X	
Spacing from trees > 20 meters:	X	
Distance from obstacles at least two times the height the obstacle protrubes above the sampler:	X	
Unrestricted air flow 270° around the sampler:	X	
No furnace or incineration flues within 10 meters:	X	

Type of sampler used: Gast vacuum pump Model 0211 with 0-5L rotameter in line

Date last calibrated: Sept. 16, 1986

By Whom? ARB-QA

Is the calibration data available for review? No - available at SSD lab

Sampling Media XAD - 2

Is the sampling media protected from sunlight if necessary?	X	
If a sorbant tube, is it vertically mounted?	X	
Is the sampler operative?-	X	

If no, state reason: _____

Are all applicable tubing and wiring free of cracks, cramps or breaks?	X	

	Yes	No
Is the site clean and well maintained?	X	
Are field measurements recorded in a log book or on data forms?	X	
Are they up-to-date?	X	
Operator's initials?	X	
Initial and Final Flows?	X	
Are records maintained regarding maintenance, site visits, problems, etc.	X	
Are the inlet and outlet ports of the sampler capped when not in use?	N/A	

Field Audit

Mass Flow Meter ARB # 6853

Date Last Certified: 10-2-86

Certification Equation: Std. Airflow = 0.10120 (Display) - 0.01

Sampler ID # _____ Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run			Indicated Flow Run			Measured Flow	True Flow	Percent Difference
	1	2	3	1	2	3			
1	29.0			3.5			3.0	2.92	+2.7

Sampler ID # _____ Collocated ( )

Audit Point	Mass Flowmeter Flow, L/min Run			Indicated Flow Run			Measured Flow	True Flow	Percent Difference
	1	2	3	1	2	3			

Comments Pictures #18 - 24

State of California

Memorandum

To : Bob Barham, Manager
Source Evaluation Section
Stationary Source Division

Date : November 17, 1986

Subject : Imperial Valley Parathion Study - October 1986

Bob Kuhlman, Manager
Laboratory Services Section
Aerometric Data Division

From : Air Resources Board

RECEIVED
NOV 18 1986
Stationary Source Division
Air Resources Board

The analyses of Imperial Valley parathion samples submitted by Stationary Source Division staff during the month of October have been completed. The results are presented in two tables. Table I includes field samples into which parathion was initially spiked at nominal levels of 2.0 and 0.5 micrograms. The purpose was to determine the extent of breakdown of parathion during sampling. Table II includes the results of analyses on all other field samples submitted to the laboratory.

Note that while several incoming samples were received with identical sample codes, all samples were reidentified by the laboratory, as received, with a sequential Lab I.D. number.

All quality control procedures were in effect during the period of analysis. The analytical system was audited by the Quality Assurance Section and the results of that audit will be reported by them.

Attachments

bcc: Mike Poore
Tom Parker
Lynn Baker
Dave Hartmann

TABLE I

(Spiked Field Samples)

Sample Code	Lab I.D. No.	Parathion Spike Added µg	Parathion Measured µg	Paraoxon Measured µg
ELC-1S	6394	2.0	1.76	0.09
ELC-1AS	6395	0.5	0.45	< 0.08
ELC-1	6396	--	< 0.04	< 0.08
ELC-25	6397	2.0	1.88	0.10
ELC-2AS	6398	0.5	0.43	< 0.08
ELC-2	6399	--	< 0.04	< 0.08
ELC-35	6400	2.0	1.95	0.11
ELC-3AS	6401	0.5	0.46	< 0.08
ELC-3	6402	--	< 0.04	< 0.08

TABLE II

(Regular Field Samples)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
HEB-1	6403	0.39	*	*	0.35	*
HOL-1	6404	*	*	*	*	0.13
BRS-1	6405	*	*	*	*	0.14
BRA-1	6406	0.11	*	*	*	0.15
CAL1-1	6407	*	*	*	*	0.10
CAL2-1	6408	*	*	*	*	0.12
ELC-1	6409	*	*	*	*	*
BLANK	6410	*	*	*	*	*
HEB-2	6411	*	*	*	*	*
HOL-2	6412	*	*	*	*	0.06
BRS-2	6413	0.11	*	*	*	0.20
BRA-2	6414	*	*	*	*	0.07
CAL1-2	6415	*	*	*	*	0.10
CAL2-2	6416	*	*	*	*	0.11
ELC-2	6417	*	*	*	*	*
HEB-3	6418	*	*	*	*	*
HOL-3	6419	*	*	*	*	*
BRS-3	6420	*	*	*	*	*
BRA-3	6421	*	*	*	*	0.07
CAL1-3	6422	*	*	*	*	*
CAL2-3	6423	*	*	*	*	*
ELC-3	6424	*	*	*	*	*
HEB-4	6425	*	*	*	*	*

TABLE II
(continued)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
HOL-4	6426	*	*	*	*	*
BRS-4	6427	*	*	*	*	*
BRA-4	6428	*	*	*	*	0.07
CAL1-4	6429	*	*	*	*	*
CAL2-4	6430	*	*	*	*	*
ELC-4	6431	*	*	*	*	*
HEB-1	6432	*	*	*	*	0.08
BRS-1	6433	*	*	*	*	0.04
HOL-2	6434	0.09	0.06	*	*	0.13
BRA-1	6435	0.15	*	*	*	0.08
CAL1-1	6436	0.13	0.15	*	*	0.72
CAL2-1	6437	VIAL BROKEN IN TUBE				
ELC-1	6438	*	*	*	*	*
HEB-2	6439	0.08	*	*	*	0.16
HOL-1	6440	0.10	*	*	*	0.04
BRS-2	6441	0.08	*	*	*	0.08
BRA-2	6442	0.28	*	*	*	0.11
CAL1-2	6443	*	*	*	*	0.23
CAL2-2	6444	*	*	*	*	0.21
ELC-2	6445	*	*	*	*	0.07
BLANK	6446	*	*	*	*	*
HEB-3	6447	*	*	*	*	0.06
HOL-3	6448	*	*	*	*	*

TABLE II
(continued)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
BRS-3	6449	0.19	*	*	*	0.11
BRA-3	6450	0.08	*	*	*	0.13
CAL1-3	6451	*	*	*	*	0.19
CAL2-3	6452	*	*	*	*	0.19
ELC-3	6453	*	*	*	*	0.05
BLANK	6454	*	*	*	*	*
HEB-4	6455	*	*	*	*	0.08
BRS-4	6456	*	*	*	*	0.04
BRA-4	6457	*	*	*	*	0.06
CAL1-4	6458			TEST FAILURE		
CAL2-4	6459			TEST FAILURE		
ELC-4	6460	*	*	*	*	*
HEB-5	6461	*	*	*	*	*
HOL-5	6462	*	*	*	*	*
BRS-5	6463	0.10	*	*	*	0.08
BRA-5	6464	0.13	*	*	*	0.07
CAL1-5	6465	*	*	*	*	*
CAL2-5	6466	*	*	*	*	*
ELC-5	6467	*	*	*	*	*
HEB-6	6468	0.55	*	*	*	0.36
HOL-6	6469	*	*	*	*	0.06
BRS-6	6470	*	*	*	*	0.09
BRA-6	6471	*	*	*	*	0.09

TABLE II
(continued)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
CAL1-6	6472	*	*	*	*	0.10
CAL2-6	6473	*	*	*	*	0.12
ELC-6	6474	*	*	*	*	*
HEB-7	6475	0.42	*	*	*	0.45
HOL-7	6476	*	*	*	*	*
BRS-7	6477	*	*	*	*	*
BRA-7	6478	*	*	*	*	*
CAL1-7	6479	*	*	*	*	*
CAL2-7	6480	*	*	*	*	*
ELC-7	6481	*	*	*	*	*
BLANK	6482	*	*	*	*	*
ELC-8	6752	*	*	*	*	*
HEB-8	6753	*	*	*	*	0.10
HOL-8	6754	*	*	*	*	*
BRS-8	6755	*	*	*	*	*
BRA-8	6756	*	*	*	*	*
CAL-1-8	6757	*	*	*	*	*
CAL-2-8	6758	*	*	*	*	0.06
BLANK	6759	*	*	*	*	*
ELC-9	6760	*	*	*	*	*
HEB-9	6761	0.17	*	*	*	0.09
HOL-9	6762	*	*	*	*	*
BRS-9	6763	*	*	*	*	*

TABLE II
(continued)

Sample Code	I.D. No.	Diazinon µg	Methyl Parathion µg	Paraoxon µg	Malathion µg	Parathion µg
BRA-9	6764	*	*	*	*	0.05
CAL-1-9	6765	*	*	*	*	0.12
CAL-2-9	6766	*	*	*	*	0.20
ELC-10	6767	*	*	*	*	*
HEB-10	6768	*	*	*	*	0.05
HOL-10	6769	*	*	*	*	0.07
BRS-10	6770	*	*	*	*	0.04
BRA-10	6771	*	*	*	*	0.10
CAL-1-10	6772	*	*	*	*	0.15
CAL-2-10	6773	0.09	*	*	*	0.19

* Not detected

Detection Limits:

Diazinon:	0.08 µg
Methyl Parathion:	0.04 µg
Paraoxon:	0.08 µg
Malathion:	0.08 µg
Parathion:	0.04 µg

State of California

Memorandum

To : Peter Venturini, Chief
Stationary Source Division

Date : January 7, 1987

Subject : ADD Laboratory Audit - Parathion Project

From : Spencer Duckworth, Chief
Aerometric Data Division
Air Resources Board

Attached you will find a summary report of the laboratory audit conducted by my staff at SSD's request for the Parathion monitoring project. The laboratory audit consisted of both an analytical performance check and a procedural review.

Based on our evaluation of both the laboratory and field operations, we believe that the Parathion data are reliable. Sufficient effort was devoted to quality control activities both in the laboratory and field operations to allow for the generation of high quality environmental data.

A more detailed audit report is on file in the ADD-QA Section along with comments on the report made by ADD laboratory staff. If you have further questions on this audit or wish to see a copy of the full report, please contact Bob Effa at 2-3726.

Attachment

cc: Bill Loscutoff
Don Crowe
Bob Effa
Bob Barham
Bob Kuhlman

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- 1987
Stationary Source Division
Air Resources Board

January 7, 1987

Laboratory Audit Report Summary
Aerometric Data Division Laboratory
Parathion Air Monitoring Project
Imperial County, California

On Friday, October 31, 1986, the Quality Assurance Section conducted an audit of the ADD laboratory operations which was providing the analytical support for the Imperial County Parathion Air Monitoring Project. The audit consisted of two parts: a system audit of the laboratory activities relevant to the Parathion analysis, and a performance audit of the analytical method.

The system audit reviewed the quality control measures for sample handling, analysis and data documentation. The laboratory facilities were also evaluated for safety features and for chemical handling and storage equipment. No serious deficiencies were observed during the audit; however, there were several items noted that would have improved the analytical reliability and laboratory operations.

Instrumentation used for the Parathion analysis included a Varian 3400 gas chromatograph equipped with a Varian 8000 autosampler, thermionic specific detector, and computer interface for data handling. The equipment is less than two years old, representing state-of-the-art technology and is maintained under a service contract to Varian, Inc. The analytical procedure for the analysis of Parathion is documented in Standard Operating Procedure ADDL003 entitled "Method for the Determination of Selected Organic Phosphate Pesticides in Ambient Air". Briefly, the method entailed sampling ambient air through a SKC supplied XAD-2 adsorbant trap, extraction of the adsorbant media with a 80/20 iso-octane/acetone mixture and analysis of the extract by gas chromatography-thermionic specific detector.

Quality control activities performed on a regular basis to monitor and document the data validity included daily instrument calibrations, surrogate additions, field duplicates, trip blanks, spiked sampled and control sample analysis. Samples were not analyzed in duplicate to document method precision and confirmation of the samples by GC/MS or another analytical method was not attempted.

The performance of the analytical method was checked by submitting adsorbant tubes spiked with known levels of Parathion to the lab for analysis. The Parathion standard was obtained from Chem Services, Inc., and certified to be 99% pure. Four samples were given to the laboratory in the concentration range of 0-4 ug. The results reported by the laboratory are summarized in Table I. The reported values show acceptable agreement with the assigned values; all were within 12% of the audit values.

Table I

Parathion Performance Audit Results
Aerometric Data Division Laboratory

Sample Identification	Assigned Concentration (ug)	Laboratory Measured Concentration (ug)	Percent* Bias
A	0.33	0.31	-6.1
B	0.25	0.24	-4.0
C	Blank	< 0.04	----
D	0.25	0.22	-12.0

* Percent Bias = $\frac{\text{Measured Concentration} - \text{Assigned Concentration}}{\text{Assigned Concentration}} \times 100$