

Appendix L. Chemical Analytical Method
Chloropicrin - sorbent tubes
California Department of Health Services Laboratory

METHOD RESOLUTION REQUEST

METHOD NO: Chloropicrin in Air by Dept of Toxicology, University of California, Davis, Contract # A5-169-43

VERSION DATE: 10/28/87

SECTION NO: Instrumentation

PROBLEM: Method uses an electrolytic conductivity detector and a packed column. We do not have this detector and packed columns are obsolete.

SUGGESTED RESOLUTION: An electron capture detector will be used, which is more sensitive than the electrolytic conductivity detector for this compound. A DB-5 capillary column will replace the packed column. The DB-5 column is to be 30 meters long, 0.25 mm i.d., and with a 1.0 um film thickness. The column operating conditions are: He flow rate = 1 cc/min, nitrogen make-up = 32 cc/min, injector temperature = 225 °C, detector temperature = 350 °C (detector range set at maximum sensitivity), and the oven temperature program is: 40 °C for 1min, 10 °C/min to 250 °C with no hold time.

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EHLB Analyst

11/5/99

Date

APPROVED RESOLUTION:

DPR Representative

Date

DPR Discussion:

Final Report to the Air Resources Board

Pilot Analysis of Chloropicrin in Air

Contract # A5-169-43

Date: October 28, 1987

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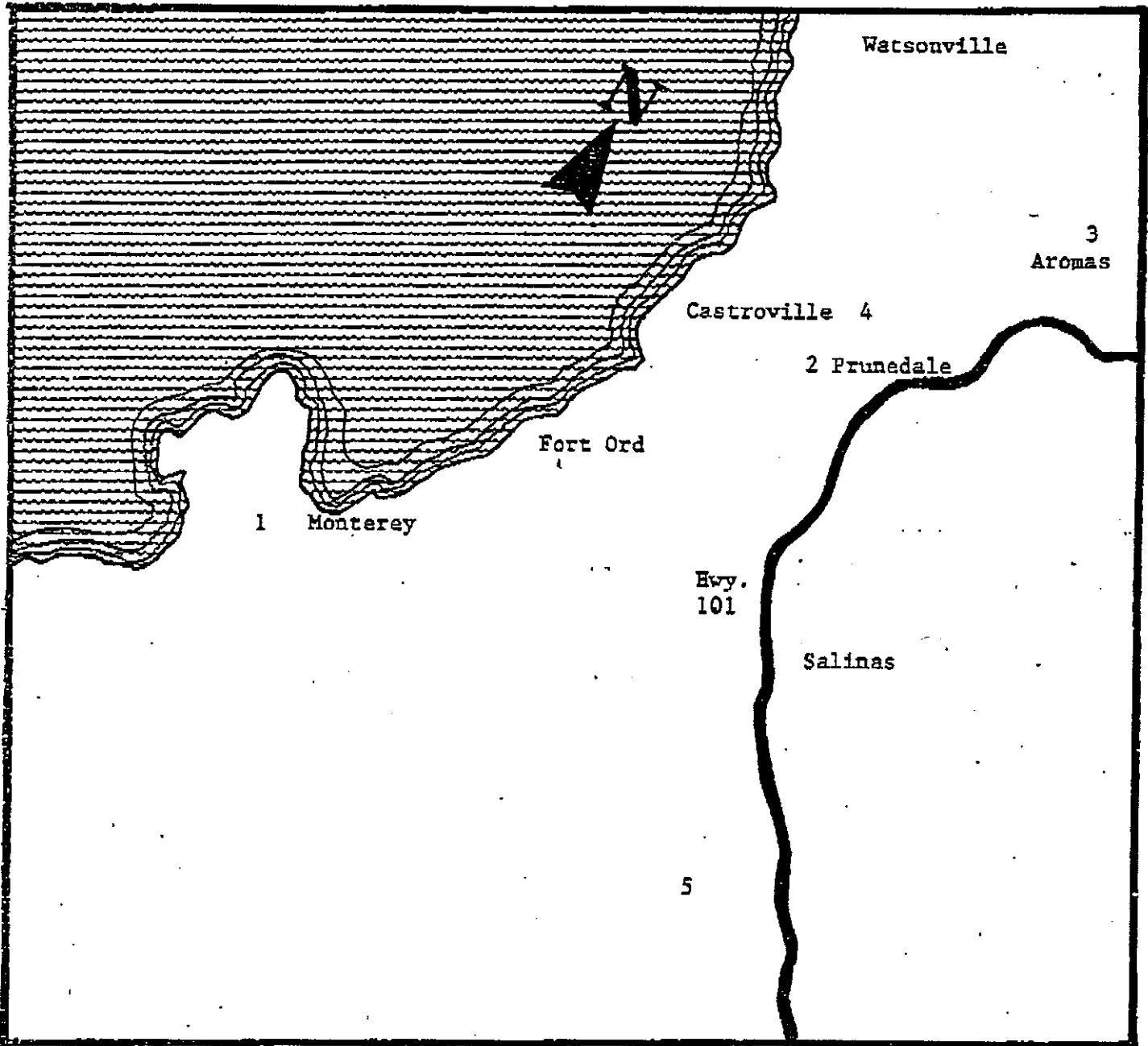
University of California, Davis

Summary

Air sampling for chloropicrin was conducted during August and September, 1986, at three ambient locations in Monterey County (Figure 1). A background site was established in the city of Monterey. Samples were also collected at an application site located at Fennell Farms on River Road south of Salinas prior to, during and four days after the application of chloropicrin to strawberry fields.

The samples were collected in XAD-4 samplers and analyzed by a gas chromatographic method. Table 1 has the summary of results. The highest concentrations of chloropicrin (23.8 parts per billion) were found at the Fennell Farms application site; the average of all samples at this site was 1.2 ppb. There were several samples that gave positive responses at or above the minimum detection limit (MDL) of 13 ppt at the ambient sites.

Figure 1. Map of Sampling Locations in Monterey County.



Scale

↔ 5 Miles ↔

Monitoring Sites

- 1 Background
- 2 Old Corral Flea Market
- 3 Aromas School
- 4 Elkhorn School
- 5 Application Sites

Table 1. Summary of Air Concentrations of Chloropicrin in Parts Per Trillion Volume

	Maximum Positive ^a	Second Highest Positive ^a	Average All Samples above MDL	Total # of Samples analyzed	# Above MDL ^b
Aromas	681	279	110	48	26
Elkhorn	57.2	22.5	39.9	46	4
Flea Market	191	99.7	75.8	48	10
M. P. Hospital	<MDL	<MDL	<MDL	42	0
Fennell Farms					
Site A	730	110	170	22	12
Site B	9080	8100	1400	38	36
Site C	23800	3430	1970	36	32

^aAverage of two replicates

^bMDL = minimum detection limit (13 ppt)

Introduction

Chloropicrin is extensively used in agriculture (1,614,000 lbs. for 1985 in California alone, [1]) as a fumigant to control nematodes, weeds, and fungi in soil and insect pests in harvested grains and nuts. Given its relative volatility, chloropicrin will readily diffuse somewhat if not rigorously contained. When used as a soil fumigant, where the material is injected into the soil and immediately covered with a plastic tarp, some escape to air may be expected; subsequent tarp removal may result in further releases to the atmosphere. The time-weighted average (8 hr/day, 40 hr/wk) threshold limit value for chloropicrin in air is 0.1 ppm [2].

In this study low volume (1.0 L/min) ambient air samples were collected in Monterey County for chloropicrin analysis at three sites plus a background site. Also, an application site was monitored prior to, during, and four days following completion of the application. Ambient air samples were taken over a four week period from August 26 to September 18, 1986.

Sampling for methyl bromide was also conducted at each site and is the subject of a separate report.

Experimental

Site Selection and Sampling

Ambient Sites

Three sites were selected in Monterey County. Roof tops of the elementary schools in Aromas and Elkhorn were utilized. The roof top of the Old Corral Flea Market located on Highway 156 approximately two miles west of highway 101 was the third site. A background site was located at the Monterey Peninsula Hospital in Monterey.

Sampling

Three replicates were collected at the Flea Market site; two replicate samples were taken at the other sites. Replicate samples were taken two meters apart and 1.67 meters above the roof top. One sampler was marked "A" and designated as the primary sample (as per ARB protocol) while the "B" sampler was the replicate. The samplers were connected to high volume sampling pumps via 3/8 inch Tygon tubing and a "T" open to the air. The "T" was needed to step down to the desired flow rate for chloropicrin. The flow rates were regulated by pinch clamps on the open end of the "T". Flow rates were measured by attaching flow meters to the top (open) end of each sampler at the beginning and the end of the sampling period. Each site met the ARB siting criteria and passed the ARB site audit performed on September 3, 1986. Trapping studies, completed prior to any sampling, showed that the maximum sampling period without breakthrough was 4 hrs with a flow rate of 1.0 LPM. A listing of sources of equipment and supplies used for field sampling is in Table 2.

Table 2. List of Equipment for Field Work

1. Wind Profile Register system, Model 104-LED-LM-DC CWT-1791, Thornwaite and Associates, Elmer, NJ
2. Microdatalogger, Model CR-21X, Campbell Scientific, Logan, UT
3. Temperature probe, Model 107, Campbell Scientific, Logan, UT
4. High Volume air samplers, Model U-1/AT, BGI, Inc., Waltham, MA
5. High volume air sampler, Bendix Co., Baltimore, MD
6. Reagent-Grade Methanol, Acetone, Ethyl Acetate, Methylene Chloride, Baker Chemical Co.
7. Rotameter, Model VFA 21, Dwyer Instruments, Inc., Michigan City, IN.
8. Battery powered low volume pumps.
9. XAD-4 Resin, Rohm and Haas,

Chloropicrin samples consisted of a 7.5 cm X 1.8 cm tube connected to a sintered glass funnel via a rubber gasket. Each tube contained 10 ml of XAD-4 resin (Figure 2). The top tube was the primary trap while the bottom tube was the back-up. The tubes were connected to the pump by 3/8 inch Tygon tubing. The entire "sample" was wrapped in aluminum foil to prevent sunlight from striking the tubes and thus heating them or causing photodegradation. After sampling was completed the tubes were frozen (-20°C) until analyzed.

Application Site

Samplers were located upwind and downwind of a field prior to application of methyl bromide and chloropicrin (Figure 3). Three sampling sites were set out during and following application. Site A was located ca. 275 m on the northwest side near a migrant trailer housing. Sites B and C were located on the southeast side 67 m and 175 m, respectively, from the edge of the field. Battery-powered personnel air samplers were used exclusively at site A (the expected upwind site). Sites B and C were powered by gasoline generators. The prevailing wind was from the northwest.

The wind patterns changed during the day with the wind coming from the southeast during the early to midmorning, then changing direction and becoming very strong out of the northwest during the late afternoon. Thus, site A was the downwind site in the early morning and the upwind site during the late morning and afternoon.

Application was started at 6:30 a.m. on September 11 but only one third of the field was fumigated due to high wind conditions. The application was completed on September 12. The field was tarped until the morning of September 15 when the tarp from one-third of the field was removed. The rest of the tarp was removed over the next two days.

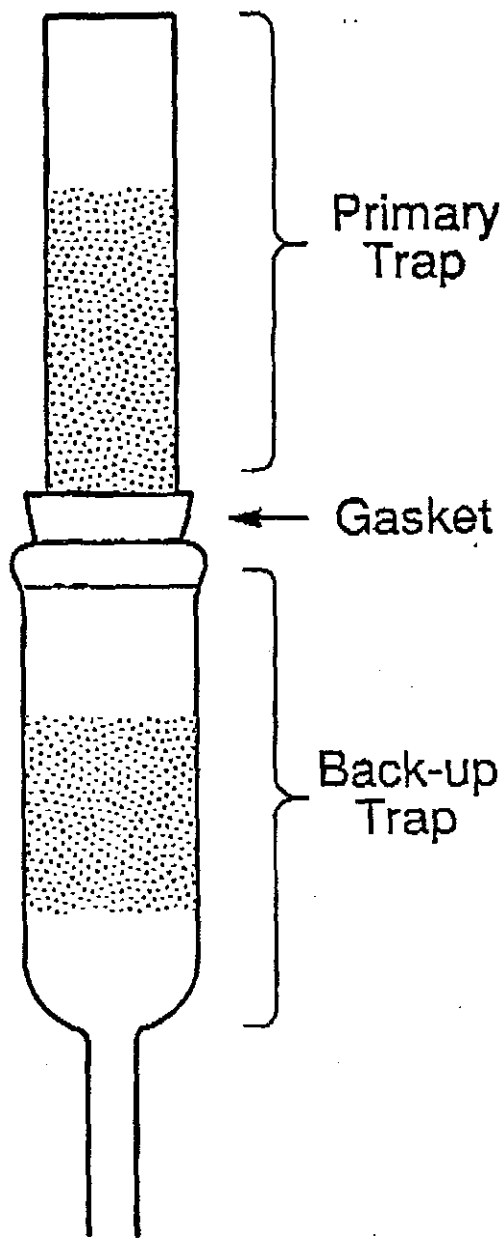
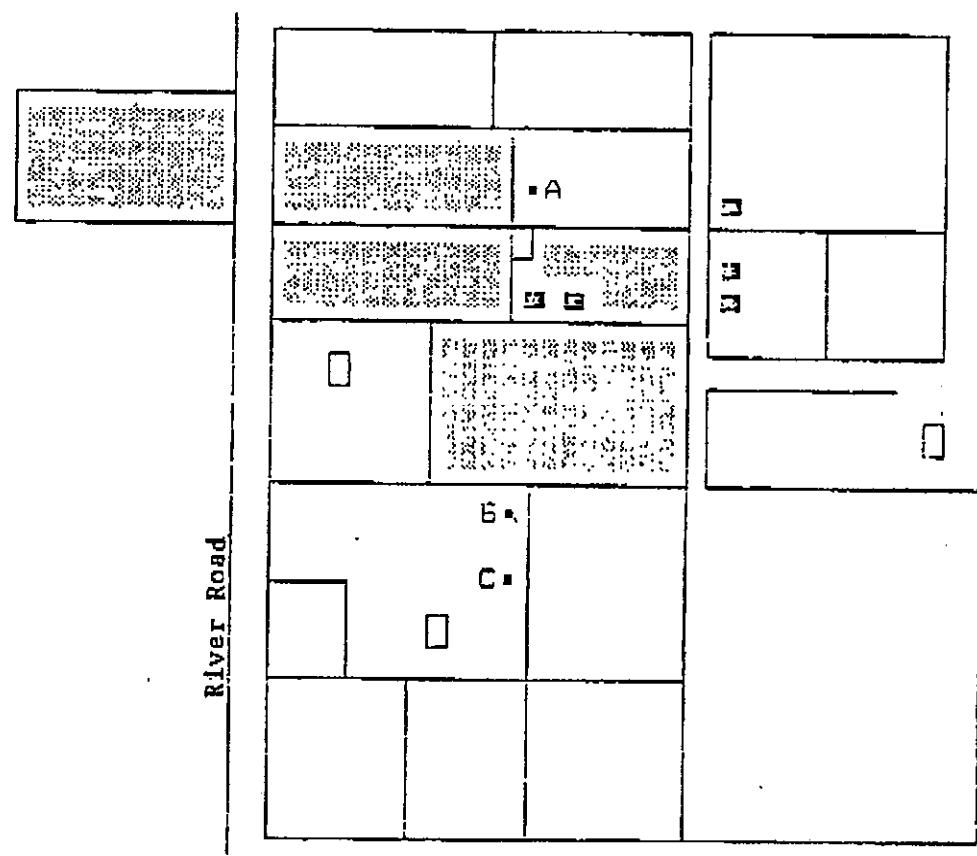
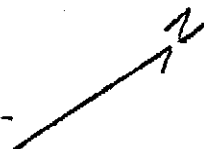


Figure 2. XAD-4 resin trap.

Figure 3. MAP OF FENNEL FIELDS APPLICATION SITE ON RIVER ROAD



- ▨ Strawberries
- Buildings
- Houses
- : site A
- : site B
- : site C
- ▨ Applied field

0.2 mile

Sampling was done on this field the day before the application began and for two 4-hour periods during the first day of application and for three 3-hour periods during the second day of application. Two 4-hour samples were collected while the field was tarped and for four 4-hour periods on the 15th, the first day that one third of the tarps were removed.

Sample Coding

Samples were coded in the following manner: The first number refers to the month of the year and the next one or two, depending on the date, refers to the day of the month. The letter refers to the site where the sample was taken: A, Aromas Elementary School; E, Elkhorn Elementary School; FM, Old Corral Flea Market; M, Monterey Peninsula Hospital. The next number is the period (either 1 or 2) and the letter following indicates whether the sample is from the "A" or "B" sampler. Therefore, 827M2A indicates that the sample was taken on August 27 at Monterey Peninsula Hospital and that it was the second sampling period on that day from the "A" sampling site.

The application site had the same coding system with the exception that the letter following the sampling period designated the site (A, B or C) then the sample (A or B).

Quality Control

To test trapping efficiency, sampling tubes were filled with 10 ml each of XAD-4 and glass wool was placed above the resin. The glass wool in each tube was spiked in duplicate with 100 and 250 ng each of chloropicrin. Each sampler had a 10 ml backup sampler. The sampling train was connected via a manifold to a modified AC-powered high-volume air sampler which pulled air at 1.0 LPM through the resin tubes for 4 hrs. Commercial sampling tubes filled with 2 ml of XAD-2 resin were also spiked. The results are in Table 3. Laboratory spiking and recoveries for chloropicrin are listed in Table 4. Table 5 has the results of the freezer stability study in which spiked samples were stored at -20°C for 42 days before analysis. This simulated the longest holding time of field samples.

Table 3. Air Trapping Efficiencies for Chloropicrin

Resin Type (Volume)	Amount Spiked (ng)	Flow Rate (L/min)	Sampling Period (hours)	Recovered (%)		avg
				A	B	
XAD-2A (2 ml)	100	1.0	4	0	0	0
XAD-4 (10 ml)	250	1.0	4	83	98	91
XAD-4 (10 ml)	100	1.0	4	85	81	83

A: Pre-packed commercial sample tube

Table 4. Spiking and Recovery

Level (ng)	1	Replicate 2	3	Average	% Recovery	Standard Deviation
1000	933	875	912	904	90.4	29
700	680	---	---	---	97.1	---
500	495	---	---	---	99.0	---
300	262	---	---	---	87.3	---
100	114	75	92	94	93.8	19

Table 5. Freezer Study^A

Spike Level (ng)	1	Replicate 2	3	Average Recovery	% Recovery	Standard Deviation
500	492	512	492	498	99.2	11.
200	186	179	179	181	90.7	4.0

A: Scored at -20°C for 42 days

LAB ANALYSIS**Instrumentation**

Chloropicrin was analyzed via Vista 402 Controlled Varian 6000 Gas chromatograph equipped with 13' x 2 mm ID glass column packed with 5% UCON-50-HP2000 liquid phase on Gas Chrom Q 60/80 mesh operated at 60°C and a carrier gas of helium at 20 ml/minute. The chloropicrin was detected using a Hall Electrolytic Conductivity Detector (Model 700A) in the chlorine reductive mode.

Inlet temperature:	225°C
Reactor base:	250°C
Reactor:	910°C
Reaction gas:	H ₂ 50 ml/minute
Solvent:	2-propanol at 0.5 ml/minute

Sample Preparation

Samples were removed from freezer November 11, 1986. Nanograde hexane (10 ml) was added using a 10 ml Volumetric pipette to each 20 ml scintillation vial containing the spiked XAD-4 resin. The vials were recapped tightly and vibrated on the Deluxe Mixer, Cat. No. 58220 (Scientific Products) for one minute. An appropriate variable volume injection, using a 10 µL Hamilton syringe was utilized. Peak heights (mm) from chromatograms were compared to standard curve peak heights vs. picograms of chloropicrin and total chloropicrin in each sample was calculated from the following equation:

$$\frac{\text{Picogram from Std Curve}}{\# \mu\text{L injected}} \times 10 \text{ ml Hexane} = \text{total nanograms}$$

The first tube was used to determine the amount of chloropicrin in air. The second tube was a back-up to determine whether breakthrough occurred. If at least 25% of the total trapped material appeared in the back-up tube, then the concentration in air would be reported as a "greater than" number.

Essentially all of the chloropicrin was trapped in the first tube. The good recovery was partly due to a relatively low field air temperature (~16°C) compared to the spiked recovery studies (21-30°C).

Field Samples

Results

Table 6 summarizes the field samples collected. Table 7 contains the air flow, period nanograms, micrograms per cubic meter and parts per trillion of chloropicrin found at the ambient sites. Thirty acres of strawberries, located approximately 0.25 mile upwind from the Aromas sampling site, were tarped during the first week of sampling. Table 9 contains the average values of chloropicrin at the ambient sites while Table 8 contains the comparison of the replicators.

The concentrations of chloropicrin were highest at the application site (Table 12). Air flows were measured at the beginning and the end of each period. The flows were adjusted to 100 ml/min at the beginning of each period. The highest average concentration (23.8 ppb) occurred at site C during the second day of application. The concentration at site B reached 9.11 ppb while site A, the site northwest of the treated area, yielded a concentration of 0.114 ppb on the second day of application. Within 15 days after application air concentrations of chloropicrin were greatly reduced.