State of California
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AIR RESOURCES BOARD

Ambient Air Monitoring for Mancozeb in Kern County During Spring 1993

Engineering Evaluation Branch

Monitoring and Laboratory Division

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Ambient Air Monitoring for Mancozeb in Kern County
During Spring 1993

This report presents the results of ambient air monitoring for mancozeb and its primary breakdown product, ethylenethiourea (ETU), during the month of peak use, in the county of peak use. Samplers were set up in various towns near expected application sites. Of the more than 50 samples taken, none were found to be above the minimum detection limit, 0.5 ug/sample (approximately 0.025 ug/m^3 for a 24-hour sample) for mancozeb. No ETU was detected, but it was later determined that the incorrect sampling medium (XAD resin) was used.

Acknowledgments

Jack Rogers, LaJuan Taylor and Ken Lewis were the Instrument Technicians. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Toxic Air Contaminant Identification Branch as well as the Kern County Agricultural Commissioner's Office. Chemical analyses were performed by the Department of Environmental Toxicology at U.C. Davis.

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Ambient Air Monitoring for Mancozeb in Kern County
During Spring 1993

I. INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted a three week ambient monitoring program for mancozeb and its primary breakdown product, ethylenethiourea (ETU) in Kern County during the Spring of 1993. This monitoring occurred from April 20 through May 7, 1993. As required by the Food and Agricultural Code 14021, this monitoring was conducted to provide DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

II. DESCRIPTION

Mancozeb is a broad spectrum fungicide used on various crops. It is a polymeric salt of ethylenebisdithiocarbamic acid containing approx. 20% manganese and 2.5% zinc. The fungicide is a yellow powder, and has virtually no odor and negligible volatility at room temperature. It is nearly insoluble in water and most organic solvents. The oral LD_{50} for rats is 11,200 mg/kg and the dermal LD_{50} for rats is >15,000 mg/kg (1990 Farm Chemicals Handbook). Mancozeb is not regulated as a restricted use material under Section 6400, Title 3 of the California Code of Regulations.

III. SAMPLING LOCATIONS

The most recently available Pesticide Use Report (PUR) was used to determine areas of high usage and peak periods of application. This information along with the recommendations of the Kern County Agricultural Commissioner's Office was used to determine which locations would be expected to be near mancozeb applications. As a result four sites were initially selected: one in Weed Patch (site V), two in Lamont (sites L and M), and one in Edison (site E). After the first week, one of the samplers in Lamont was moved to Bakersfield (site BF). The intent of moving the sampler was to assess possible exposure in a major urban area rather than have two samplers in an area of more likely exposure. TABLE I lists the addresses of the monitoring sites. TABLE II lists the results and the sample identifications. FIGURE I shows the location of these monitoring sites. In addition, a "rover" was moved among the sampling sites to obtain duplicate collocated samples which were used to evaluate the precision of the data.

The sites were chosen on the basis of the criterion listed in the QA Plan for Pesticide Monitoring (APPENDIX I). Other considerations in selecting the monitoring sites were: proximity to expected application sites, possible population exposure, reasonable access, availability of AC power and security.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through a glass fiber filter followed by a bed of XAD-4 resin (see APPENDIX II). Both holders were made of Teflon. The resin holders contained approximately 30 cc of resin. The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any mancozeb present in the sampled ambient air was captured by the glass fiber filter while the more volatile ETU was expected to be captured by the XAD-4 adsorbent. Subsequent to sampling, the filter and the resin were transported on dry ice to the Department of Environmental Toxicology (DET), U.C. Davis for analysis.

Each sample train consisted of a filter holder, an XAD-4 resin holder, Teflon fittings and tubing, control valve, train support, and a 115VAC powered vacuum pump. A diagram of the sampling train is shown in FIGURE II. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through the holders adjusted with a metering valve to an indicated reading of 12.4 on a calibrated flow meter. This was accomplished by attaching the calibrated flow meter to the inlet of the filter holder. A leak check was performed by blocking off the flow meter inlet. Upon completion of a successful leak check, the indicated flow rate was again set at 12.4 and was recorded (if different from the planned setting) along with date, time and site location. Calibration prior to use in the field indicated that an average flow rate of 16.2 lpm was actually achieved when the flow meter was set to 12.4. Each sampler was run at this rate for approximately 24 hours. Samples were run Monday through Friday, collecting four samples per week.

At the end of each sampling period the final indicated flow rate (if different than the set 12.4), the stop date and time were recorded. The filter and XAD-4 resin were then removed from the holders, transferred to separate pre-cleaned jars with a Teflon lined lid and an identification label affixed to each jar. Each jar was then placed in an ice chest containing dry ice until the jars were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The filter and the XAD-4 resin recovered from each sampler were analyzed by the DET staff. Any mancozeb present on the glass fiber filter was converted to carbon disulfide and measured using gas chromatography with a flame photometric detector (GC/FPD). The filters

were reacted with 37% hydrochloric acid containing 3% stannous chloride. The sealed vials also contained 2 ml iso-octane to extract the resultant carbon disulfide. The XAD-4 was extracted with 75 ml of ethyl acetate, concentrated, followed by GC separation on a DB-5 megabore column and measurement by a Thermionic Specific (nitrogen/phosphorous) Detector (TSD) (see APPENDIX III for details.)

VI. RESULTS

Results for mancozeb are shown in TABLE II and APPENDIX III. Many of the flow rates decreased from the original set value (TABLE III). The reported values (TABLE II) were calculated using the average of the concentrations based on the beginning and ending flow rates. The final concentrations were also calculated using the beginning flow rate and the final flow rate separately (TABLE III). This gives minimum and maximum concentrations possible, based on changes in the flow rates. As TABLE II indicates, no mancozeb was found above the detection limit (0.5 ug/sample or approximately 0.025 ug/m^3.)

No ETU was detected, but after the analysis it was determined that the incorrect sampling medium (XAD-4 resin) was used. Prior to sampling there was insufficient time to conduct the quality assurance measures required by the Quality Assurance Plan. The "best guess" for ETU collection was the XAD-4 resin. Unfortunately, it was discovered that the ETU could not later be desorbed from the resin. Subsequent research has indicated that a water trap might be appropriate, but further research is still required.

Pursuant to the Food and Agricultural Code Section 14021, mancozeb has recently been designated as a toxic air contaminant. The DPR has indicated that no further monitoring of ETU will be required, based on this decision.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Laboratory Report for mancozeb (APPENDIX III).

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX I) were followed except no field spikes were prepared. Laboratory spikes were prepared by the Quality Management and Operations Support Branch of the ARB. The results are shown in APPENDIX IV.

TABLE I. Mancozeb Ambient Monitoring Sites

Site ID	Address
V	Vineland School 14713 Weedpatch Hwy. Bakersfield, CA 93307
L	Lamont School 8201 Palm Avenue Lamont, CA 93241
M	Mountain View School Mountain View Rd. and Hwy. 184 Lamont, CA 93241
E	Edison School 721 Edison Rd. Bakersfield, CA 93307
BF	ARB Ambient Monitoring Station 225 Chester Avenue Bakersfield, CA 93301

TABLE II. Mancozeb Ambient Monitoring Data

Sample ID	Time (min.)	Volume (m^3)	Detected (ug)	Concentration (ug/m^3)	Date Collected
1V	1360	22.03	ND	--	4/20/93
1L	1360	22.03	ND	--	"
1M	1365	22.11	ND	--	"
1E-1	1360	22.03	ND	--	"
1E-2	1360	22.03	ND	--	"
2V	1380	22.36	ND	--	4/21/93
2L	1380	22.36	ND	--	"
2M	1380	22.36	ND	--	"
2E-1	1380	22.36	ND	--	"
2E-2	1380	22.36	ND	--	"
2B	BLANK	--	ND	--	"
3V	1370	22.19	ND	--	4/22/93
3L	1370	22.19	ND	--	"
3M	1365	22.11	ND	--	"
3E-1	1370	22.19	ND	--	"
3E-2	1370	22.19	ND	--	"
4V	1420	23.00	ND	--	4/23/93
4L	1440	23.33	ND	--	"
4M	1345	21.79	ND	--	"
4E-1	1290	20.90	ND	--	"
4E-2	1290	20.90	ND	--	"
5V	1455	23.57	ND	--	4/27/93
5L-1	1415	22.92	ND	--	"
5L-2	1415	22.92*	ND	--	"
5E	1375	21.86*	ND	--	"
5BF	1425	23.16	ND	--	"
5B	BLANK	--	ND	--	"
6E	1380	22.36	ND	--	4/28/93
6L-1	1380	22.36	ND	--	"
6L-2	1380	22.36	ND	--	"
6V	1375	22.28	ND	--	"
6BF	1375	22.28	ND	--	"
7E	1380	22.36*	ND	--	4/29/93
7L-1	1380	21.94*	ND	--	"
7L-2	1380	21.94	ND	--	"
7V	1435	23.25	ND	--	"
7BF	1385	22.44	ND	--	"

*Average of beginning and ending flow rates.

ND = not detected, less than 0.5 ug/sample (<0.025 ug/m^3 for a 20 m^3 sample volume).

No values have been corrected for recovery levels.

TABLE II. Mancozeb Ambient Monitoring Data (cont.)

Sample ID	Time (min.)	Volume (m^3)	Detected (ug)	Concentration (ug/m^3)	Date Collected
8E	1365	21.16*	ND	--	4/30/93
8L-1	1365	22.11	ND	--	"
8L-2	1365	22.11	ND	--	"
8V	1375	22.28	ND	--	"
8BF	1425	23.09	ND	--	"
9E	1425	23.09	ND	--	5/4/93
9V-1	1425	23.09	ND	--	"
9V-2	1425	23.09	ND	--	"
9L	1440	23.33	ND	--	"
9BF	1430	23.17*	ND	--	"
10E	1360	21.76	ND	--	5/5/93
10V-1	1370	22.19	ND	--	"
10V-2	1370	22.19*	ND	--	"
10L	1355	21.54	ND	--	"
10BF	1345	19.16	ND	--	"
11E	1435	23.25	ND	--	5/6/93
11V-1	1320	21.38	ND	--	"
11V-2	1320	21.38*	ND	--	"
11L	1365	18.12	ND	--	"
11BF	1415	22.92	ND	--	"
12E	1345	19.97	ND	--	5/7/93
12V-1	Sample not taken				"
12V-2	Sample not taken				"
12L	Sample not taken				"
12BF	1325	19.68	ND	--	"

*Average of beginning and ending flow rates.

ND = not detected, less than 0.5 ug/sample (<0.025 ug/m^3 for a 20 m^3 sample volume).

No values have been corrected for recovery levels.

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TABLE III. Mancozeb Maximum/Minimum Flow Data

Sample ID	Time (min.)	volume (m^3) Start*	Avg**	Final	Final Flow (lpm)
5E	1375	22.28	21.86	21.45	12.0
5BF	1425	23.09	23.16	23.23	12.5
7L-1	1380	22.36	21.91	21.53	12.0
7L-2	1380	22.36	21.91	21.53	12.0
8E	1365	22.11	21.16	20.20	11.5
10E	1360	22.30	21.76	21.22	12.0
10L	1355	21.95	21.54	21.14	12.0
10BF	1345	21.79	19.16	16.52	9.8
11L	1365	21.11	18.12	15.14	9.0

*Starting flow rate = 16.2 lpm.

**Due to decreases in flow rate from the initial setting for some samples, the volume for these samples was calculated using the initial and final flow rates separately. This value is the average of those volumes.

FIGURE I. Mancozeb Monitoring Area

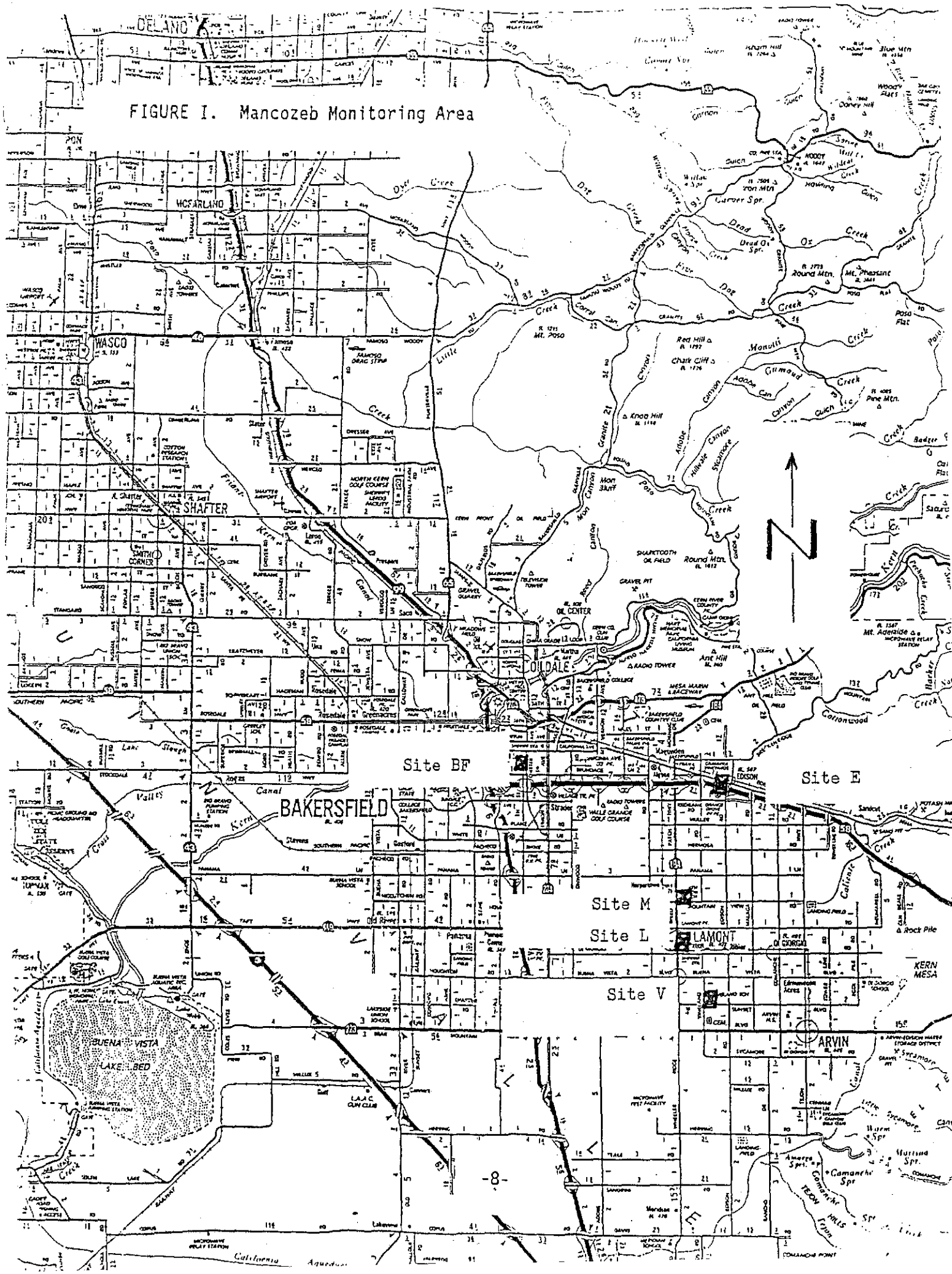
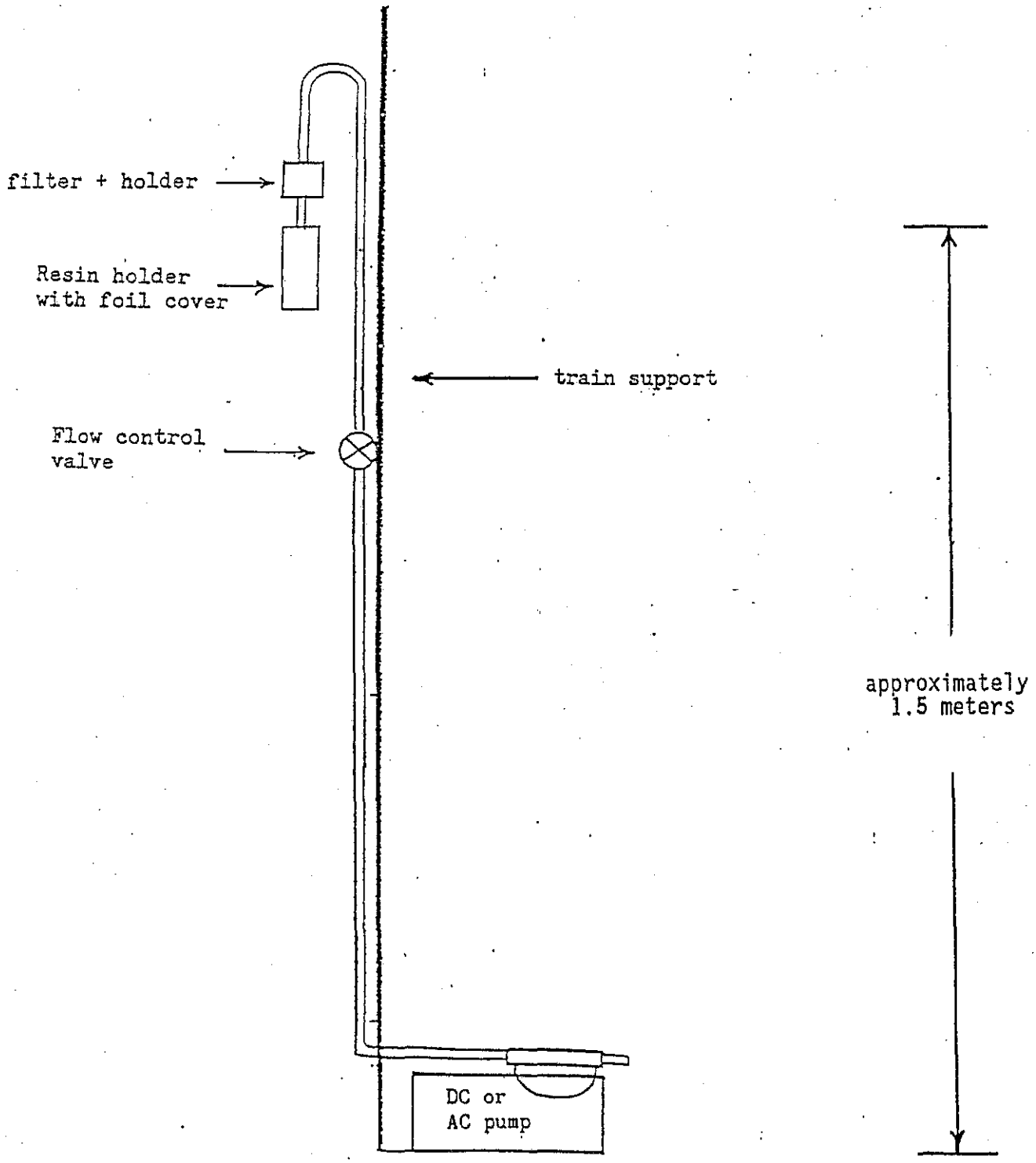


FIGURE II. Mancozeb Monitoring Apparatus



APPENDIX I

QUALITY ASSURANCE PLAN

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN

FOR PESTICIDE MONITORING

Prepared by the

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Revised: February 4, 1994

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This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signifiy that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABL 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial us

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TAB 1). In addition, the placement of the application samplers should be to obta upwind and downwind concentrations of the pesticide. Since winds are variab and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

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

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters 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 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.

4. Description of the analytical method.

5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

   A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

   Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

   The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

   Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

   The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

   All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: ____/____/____
Sample/Run #: _____ Time: _____
Job name: _____
Sample Location: _____
Type of Sample: _____
Log #'s: _____

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected					
			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: _____

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX II

SAMPLING PROTOCOL

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

Mancozeb Monitoring in Kern County during April, 1993

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C93-012A

Date: April 12, 1993

APPROVED:

_____, Project Engineer
Testing Section

_____, Manager
Testing Section

_____, Chief
Engineering Evaluation Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Protocol for Mancozeb Monitoring
in Kern County during Spring, 1993

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) will conduct a 3-day source impacted ambient monitoring program upwind and downwind of an application of mancozeb as well as a four week ambient study to determine possible exposure to population centers near the site of applications. Mancozeb is a fungicide widely used on a wide variety of fruit, vegetable, nut and field crops. A report on the measured concentrations will be submitted to DPR.

II. Sampling

A stainless steel valve downstream of the sampling medium will be used to control all sample flow rates. The flow rate will be set and checked with a calibrated flowmeter. A glass fiber filter followed by a bed of XAD-4 resin will be used to collect the fungicide and its breakdown product, ethylenethiourea. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. Any change in the flow rates will be recorded in a log book, along with any other pertinent information.

A. Application

Prior to application, background samples will be taken to establish if any mancozeb is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Samples will be collected with DC-powered pumps capable of flows of approximately 16 liters per minute. Sample collection will follow the timetable outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" as closely as is reasonably possible.

Five samplers will be used; each approximately 15 yards from the perimeter of the field. Four will be placed at the center of each face (assuming a rectangular field) of the field. The fifth sampler will be collocated with one of the other samplers to obtain precision data. These distances are approximate and dependent on the physical obstacles surrounding the field. ARB's "Quality Assurance Plan for Pesticide Monitoring" will be followed as closely as possible.

B. Ambient

In order to determine any possible exposure to major population centers in the county of peak use, four AC powered samplers will be set up in towns near the sites of potential applications. A fifth sampler will be collocated with each

precision data. Samples will be collected at approximately 16 lpm for 24-hour intervals, Monday through Friday for a period of four weeks.

III. Analysis

All samples will be analyzed for mancozeb by the Department of Environmental Toxicology (DET), University of California, Davis by converting the dithiocarbamate fungicide to carbon disulfide (CS_2) and measuring this product using a flame photometric detector (FPD). All samples will be stored on dry ice until delivery to DET. The analytical procedure for the breakdown product, ethylenethiourea has not been finalized at this point.

IV. Quality Assurance

Field sampling and laboratory analytical quality assurance activities are described in the ARB's "Quality Assurance Plan for Pesticide Monitoring."

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. Sample flow rates will be calibrated prior to and after sampling in the field.

A chain of custody sheet will accompany all samples. A field log book will be used to record start and stop times, sample ID's and any other significant data, including field size, application rate, formulation, and length of the application.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and Jack Rogers (Instrument Technician).

APPENDIX III

LABORATORY REPORT

Analysis of Air Samples for the Fungicides Ziram and Mancozeb and the Breakdown Product Ethylenethiourea

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Final Report

Prepared for the California Air Resources Board

Under Contract #92-313

--

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--

July, 1994

DRAFT

Abstract

In an attempt to provide data for human health risk assessment, airborne residues of the dithiocarbamate fungicides ziram and mancozeb were trapped on glass fiber filters (GFFs) using air sampling at 14-16 liters/min for periods of time up to 24 hrs. Both application and ambient field situations were monitored. The trapped material was determined by treating the filters with concentrated hydrochloric acid containing 3% stannous chloride to convert the dithiocarbamates to carbon disulfide, which was subsequently assayed using sulfur-mode flame photometric gas chromatography. Detected residues were quantitated by comparison of their responses with those of standard injections of carbon disulfide resulting from acid-treated clean GFFs spiked with analytical standards of the fungicides. Limits of detection for ziram and mancozeb were about 0.3 μg and 0.5 μg per GFF, respectively. These levels were equivalent to 14-23 ng/m^3 at 15 liters/min flow rate for 24 hours of sampling. Attempts were made to also detect ethylenethiourea (ETU), a breakdown product of mancozeb; however, problems arose related to ETU stability. This report will discuss details of the analytical methodology, the selection of suitable solvents for the fungicides, stability of the fungicides and ETU on GFFs under air sampling conditions and cold (-15°C to -20°C) storage, and analytical results for the field samples.

Acknowledgments

The authors wish to acknowledge the following personnel for their guidance and assistance in this project: Professor T. Shibamoto, Chairman of the Department of Environmental Toxicology, and Ralph Propper (contract officer), Lynn Baker, Ken Bowers, Don Fitzell, and Gabriel Ruiz, all with the Air Resources Board.

This report was submitted in partial fulfillment of contract #92-313 (Analysis of Air Samples for the Fungicides Ziram and Mancozeb and the Breakdown Product Ethylenethiourea) by personnel from the University of California and the University of Nevada under the sponsorship of the California Air Resources Board. Work was completed on June 6, 1994.

Disclaimer

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein, is not to be construed as either an actual or implied endorsement of such products.

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Summary and Conclusions

The essentially non-volatile and water insoluble fungicides ziram and mancozeb, which are zinc and manganese dithiocarbamates used as protective agents for fruits and vegetable crops, can move from target sites as particulate drift during application and as a result of wind erosion of deposited residues; losses of volatile breakdown products can also occur. Because of this, there is concern over the potential impact ziram and mancozeb usage may have on human health, since these fungicides are suspect carcinogens. Of additional concern is ethylenethiourea (ETU), a breakdown product of mancozeb, which is a recognized mutagen and teratogen, is a suspect carcinogen, and will target the pituitary, liver and thyroid.

Information is lacking describing potential human exposure to the presence of dithiocarbamates and related residues in the air resulting from agricultural usage. In part, this is because of the lack of a method for determining their air residues at anticipated ambient levels. This method, and resulting analytical information, are needed to form a basis for human exposure risk assessment. To generate data for ziram, mancozeb, and ETU in air that could be used as a basis for exposure levels in the assessment of risk to human health, dynamic air sampling techniques were used with glass fiber filters alone to trap ziram from air and with a combination of glass fiber filter followed by XAD-4 polymeric adsorbent to trap mancozeb and relatively volatile ETU during and after commercial applications. Sampling flow rates were in the range 14-16 liters/min for times as short as 2 hours (1.7-1.9 m^3) and as long as 24 hours (20.2-23.0 m^3). The fungicides trapped on glass fiber filters were determined by converting

them to carbon disulfide (CS_2), based on techniques reported earlier (Lowen and Pease, 1964; Keppel, 1971; Mumma et al., 1985; Maini and Boni, 1986), and analyzing the CS_2, trapped in iso-octane solvent, by sulfur-mode flame photometric detection gas chromatography on a DB-1 megabore column. The minimum detection limits (MDLs) were about 0.3 µg ziram and 0.5 µg mancozeb. Assuming an average sampling flow rate of 15 liters/min, these detection limits were equivalent to 167 ng/m^3 and 278 ng/m^3 (two hours sampling) and 14 ng/m^3 and 23 ng/m^3 (24 hours sampling) for ziram and mancozeb, respectively. All sample and standard chromatograms appeared to be "clean", meaning that only CS_2 and iso-octane solvent peaks were evident (Figure S-1). When fungicide levels were less than the MDL, the chromatograms were essentially flat lines up to solvent elution.

Freezer spikes of ziram and mancozeb standards on glass fiber filters were stored at -15°C to -20°C, along with the field samples. These fungicides appeared to be stable (92-97% recovered) for storage periods of as little as two weeks (ziram and mancozeb) to as long as two months (ziram). Ziram and mancozeb standards were also stable on filters under dynamic flow conditions; both compounds showed recoveries in the range 88-100% after 15 liters/min flow for 24 hours (23°C). However, stability of these compounds under both freezer and air sampling conditions was affected by the type of solvent used to prepare the standards. Solubilizing dithiocarbamate fungicides, which are metal salt/complexes, often destabilizes them. For example, when mancozeb was dissolved in 0.1 M EDTA, only 15-20% of the original spikes were recovered when chelated mancozeb was spiked to glass fiber filters and stored at -20°C for about two weeks. Furthermore, only about 16% of ziram dissolved in acetone

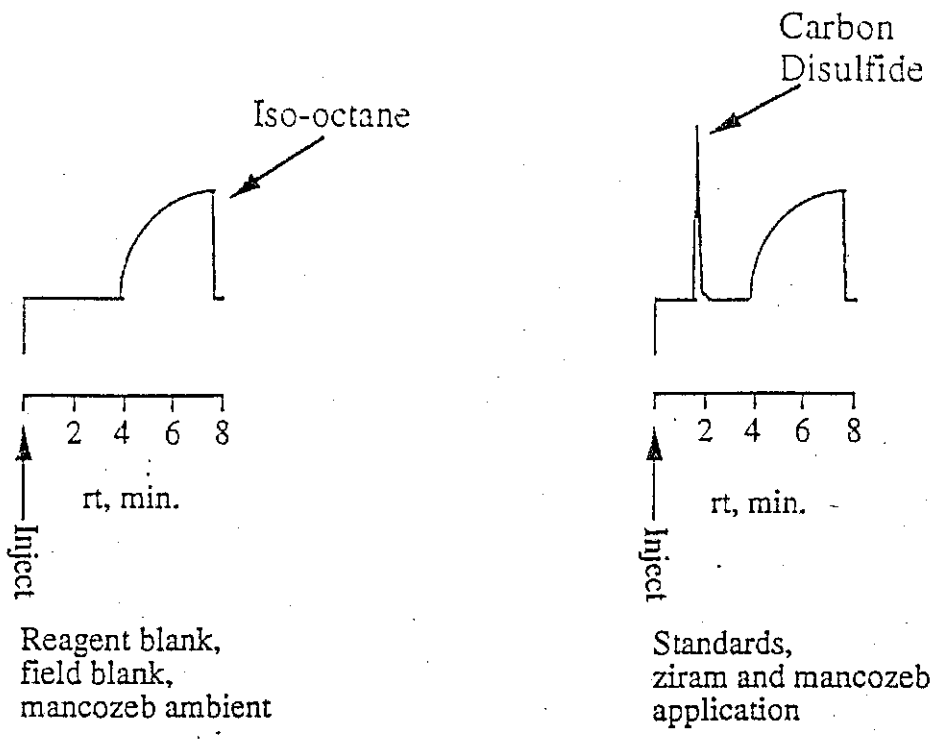


Figure S-1. Gas chromatograms of carbon disulfide derived from ziram and mancozeb fungicide field samples, including standards and blanks.

was recovered from spiked glass fiber filters under air sampling conditions of 15 liters/min for 24 hours. Quantitative recovery of both compounds was achieved only when filters were spiked with solvent suspensions, not solutions, of the fungicides.

Analytical results for the fungicide application field samples are summarized in Tables S-1 and S-2. While ziram and mancozeb residues were less than the MDL in the pre-application samples, as would be expected, residues greater than the MDL were detected in almost every sampling period thereafter (during and post-application), and residues were consistently detected in the later sampling periods. This latter result may have been due to wind erosion of dried, deposited residues. In addition to the application samples, mancozeb ambient samples were collected as well, but these samples did not show any residues above the MDL.

While ziram and mancozeb concentrations declined rapidly during the day of application, measurable residues persisted up to the fourth day (Figure S-2). Log-linear plots of average concentration vs sampling period indicated that the minimum detection limit would be reached after about 7 sampling periods (4 days) and 10-11 sampling periods (6-7 days) for ziram and mancozeb, respectively (Figure S-3). These results imply that residues remained suspended and/or deposited residues were re-suspended as a result of wind erosion.

ETU was quantitatively recovered (~90%) from spiked glass fiber filters after they had been stored at -20°C for at least two months. However, when ETU was spiked to XAD-4 polymeric adsorbent, ETU interacted with the adsorbent leading to irreversible adsorption and/or breakdown and low recovery. The unusual interaction of ETU with the adsorbent was demonstrated by adding an aliquot of the adsorbent to a

Table S-1. Analysis of glass fiber filters for ziram fungicide residues trapped during application.

Sample ID #	LOG #	Ziram/GFF, µg
0W	1	<MDL*
0S1	2	<MDL
0S2	3	<MDL
0E	4	<MDL
0N	5	<MDL
1W	6	0.647
1S1	7	1.80
1S2	8	1.80
1E	9	8.30
1N	10	9.98
1B	11	<MDL
2W	12	<MDL
2S1	13	<MDL
2S2	14	<MDL
2E	15	<MDL
2N	16	1.65
3W	17	<MDL
3S1	18	<MDL
3S2	19	<MDL
3E	20	<MDL
3N	21	0.831
4W	22	<MDL
4S1	23	<MDL
4S2	24	<MDL
4E	25	<MDL
4N	26	0.325
5W	27	0.488
5S1	28	0.455
5S2	29	0.422
5E	30	0.688
5N	31	0.729
6W	32	0.442
6S1	33	0.455
6S2	34	0.303
6E	35	0.411
6N	36	0.343
7W	37	<MDL
7S1	38	<MDL
7S2	39	<MDL
7E	40	<MDL
7N	41	0.312

*MDL= 0.3 µg Ziram/GFF (equivalent to ~167 ng/m^3 at 15 liters/min for 2 hours).

Table S-2. Analysis of glass fiber filters for mancozeb fungicide residues trapped during application.

Sample ID#	LOG #	Total Mancozeb, µg	Description
0S-1	1	<MDL*	pre-application
0S-2	2	"	"
0N	3	"	"
0E	4	"	"
1N	5	"	during/post app'n
1S-1	6	1.99	"
1S-2	7	2.72	"
1E	8	1.34	"
2N	9	<MDL	"
2S-1	10	"	"
2S-2	11	"	"
2E	12	"	"
2B	13	"	"
3N	14	1.00	"
3S-1	15	1.20	"
3S-2	16	<MDL	"
3E	17	2.86	"
4N	18	<MDL	"
4S-1	19	0.931	"
4S-2	20	1.59	"
4E	21	0.522	"
5N	22	0.593	"
5S-1	23	1.41	"
5S-2	24	2.42	"
5E	25	<MDL	"
6N	26	4.58	"
6S-1	27	2.60	"
6S-2	28	3.10	"
6E	29	3.76	"
7N	30	<MDL	"
7S-1	31	1.82	"
7S-2	32	2.44	"
7E	33	0.890	"

*0.5 µg mancozeb (equivalent to ~278 ng/m^3 at 15 LPM for 2 hours).

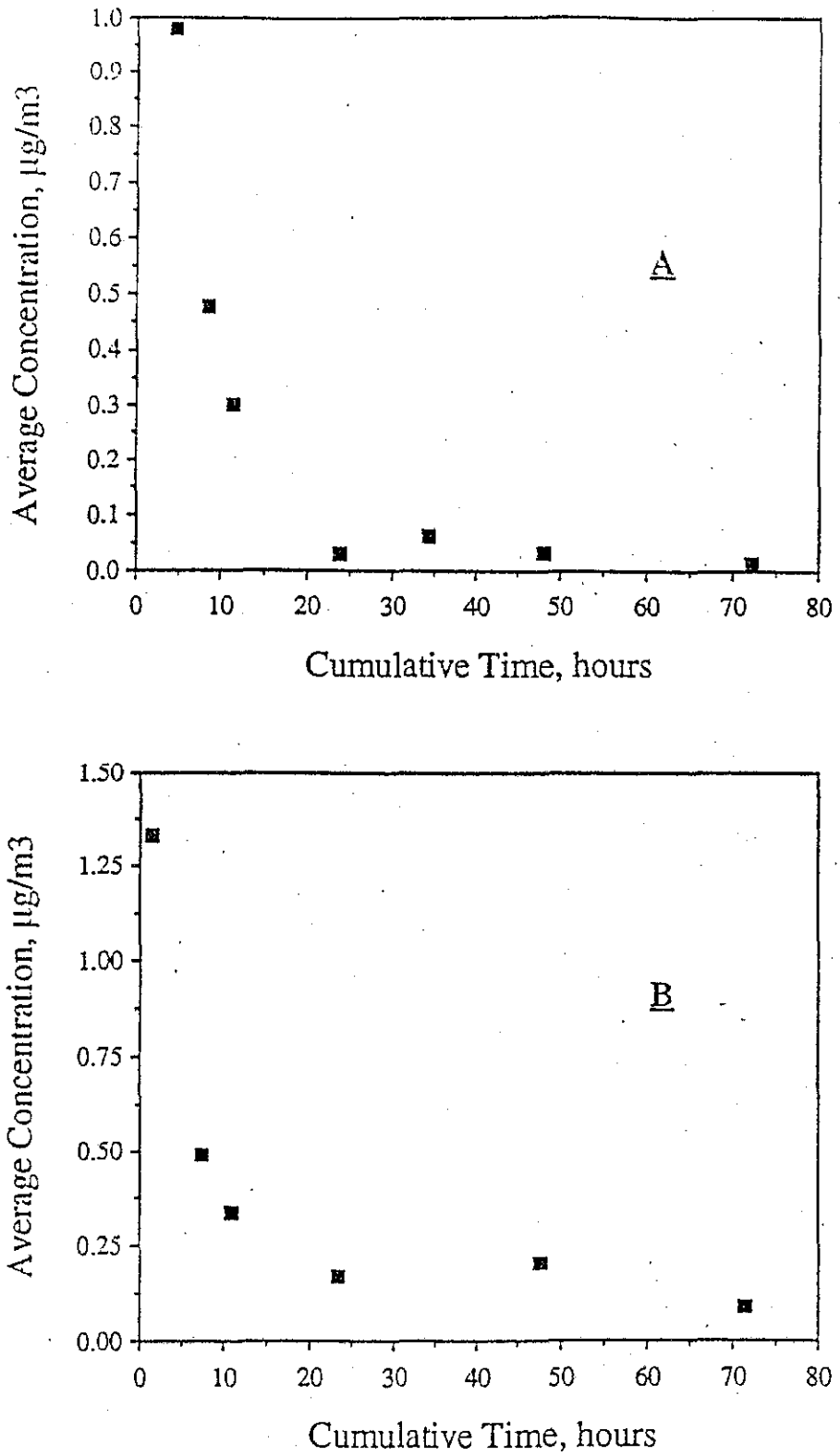
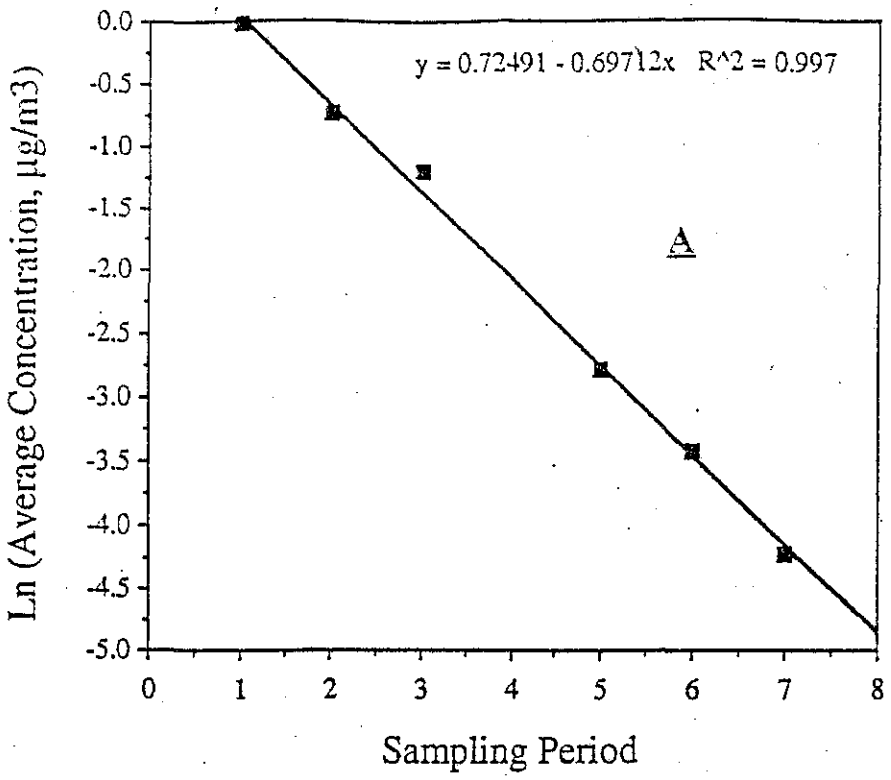


Figure S-2. Decline of ziram (A) and mancozeb (B) residues in air following application.



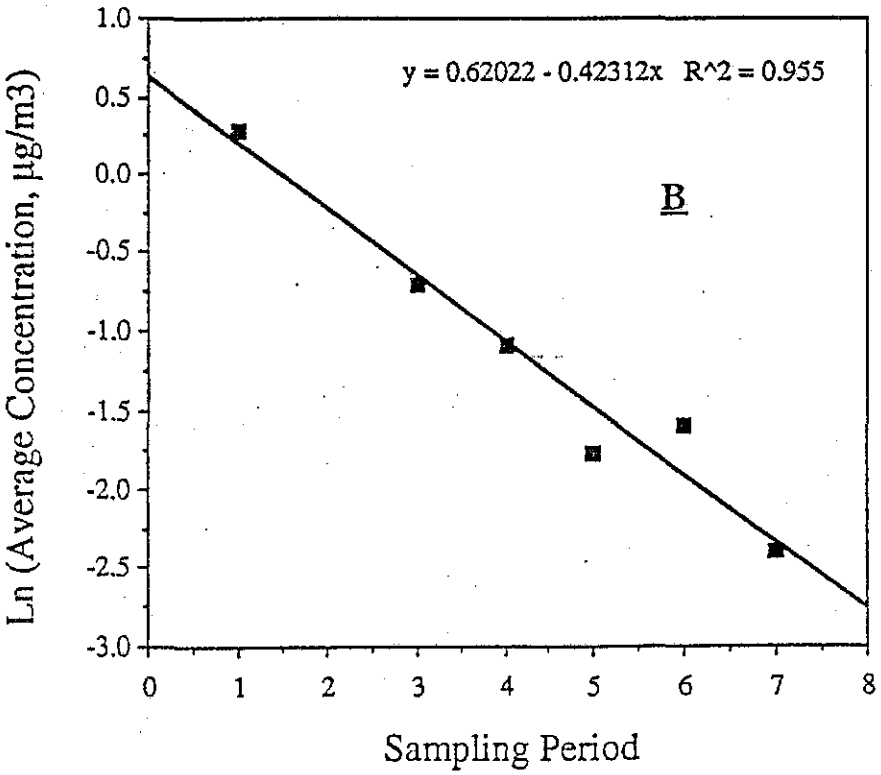


Figure S-3. Ziram (A) and mancozeb (B) concentrations in air vs the sampling period.

solution of ETU in an organic solvent: the result was a decline in concentration of ETU to below detection limits after about 24 hours. Furthermore, little or no ETU could be recovered from spiked adsorbent when treated with pure solvent immediately after spiking. However, consistent, but low (~19-20%), recoveries were achieved when methyl alcohol containing 3-4% glacial acetic acid was used as the extractant. These recoveries fell to less than 10% if air was drawn through the spiked adsorbent at 15 liters/min for 2 hours prior to extraction with the alcohol/acid mixture. These results indicate that the XAD-4 adsorbent was a poor choice as a trapping medium for ETU.

In addition to the problem with the adsorbent, ETU spiked to glass fiber filters and exposed to an air flow of 15 liters/min showed a linear decline, with 50% loss occurring in 51 min. In other tests, EU spiked to filters showed a similar, but exponential, decline under the same flow conditions, with a half-life of about 44-45 min. For ETU, the linear dissipation curve probably reflected two simultaneous processes: 1) volatilization of ETU and 2) oxidation of ETU to EU. Filters spiked with ETU were also analyzed for EU after exposure to dynamic sampling, but no measureable residues were detected, since EU did not accumulate to detectable levels under the dynamic flow conditions of the test. This was probably due to the rapid volatilization of EU upon formation from ETU and to ETU breakdown leading to products other than EU.

A water-filled glass impinger showed promise as an alternative sampler when ETU, spiked to water and exposed to an air flow of 15 liters/min for 2 hours, appeared to be quantitatively recovered (relative to spiked water without air), without any detectable conversion to the oxidation product ethyleneurea (EU). These results are tempered by the

fact that absolute recoveries of ETU from water declined with ETU concentration (e.g., >90% for 1ppm, ~50% for 0.3 ppm) when solid-phase extraction cartridges were used to extract spiked water.

Work by other investigators has shown that ETU can be quantitatively (~80%) recovered from water at concentrations as low as 10 ppb by extractive acylation (Singh et al., 1979). We pursued this approach and confirmed the results of these investigators. However, we found that ETU residues in water (~0.02 μg/ml) did not survive dynamic air sampling for more than a few hours. We replaced water with ethylene glycol (EG) and were able to recover about 38-62% of the original ETU spikes under dynamic air sampling conditions after 2-4 hours at room temperature. It was assumed that the unrecovered ETU had been converted to EU, with some losses possibly due to volatilization. While acylation of ETU was straightforward, EU appeared to be somewhat less reactive. However, we were able to obtain a derivative of EU, confirmed by mass spectrometry, by treating the EG with the acylating reagent prior to dilution with aqueous sodium sulfate and extraction with methylene chloride.

Taken together, the results of the laboratory tests with ETU/EU invalidate the field samples taken with glass fiber filters and XAD-4 adsorbent, while they point toward the use of EG-filled impingers with derivatization as the most promising approach to determining ETU/EU in air. However for this latter approach, much work remains to be done to validate the extractive acylation technique. Many of the mancozeb filters that were analyzed anyway for ETU had chromatograms that were free of peaks in the retention window for ETU. A number of the samples did show peaks in this critical region, but the field blanks had the same peaks.

No attempt was made to analyze the adsorbent field samples because of the demonstrated low recovery of ETU from the adsorbent.

Recommendations

Based on the results of this study, we make the following recommendations:

1). The glass microfiber filters used in this study have been shown by the manufacturer to be quantitatively efficient for trapping particulates with diameters less than 0.5 μm.. Therefore, these filters, or their equivalent, should be used to quantitatively trap ziram and mancozeb, and possibly other dithiocarbamate fungicides, for their determination in air.

2). The analytical method used to determine the fungicides, by converting them to carbon disulfide, gave acceptable sensitivity. Several field samples provided by CARB were analyzed, with quantifiable results for the parent fungicides. However, refinements to this method probably should be pursued in an attempt to lower the detection limit by optimizing gas chromatographic conditions for the detection of CS_2, using more sensitive GC detectors, and improving the efficiency of conversion to carbon disulfide at low fungicide residue levels by altering reaction conditions.

3). Preliminary tests with EG-filled impingers as a sampler for ETU/EU were promising. Further tests need to be done to determine the trapping efficiency of EG-filled impingers for ETU/EU, to establish the stability of these compounds in EG under prolonged dynamic flow conditions (we might consider chilling the impingers in ice to enhance the stability of ETU), and to determine recovery efficiencies for ETU/EU

from EG, especially at low residue levels (<0.5μg). The extractive acylation method of Singh et al. (1979) appears to be the most promising for recovering ETU/EU from EG. However, validation of this approach, especially for EU, needs to be done.

Introduction

The dithiocarbamate fungicides have wide usage as protective agents for fruits and vegetable crops. Two common agents, ziram and mancozeb, are zinc and manganese dithiocarbamates that are practically insoluble in water and have negligible vapor pressures. Movement from the target site could occur as a result of drift of compound particulates during application, wind erosion of deposited particulate residues, and losses of volatile breakdown products.

There is concern over the potential impact ziram and mancozeb usage may have on human health. Furthermore, mancozeb will break down under warm and moist conditions to ethylenethiourea (ETU), which is a recognized mutagen and teratogen, is a suspect carcinogen, and will target the pituitary, liver, and thyroid. Information is lacking describing potential human exposure to the presence of dithiocarbamates and related residues in the air resulting from agricultural usage. In part, this is because of the lack of a method for determining their air residues at anticipated ambient levels. This method, and resulting analytical information, are needed to form a basis for human exposure risk assessment.

A main objective of the project was to generate data for ziram, mancozeb, and ETU in air that could be used as exposure levels in the assessment of risk to human health. So, a primary focus of our efforts was the development of analytical methods for the analysis of the fungicides and ETU trapped on glass fiber filters and also of ETU that might break through the filters to a backup polymeric adsorbent trap.

For the fungicides, we proposed treating the dithiocarbamates on glass fiber filters with concentrated hydrochloric acid, containing stannous chloride, to evolve carbon disulfide, which would then be assayed directly without derivatization (Maini and Boni, 1986), in contrast to some colorimetric techniques (Lowen and Pease, 1964; Keppel, 1971; Mumma et al., 1985). Many of the published methods for ETU involve derivatization of the material prior to analysis (Keppel, 1971; Haines and Adler, 1973; King, 1977; Mumma et al., 1985; Savolainen et al., 1989). We decided to determine ETU without derivatization based on other work (Camoni et al., 1988) and after our own preliminary investigations indicated that underivatized residues as low as 0.27 ng could be easily determined by gas chromatography. We proposed recovering ETU from the filters and polymeric adsorbent by solvent extraction.

Materials and Methods

Fungicide and related residues in air were trapped on 47 mm diameter glass fiber filters (Fisher, Fair Lawn, NJ) at air sampling rates of about 15 liters/min using 12 VDC Teflon® membrane pumps (Thomas, Santa Clara, CA). In the case of mancozeb, the filter was followed by an XAD-4 (20-50 mesh, macroreticular cross-linked polystyrene, divinylbenzene copolymer; Rohm and Haas, Philadelphia, PA) adsorbent trap for any residues of ETU that might pass through the filter (Figure 1). After sampling, the filters were sealed in screw-cap glass jars and transported over dry ice to UC Davis and UN Reno, where they were immediately stored at -15°C to -20°C. Clean samples of filters and adsorbent were spiked with standards of the fungicides and ETU and the

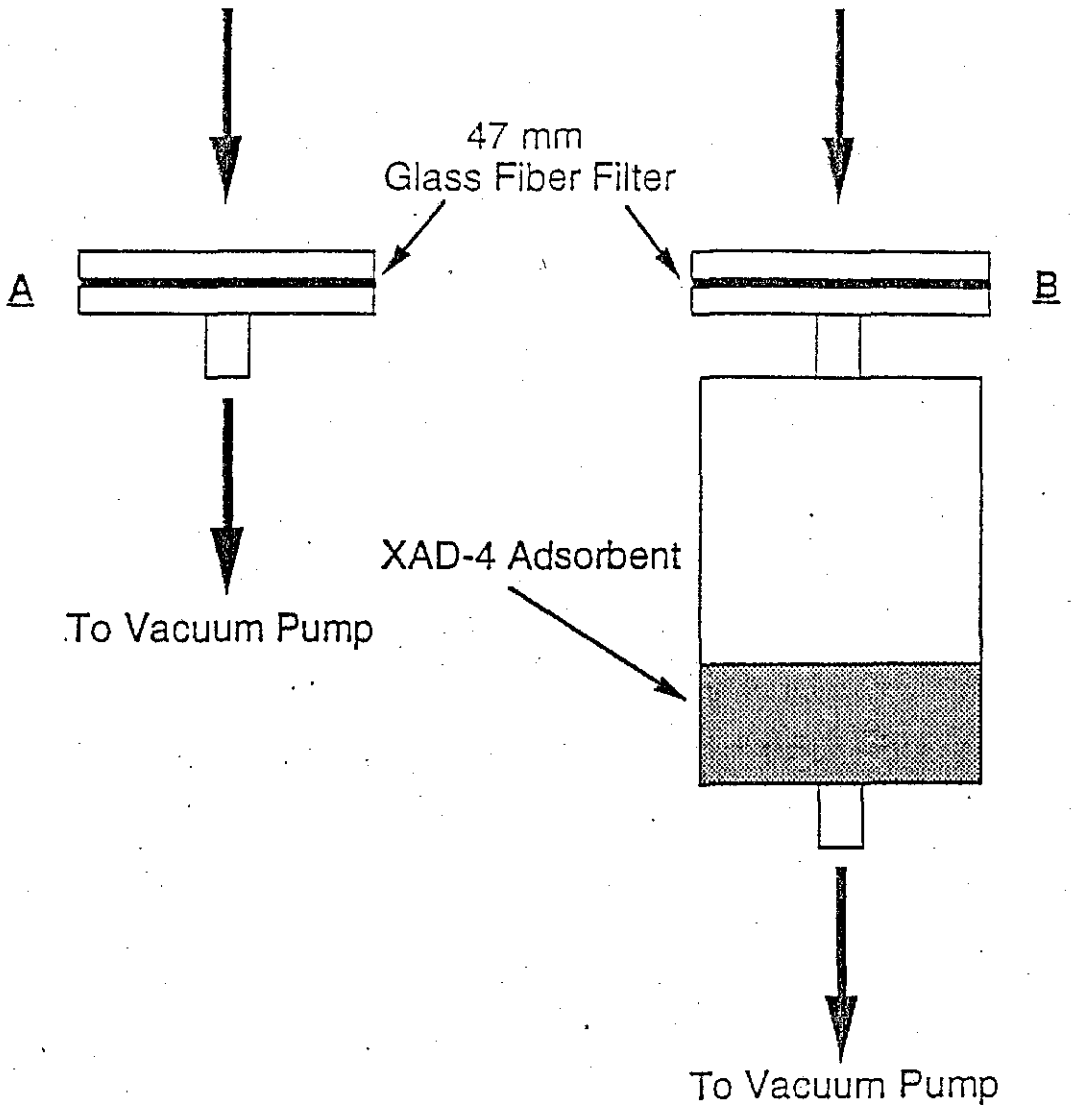


Figure 1. Air sampling apparatus for trapping ziram (A) an mancozeb/ethylenethiourea (B).

spiked samples were placed in the same freezer along with the field samples.

The glass fiber filters containing fungicide residues (whole filters for ziram and half filters for mancozeb) were placed in 22 ml glass headspace vials (Perkin-Elmer, Norwalk, CT), 2 ml iso-octane (Fisher) and 5-10 ml of a mixture of concentrated HCl (37%; Fisher) and 3% (w/v) $SnCl_2$ (Aldrich Chemical Company, Milwaukee, WI) were added to each vial, and the vials were sealed with crimped caps containing Teflon-lined silicone rubber septa (Perkin-Elmer) (Figure 2). The vials were then placed in an oven heated to 80°C and after an hour were removed and allowed to cool to room temperature; during cooling and just prior to removing the caps, the vials were shaken to help partition the CS_2 into the iso-octane layer. After the caps were removed, the iso-octane layer was pipetted into screw cap sealed 4 ml vials, 2 ml distilled water was added, and the vials were sealed and shaken vigorously to wash the iso-octane.

Residues of CS_2 in iso-octane were chromatographed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 30 m x 0.53 mm (id) DB-1 megabore fused silica column (J&W Scientific) and a flame photometric detector (FPD) in the sulfur mode (394 nm filter). The carrier gas (helium) flow was set at about 4.5-5.0 ml/min, and the column, injection port, and detector temperatures were set at 45°C, 120°C, and 230°C, respectively. Carbon disulfide retention time typically fell in the range 1.8-2.3 min, as determined by injections of pure carbon disulfide (Aldrich) dissolved in iso-octane; iso-octane eluted as a misshapened peak beginning about 4 min after injection. Residues were determined by comparing instrument responses with those of standard injections. Carbon disulfide standards for quantitation were prepared by spiking a series of

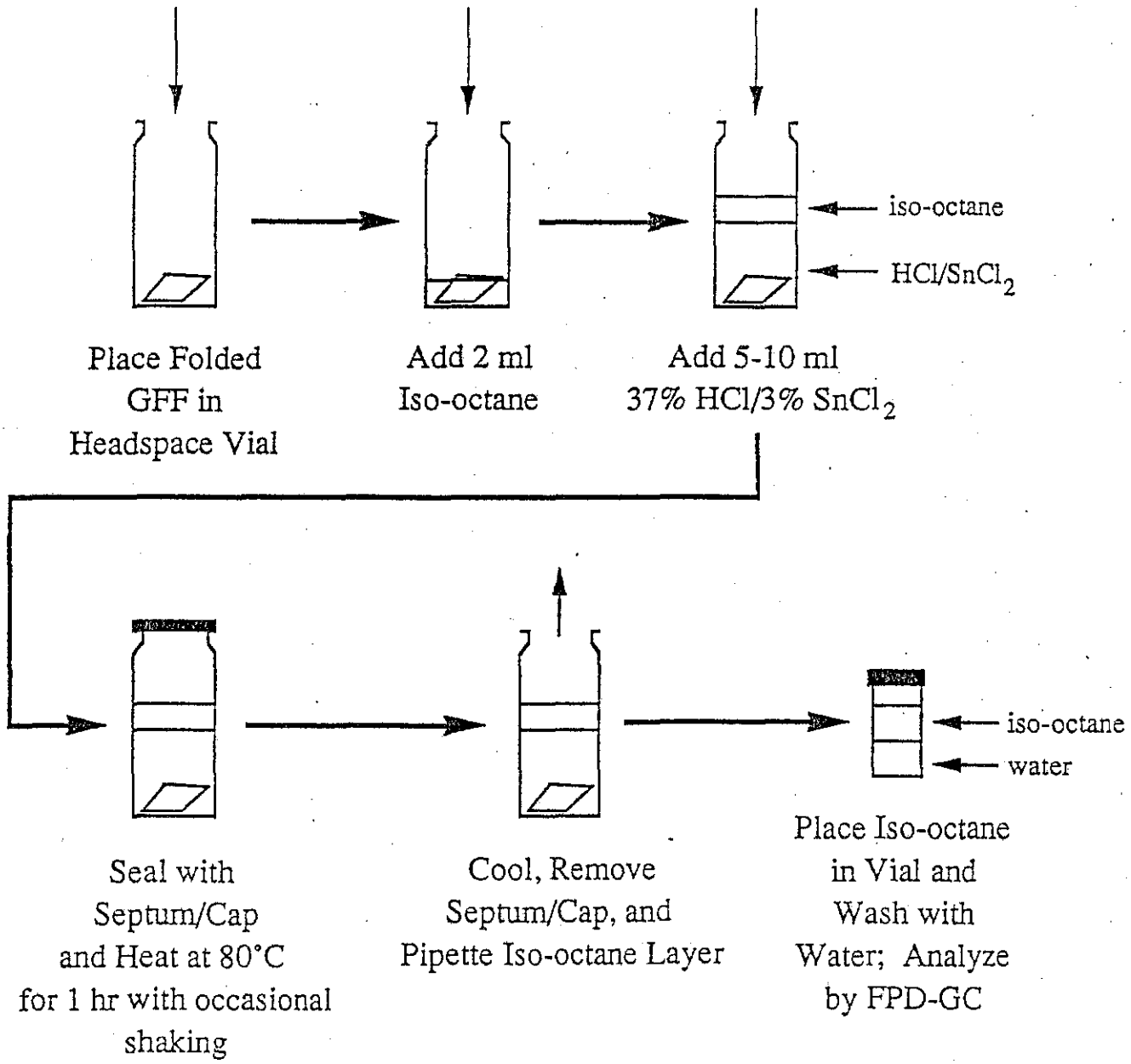


Figure 2. Sample preparation scheme for analysis of dithiocarbamate fungicides ziram and mancozeb trapped on glass fiber filters.

clean glass fiber filters with varying amounts of the fungicides dissolved in suitable solvents and treating the spiked filters using the procedure described for the preparation of the field samples for analysis. Typical chromatograms are shown in Figure 3.

The remaining halves of the mancozeb filters were placed in 4 ml vials, 2 ml ethyl acetate was added to each vial, the vials were sealed, and extraction of the filters was allowed to proceed under ambient conditions for 30-60 min with intermittent shaking. The extracts were determined using a Hewlett-Packard 5890 gas chromatograph equipped with a 30 m x 0.53 mm (id) DB-5 FSOT at 200°C and a nitrogen-phosphorus thermionic detector (NPD) at 230°C. Chromatograms of the field samples were compared with those of filters spiked with ETU standard (in methyl alcohol) and extracted in the same way as the field samples.

To determine the stability of ETU and EU on glass fiber filters during air sampling, filters were spiked with either 8.9 μg ETU or 10.1 μg EU and air was pulled through the filters at 15 liters/min over a 90 min period at 23°C. The filters were then carefully folded, placed in screw-cap vials, 4 ml ethyl acetate was added to each vial, and the filters were extracted over a 30-60 min period with intermittent shaking. Extracted residues were determined using NPD/GC with the DB-5 column at 200°C (ETU) or at 170°C (EU).

To determine ETU recovery from XAD-4 adsorbent, 30 ml of the adsorbent was spiked with 17.8 μg ETU in methyl alcohol and the adsorbent was extracted three times with 50 ml methyl alcohol, 20 min per extraction, using a rotary shaker. The extracts were combined, taken to dryness on a rotary evaporator, the residue was dissolved in 2 ml distilled water, the aqueous mixture was transferred to a 15 ml centrifuge tube, and

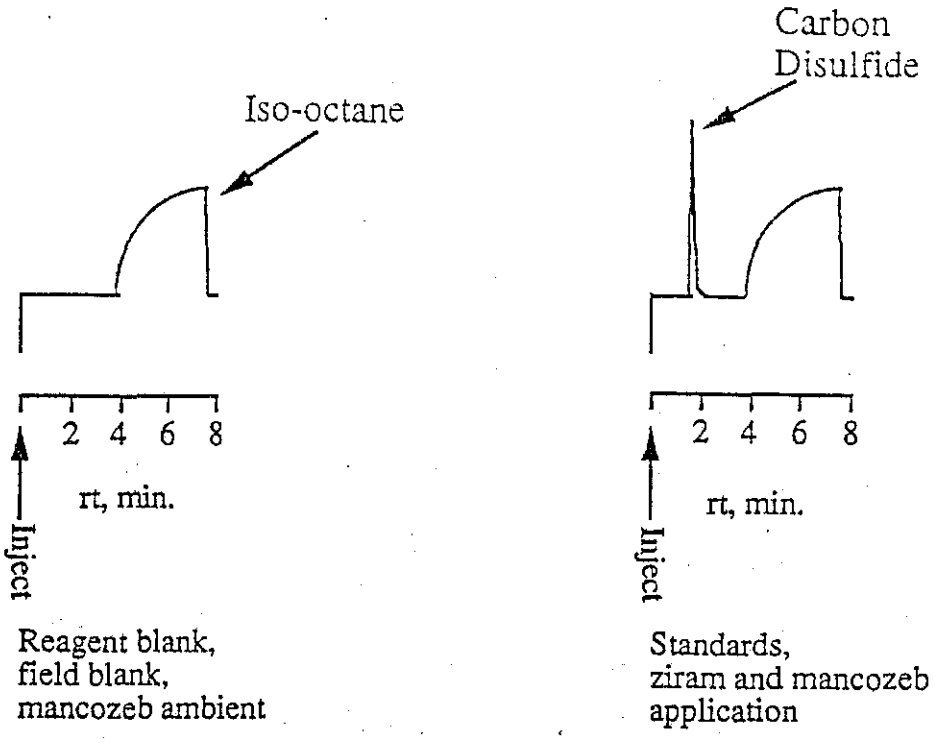


Figure 3. Gas chromatograms of carbon disulfide derived from ziram and mancozeb fungicide field samples, including standards and blanks.

excess anhydrous sodium sulfate was added to the aqueous mixture. This mixture was then extracted with 4 ml ethyl acetate by vigorously vortexing the mixture for 0.5-1 min and the extract was analyzed for ETU using NPD/GC. In a related test, 89 µg ETU was added to 50 ml ethyl acetate and the solution concentration was checked against a 1.78 ng/µl ETU standard using NPD/GC. About 30 ml XAD-4 adsorbent was added to this solution, the solution was swirled briefly, and the ETU concentration was determined again as the time = 0 value. Subsequent determinations were made at 5, 10, 15, 45, 78, 120, 175, 238, 294, 354, 419, 476, and 1406 min, and each determination was compared to ETU in solvent without the adsorbent.

Three 30 ml portions of XAD-4 were each spiked with 17.8 µg ETU and the spiked adsorbent samples were extracted for 5, 30, and 60 min with methyl alcohol containing 3-4% (v/v) glacial acetic acid. The alcohol/acid extracts were reduced to 2-3 ml on a rotary evaporator, the concentrate was transferred to a 15 ml centrifuge tube, enough sodium carbonate was added to the concentrate to neutralize the acetic acid, and the neutralized concentrate was extracted with 4 ml ethyl acetate by vigorously vortexing the mixture for 0.5-1 min. The ethyl acetate extract was analyzed using NPD/GC and extract recovery was compared to the recovery for 17.8 µg ETU spiked just to the methyl alcohol/acetic acid mixture (no XAD-4).

The XAD-4 adsorbent was spiked directly with 17.8 µg ETU, air was pulled through the adsorbent for 2 hours at 15 liters/min, and the adsorbent was extracted by swirling for <5 min using the methyl alcohol/acetic acid mixture. Glass fiber filters were spiked at the same level with ETU and air was pulled through the filters at the same flow rate and duration, with 30 ml aliquots of XAD-4 adsorbent downstream of the

filters. The filters were extracted as described above and the adsorbent was extracted by swirling for <5 min using the alcohol/acid mixture. In a third scenario, glass fiber filters were spiked with 17.8 μg ETU and air was pulled through the filters (15 liters/min, 2 hours), then through 30 ml aliquots of XAD-4 adsorbent, and finally through impingers containing either 100 ml methyl alcohol or 100 ml distilled water. Impingers containing either the alcohol or water were spiked directly with ETU and air was pulled through them to determine the suitability of the solvents for trapping and holding ETU. The alcohol was prepared for analysis using the method described above, while the water was saturated with sodium sulfate and passed through a 3 cc cyclohexyl solid phase extraction cartridge (Varian, Sunnyvale, CA), which was subsequently eluted with 4 ml ethyl acetate. Recovered ETU and related residues were determined using NPD/GC.

The suitability of impingers for trapping ETU/EU from air was investigated by filling a 125 ml glass impinger (#7542, Ace Glass, Inc., Vineland, NJ) with either 50 ml distilled water or 20 ml ethylene glycol (EG) and spiking with ETU in the range 0.28-5.65 μg. In stability/recovery tests, the impinger was operated at 10-11 liters/min for 2-4 hours, with the impinger at room temperature. The spiked water samples were prepared for analysis using the method of Singh et al. (1979), where acetonitrile (ACN, Baxter, MacGaw Park, IL) was added to 10% of the water volume and the water/ACN mixture was extracted with 15 ml methylene chloride (Baxter) containing 1.5-2.0 μl dichloroacetic anhydride (DCAA, Aldrich). The spiked EG samples were prepared for analysis by diluting the EG with 70 ml saturated aqueous sodium sulfate (Fisher Scientific, Fair Lawn, NJ) and extracting the mixture with 15-20 ml

methylene chloride containing 2.0 µl DCAA. The water and EG samples were extracted by shaking vigorously for 2 min, with frequent venting; the methylene chloride layer was allowed to separate for 3-5 min, then it was drained into a 20 ml vial, taken just to dryness under a stream of dry nitrogen, and the residues were dissolved in 1-5 ml of ethyl acetate (Baxter). Recovery of EU from EG was investigated by spiking 20 ml aliquots of EG with 5 µg EU, adding 1-2 ml methylene chloride containing 20 µl of either DCAA or dichloroacetyl chloride (DCAC, Aldrich), and shaking vigorously for 2 min. The treated EG was then diluted with 70 ml saturated aqueous sodium sulfate and extracted with 20 ml methylene chloride. The recovered derivatized residues were determined by gas chromatography using a Hewlett-Packard Series II gas chromatograph equipped with a 30 m x 0.32 mm (id) HP-5 FSOT column and an NPD. The injector and detector temperatures were 180°C and 230°C, respectively; the column was held at 150°C for 4 min, then it was heated at 10°C/min to 200°C, where it was held for 5 min. Derivatization was confirmed by gas chromatography/mass spectrometry (GC/MS) using a Varian Model 3400 gas chromatograph (Varian Instruments, Palo Alto, CA), equipped with a 30 m x 0.25 mm (id) FSOT column, coupled to a Finnigan Model SSQ 710 mass spectrometer (Finnigan MAT, San Jose, CA).

Results and Discussion

In order to analyze the dithiocarbamates using gas chromatography, it was necessary to reproducibly convert ziram and mancozeb into a volatile component that could be used to represent the mass of material

trapped from air. We found a method in the literature that showed much promise by utilizing the dithiocarbamate synthetic pathway to produce volatile carbon disulfide (CS_2). To produce dithiocarbamates, CS_2 undergoes a nucleophilic attack at the carbon atom by secondary amines in alkaline medium. Using zinc cation in combination with dimethyl amine, and zinc and manganese cations with nabam (sodium salt of the reaction product of CS_2 and ethylene diamine), the ziram and mancozeb fungicides, respectively, are formed (Figure 4). To get back to CS_2 for fungicide analysis, the fungicides may be treated with concentrated hydrochloric acid (HCl) containing about 3% stannous chloride ($SnCl_2$) (Maini and Boni, 1986). This conversion to CS_2 takes place because in concentrated chloride divalent tin exists as a trichloro species which is a mild reducing agent:

$$SnCl_2 + Cl^- \text{-----}> Sn^{II}Cl_3^- + 3Cl^- \text{-----}> Sn^{IV}Cl_6^{-2} + 2e^-$$

We utilized this reaction to determine ziram and mancozeb trapped on glass fiber filters by sealing the filters in glass vials along with the concentrated $HCl/SnCl_2$ mixture and iso-octane and heating the contents to promote conversion to CS_2. Since CS_2 is much more soluble in oils and hydrocarbon solvents than in aqueous media, it would partition into the iso-octane layer which could then be analyzed directly by gas chromatography. Under the gas chromatographic conditions of this study, the lower volatility of iso-octane assured its clean separation from the CS_2 analyte.

We investigated the use of electron-capture and flame photometric (FPD) detectors in combination with 30 m x 0.53 mm (id) DB-1 and DB-5 FSOT columns for the analysis of the carbon disulfide evolved from ziram and mancozeb. We found that best results were obtained with the FPD in combination with a DB-1 FSOT column. For analysis of ethylenethiourea,

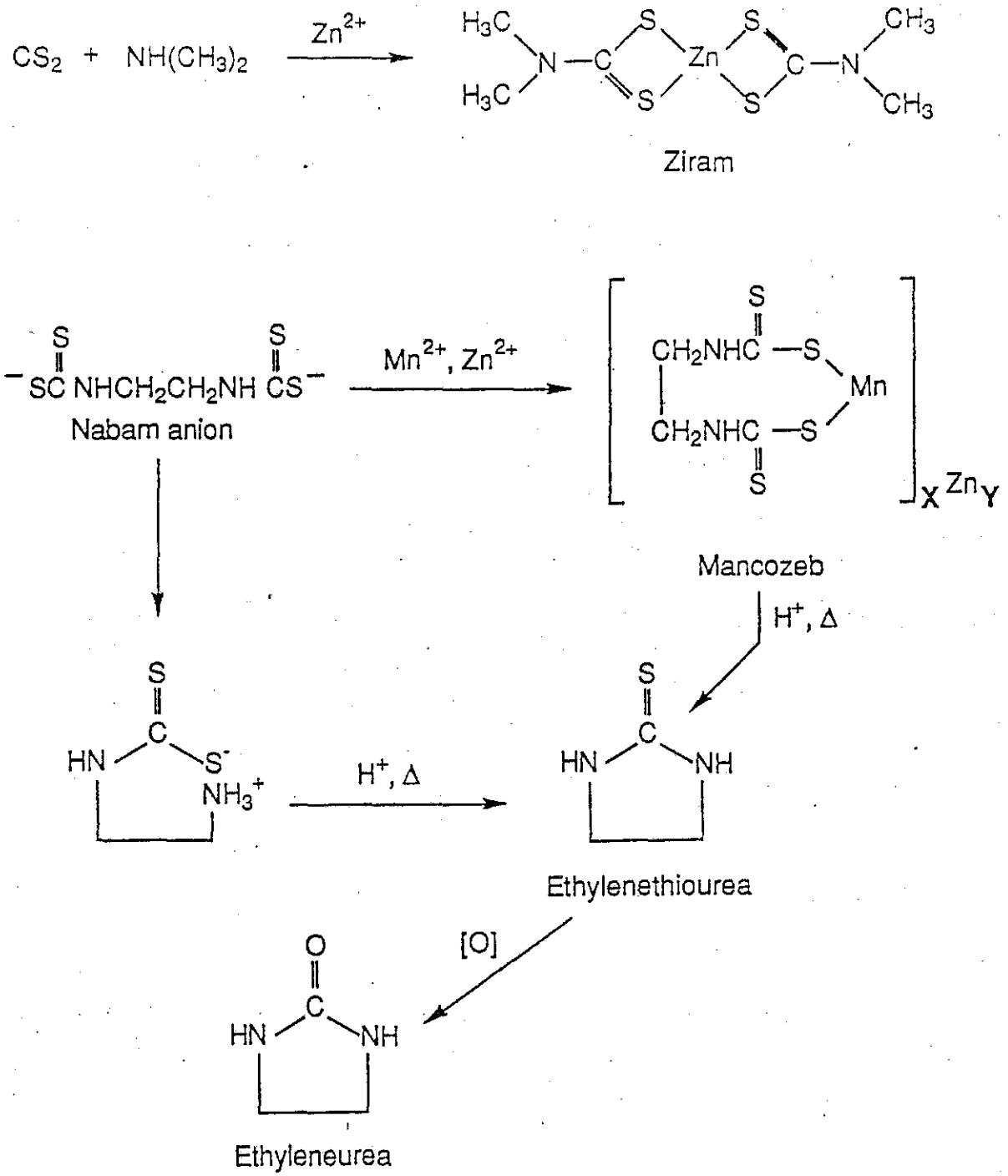


Figure 4. Synthesis of ziram and mancozeb fungicides; ethylenethiourea formation and its oxidation product ethyleneurea.

best results were obtained with a nitrogen-phosphorus detector (NPD) in combination with a 30 m x 0.53 mm (id) DB-5 FSOT.

A ziram standard was prepared in acetone, with some sonication to promote solubility, and a mancozeb standard was prepared in 0.1 M EDTA (tetrasodium salt) without sonication. Dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) were also considered as solvents for mancozeb, since these solvents often solubilize recalcitrant materials where other solvents fail. However, the fungicide proved to be unstable in DMF (no CS_2 standards could be prepared from a DMF solution) and DMSO interfered with CS_2 determination. The EDTA solution, on the other hand, appeared to be stable, and CS_2 standards could be readily prepared. Since some breakdown of mancozeb to ETU will occur in water (a few percent within 24 hours), it is recommended that the CS_2 standards be prepared soon after mancozeb has completely dissolved in the EDTA solution.

To prepare solutions of CS_2 to be used as standards for FPD/GC quantitation, varying amounts of fungicide standards were spiked to clean glass fiber filters and the spiked filters were treated with 37% HCl/3% $SnCl_2$ to produce CS_2. For ziram, the range of spiking levels was 0.48-17.3 μg, while the range for mancozeb was 0.47-20.5 μg. Stoichiometric considerations indicated that each mole of ziram would produce two moles of CS_2; this means that the evolved CS_2 would represent approximately half the mass of ziram, taking molecular weights into consideration (Figure 5). Similar considerations were not possible for mancozeb, since its composition is not clearly known (Figure 5). However, mass-for-mass mancozeb appeared to yield about half the amount of CS_2 as did ziram not only at the residue level (Figure 6), but also at higher spiking levels (e.g., 6

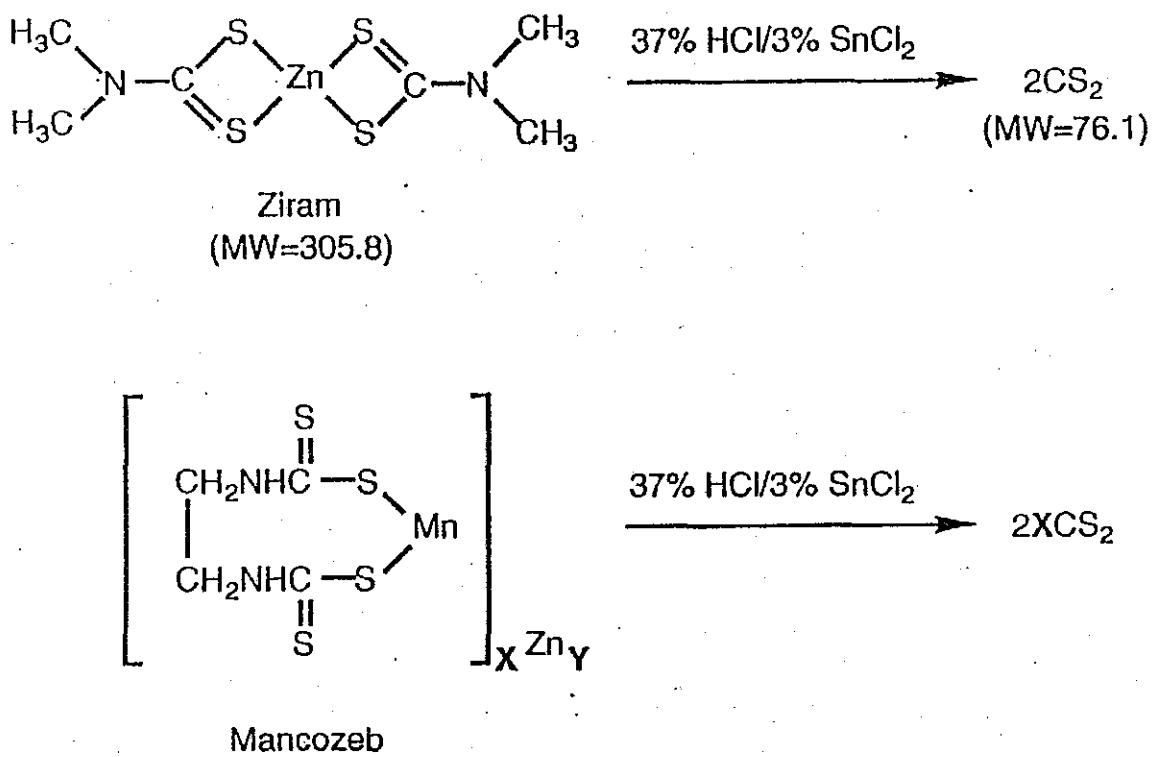


Figure 5. Conversion of ziram and mancozeb to carbon disulfide for analysis.

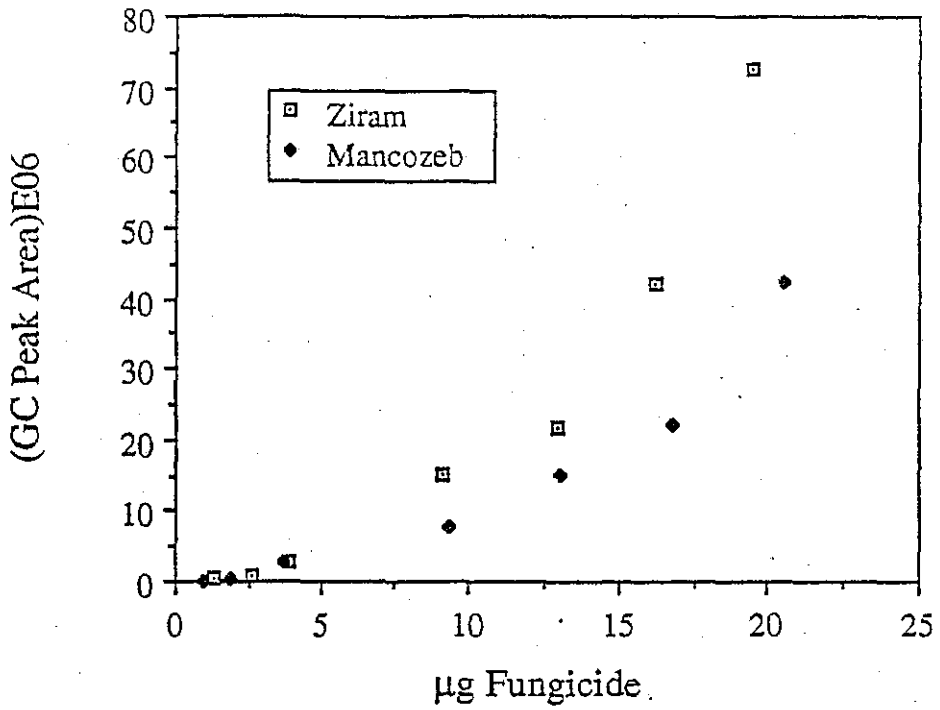


Figure 6. Comparison of ziram- and mancozeb-derived carbon disulfide responses using the flame photometric detector in the sulfur mode.

mg each of the crystalline ziram and mancozeb gave about 3 mg and 1.6 mg CS_2, respectively).

Response of the FPD/GC was typically non-linear for the sulfur mode, showing an exponential increase in response with increasing amount injected (Figure 6). The curves were best described by 2nd- and 3rd-order polynomials. While sulfur-mode FPD/GC is well known to produce an exponential response curve, a complicating factor with the fungicides that might have affected the shape of the response curve was the dependency of CS_2 evolution on the amount of fungicide in the residue. For example, at the milligram level ziram conversion to CS_2 was >90%, about 75-80% at 20 μg, and about 65% at 2-3 μg (Figure 7). Below about 2 μg, we don't know what the conversion efficiency would be. However, to avoid having to factor this varying conversion efficiency into quantitation calculations for the field samples, standard curves were prepared by spiking clean glass fiber filters with standard solutions of the fungicides, and these spikes were prepared for FPD/GC the same as for the glass fiber field samples.

The reaction conditions for synthesizing mancozeb and also the fungicide itself can lead to the formation of ETU under warm hydrolytic conditions (Figure 4). Therefore, the mancozeb formulation can contain traces of this breakdown product to be released to the environment during application and, furthermore, ETU may also form under environmental conditions after mancozeb has been applied. However, it was assumed that any residues of ETU in the environment that might be trapped by glass fiber filters would be fairly low (<1 μg total). Therefore to generate standard curves, we spiked clean glass fiber filters with standards of ETU in methyl alcohol over the range of about 0.2-1.0 μg. Different sets of these spiked filters were extracted with methyl alcohol and ethyl acetate.

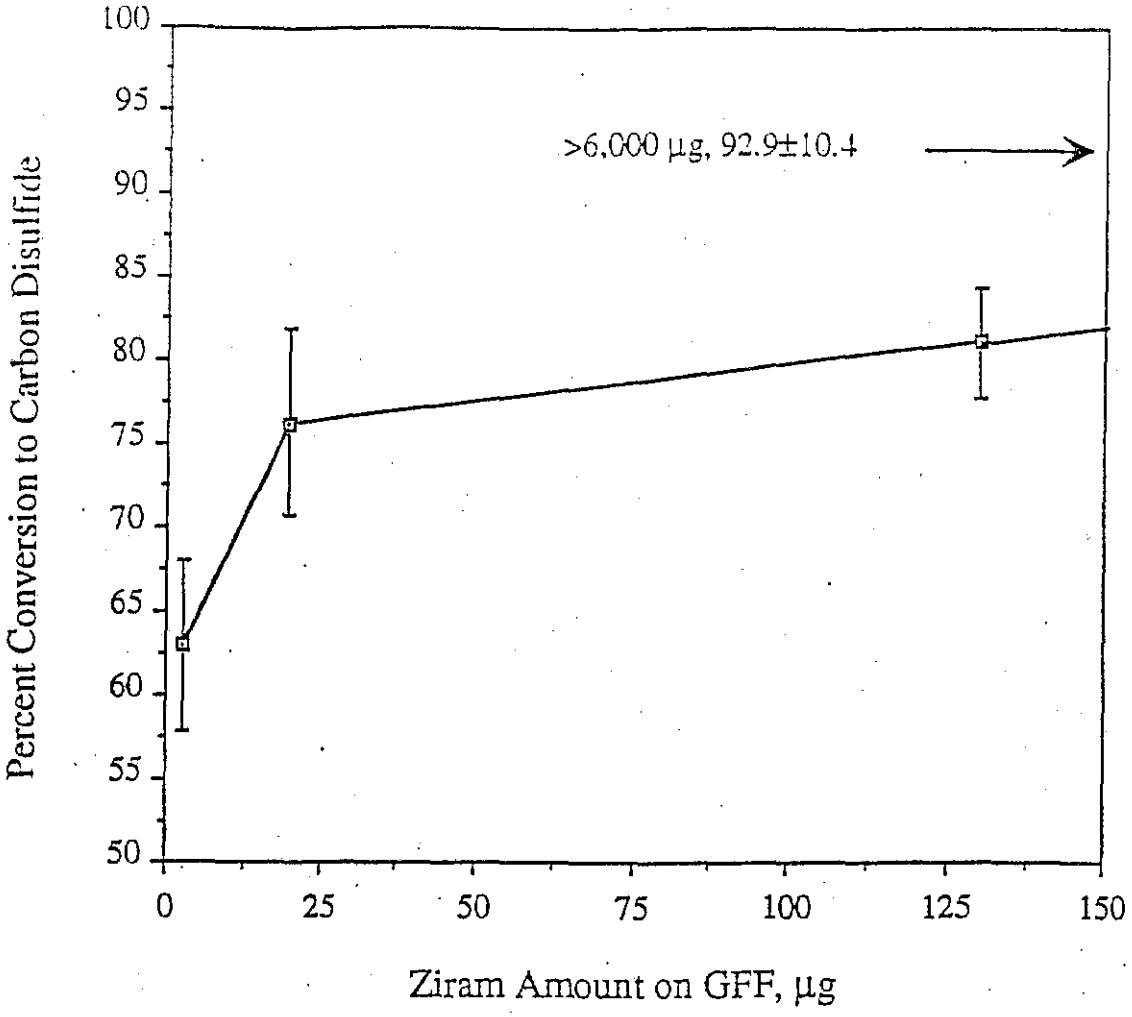


Figure 7. Extent of conversion of ziram to carbon disulfide as related to residue level.

While methyl alcohol was by far the best solvent for ETU residues on filters, we chose ethyl acetate since the alcohol seemed to decrease the sensitivity of the NPD to about half that for ethyl acetate. The standard curves resulting from spiked filters were best described by 2nd- and 3rd-order polynomials (R^2 = 0.998-1.000).

Ziram

Freezer stability. On two different occasions, a set of six glass fiber filters was spiked with 2.6 µg and a set of three glass fiber filters was spiked with 1.04 µg ziram in acetone. The filters were placed in screw cap sealed glass jars and the jars were stored in a freezer at -15°C to -20°C. Two of the 2.6 µg spikes were removed 15 days after storage and analyzed; the remaining 2.6 µg spikes were removed almost two months after storage and analyzed, while all of the 1.04 µg spikes were removed about one month after storage and analyzed. Quantitation was done against the standards used to spike the filters. The results, summarized in Table 1, indicated that ziram is stable in cold storage, for at least two months. The average recovery for all of the 2.6 µg spikes (1993) was 92.4±8.4 %, while the average recovery for the 1.04 µg spikes (1994) was 97.3±2.9%.

Air sampling stability. Pulling air through clean glass fiber filters spiked with standard ziram in acetone resulted in the apparent disappearance of the fungicide (~16% recovered after 24 hours at 15 liters/min [23°C]). Since this compound has a negligible vapor pressure, it was assumed that ziram broke down under air sampling conditions. However, the observed decline of ziram on spiked filters under dynamic flow conditions was an artifact of ziram being dissolved in acetone solvent. Solubilizing dithiocarbamate fungicides, which are metal salt/complexes,

Table 1. Freezer stability of ziram spiked to glass fiber filters.

Sample	Storage time, days	Amount found, µg[a]	Percent recovery
FS-1-1993	15	2.52	96.9
FS-2-1993	"	--b	--b
FS-3-1993	60	2.06	79.2
FS-3-1993	"	2.57	98.8
FS-4-1993	"	2.56	98.5
FS-5-1993	"	2.31	88.8
		Average:	92.4±8.4

[a] Filters spiked with 2.6 µg ziram.
[b] Sample lost.

Sample	Storage time, days	Amount found, µg[a]	Percent recovery
FS-1-1994	30	1.03	99.0
FS-2-1994	"	1.03	99.0
FS-3-1994	"	0.976	93.9
		Average:	97.3±2.9

[a] Filters spiked with 1.04 µg ziram.

often destabilizes them (see Mancozeb below). In contrast to the acetone solution, ziram, suspended (not dissolved) in iso-octane and spiked to glass fiber filters at 7-10 μg per filter, showed an average recovery of 88.2±19.4% (n=6) for an air flow of 15 liters/min for 24 hours. The relatively large uncertainty for iso-octane was due primarily to the difficulty in obtaining reproducible aliquots from the suspension, since iso-octane did not give a true solution. This uncertainty was even more dramatic for hexane, where average recovery was 109±42% for <0.5 μg spiked to glass fiber filters under the same air flow conditions. Although the uncertainty was high for hexane, again due to a lack of good reproducibility in obtaining aliquots from the suspension, the recovery was essentially quantitative for less than one-tenth of the amount used for ziram in acetone (5.6 μg). The conclusions from all of this are as follows: 1) Acetone indeed destabilizes ziram causing breakdown of the complex during simulated air sampling; and 2) non-solvated, but solvent suspended, ziram should be used to determine recovery from spiked filters under dynamic air sampling conditions. The latter would best simulate the field situation.

Field samples. The analytical results for the ziram field application samples are summarized in Table 2. Quantitation was done using an eight-point standard curve, with at least two injections per point. The standard curve spanned the range 0.48-17.3 μg ziram and was described by a 3rd-order polynomial, with a correlation coefficient (r^2) of 1.000. From the standard responses of CS_2, resulting from filters spiked with standard ziram, it was possible to read directly the mass of ziram on each filter. The minimum detection limit (MDL) was about 0.3 μg ziram (equivalent to about 167 ng/m^3 in air, assuming a flow rate of 15 liters/min

Table 2. Analysis of glass fiber filters for ziram fungicide residues trapped during application.

Sample ID #	LOG #	Ziram/GFF, µg
0W	1	<MDL*
0S1	2	<MDL
0S2	3	<MDL
0E	4	<MDL
0N	5	<MDL
1W	6	0.647
1S1	7	1.80
1S2	8	1.80
1E	9	8.30
1N	10	9.98
1B	11	<MDL
2W	12	<MDL
2S1	13	<MDL
2S2	14	<MDL
2E	15	<MDL
2N	16	1.65
3W	17	<MDL
3S1	18	<MDL
3S2	19	<MDL
3E	20	<MDL
3N	21	0.831
4W	22	<MDL
4S1	23	<MDL
4S2	24	<MDL
4E	25	<MDL
4N	26	0.325
5W	27	0.488
5S1	28	0.455
5S2	29	0.422
5E	30	0.688
5N	31	0.729
6W	32	0.442
6S1	33	0.455
6S2	34	0.303
6E	35	0.411
6N	36	0.343
7W	37	<MDL
7S1	38	<MDL
7S2	39	<MDL
7E	40	<MDL
7N	41	0.312

*MDL= 0.3 µg Ziram/GFF (equivalent to ~167 ng/m^3 at 15 liters/min for 2 hours).

for two hours, or about 14 ng/m^3 in air for a 24 hour sampling period at the same flow rate). All sample and standard chromatograms appeared to be "clean", meaning that only the CS_2 and iso-octane peaks were evident (Figure 3). When ziram levels were less than the MDL, the chromatograms were essentially flat lines up to iso-octane elution.

While ziram concentrations declined rapidly during the day of application, measurable residues persisted up to the fourth day (Figure 8). This approximate hyperbolic function reflected the rapid settling of particles with diameters greater than 10 μm. If these data are plotted as Ln (average concentration [detectable residues]) vs sampling period (Figure 9, the point for sampling period 4 appeared to be an outlier and was omitted from the plot), extrapolation indicated that the minimum detection limit (<14 ng/m^3) would be reached after about 7 sampling periods (4 days). These results imply that residues remained suspended and/or deposited residues were re-suspended as a result of wind erosion (wind speed varied between <1-6 mph [<0.45-2.7 meters/sec] during the sampling periods). Taking into consideration the settling velocities of particles of varying diameters, residues that could remain suspended in air for a prolonged period of time, or could be re-suspended by wind erosion, would probably have average diameters <1 μm (e.g., assuming a height of about 300 cm, a 1 μm particle would settle out in about 24 hours in still air). However, persistent breezes may be capable of suspending particulates of greater average diameters. In any case, ziram residues remaining in air would no doubt be respirable and thus be available to workers and residents in a region of use.

Audit spikes. Analytical results for the seven audit spikes are summarized in Table 3, where quantitation was done using ziram standards

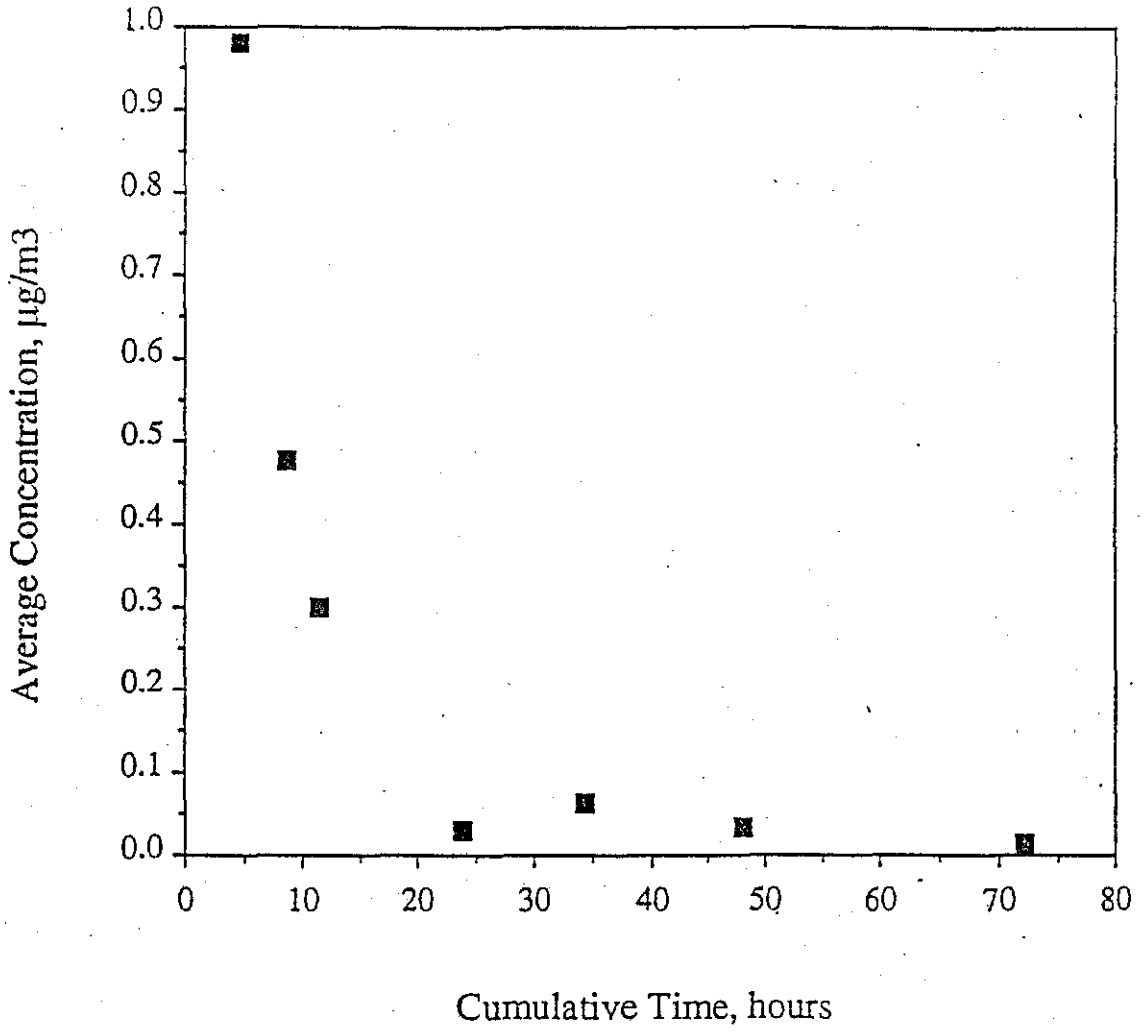


Figure 8. Decline of ziram residues in air following application.

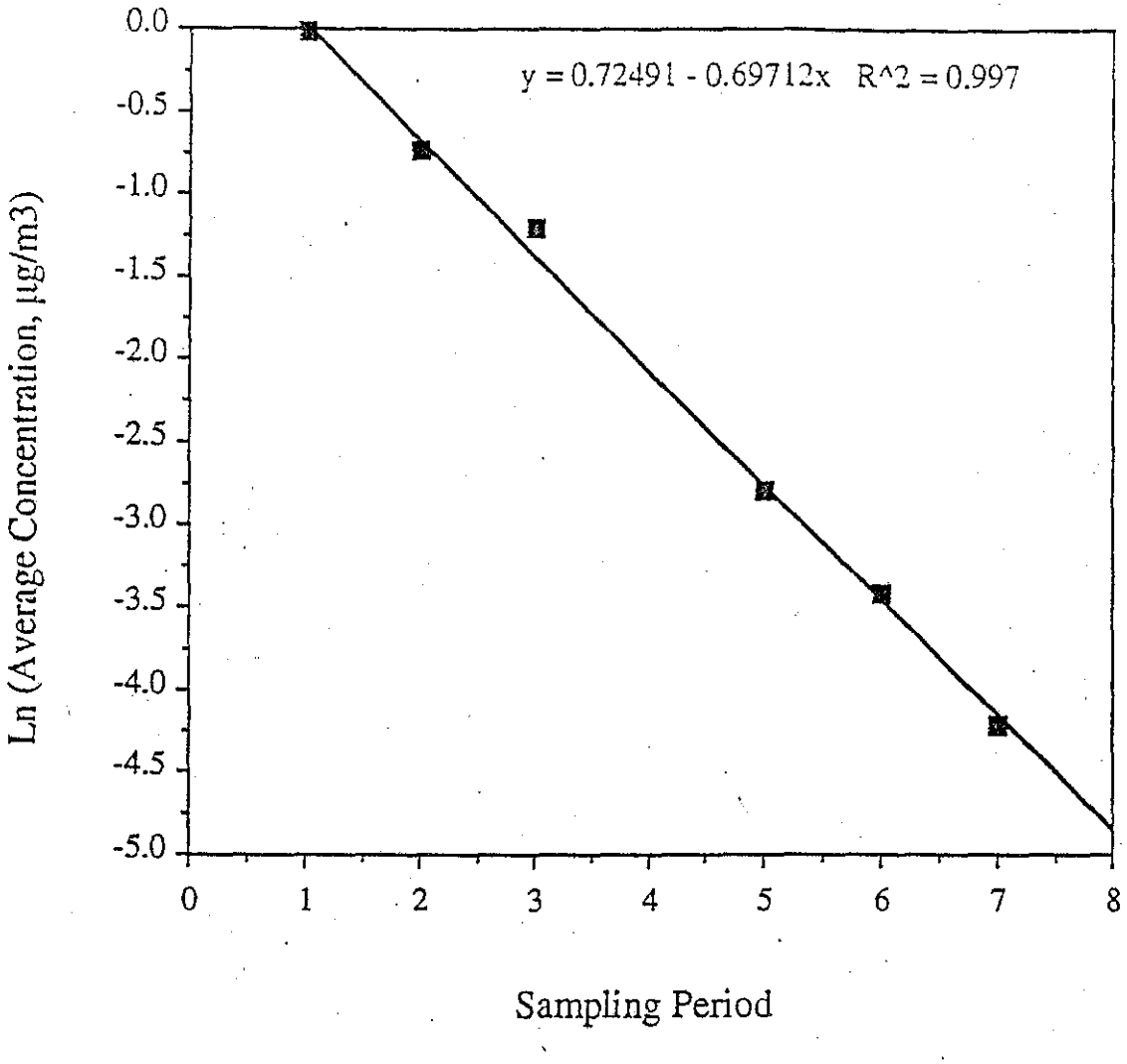


Figure 9. Ziram concentration in air vs the sampling period.

Table 3. Analysis of glass fiber filters spiked with standard ziram in acetone.

CARB samples	Amount, µg
ZRM-1	5.05 (101%)*
ZRM-2	1.01 (101%)
ZRM-3	2.10 (105%)
ZRM-4	5.89 (118%)
ZRM-5	3.00 (100%)
ZRM-6	<MDL†
ZRM-7	1.02 (102%)

*Recovery relative to intended spike.
†0.3 µg ziram.

in acetone. Results are listed as single determinations of each spiked sample. Compared to the intended spikes, analytical results fell in the range 100-118% (the average percent difference between found and intended residues was about +4.5%). Except for the one high point, these results are encouraging in light of the fact that the audit spikes were prepared by CARB personnel using a certified standard obtained from a chemical supplier, while analyses were done using a standard prepared by UN Reno personnel.

Mancozeb

Freezer stability. After spiking three glass fiber filters each with 9.32 μg mancozeb in 0.1 M EDTA, they were sealed in glass jars and then stored in a -20°C freezer. About two weeks later, the samples were removed and analyzed by comparing instrument response against that for the standard used to spike the filters. Average recovery fell in the range 15-20%, indicating that the chelated fungicide, at least, was not stable in cold storage. The freezer stability study was repeated by spiking clean filters with 5.7 μg mancozeb suspended in methyl alcohol, without chelation. These filters were analyzed after storing in a -20°C freezer for almost two weeks and the average recovery was 97.0±2.7%.

Air sampling stability. Non-chelated, solvent-suspended mancozeb on clean glass fiber filters appeared to be stable under air sampling conditions (15 liters/min, 23°C). Average recovery for about 6 μg after 24 hours of air flow was 100.9±5.4%.

Field samples. Analytical results for the mancozeb application and ambient field samples are summarized in Tables 4 and 5, respectively. Quantitation was done using standard curves generated each day mancozeb

Table 4. Analysis of glass fiber filters for mancozeb fungicide residues trapped during application.

Sample ID#	LOG #	Total Mancozeb, µg
0S-1	1	<MDL*
0S-2	2	"
0N	3	"
0E	4	"
1N	5	"
1S-1	6	1.99
1S-2	7	2.72
1E	8	1.34
2N	9	<MDL
2S-1	10	"
2S-2	11	"
2E	12	"
2B	13	"
3N	14	1.00
3S-1	15	1.20
3S-2	16	<MDL
3E	17	2.86
4N	18	<MDL
4S-1	19	0.931
4S-2	20	1.59
4E	21	0.522
5N	22	0.593
5S-1	23	1.41
5S-2	24	2.42
5E	25	<MDL
6N	26	4.58
6S-1	27	2.60
6S-2	28	3.10
6E	29	3.76
7N	30	<MDL
7S-1	31	1.82
7S-2	32	2.44
7E	33	0.890

*0.5 µg mancozeb (equivalent to ~278 ng/m^3 at 15 liters/min for 2 hours).

Table 5. Analysis of glass fiber filters for mancozeb fungicide residues trapped during ambient sampling.

Sample ID#	LOG #	Total M. µg	Sample ID#	LOG #	Total M. µg
1V	1	<MDL*	6V	32	<MDL
1L	2	"	6BF	33	"
1M	3	"	7E	34	"
1E-1	4	"	7L-1	35	"
1E-2	5	"	7L-2	36	"
2V	6	"	7V	37	"
2L	7	"	7BF	38	"
2M	8	"	8E	39	"
2E-1	9	"	8L-1	40	"
2E-2	10	"	8L-2	41	"
2B	11	"	8V	42	"
3V	12	"	8BF	43	"
3L	13	"	9E	44	"
3M	14	"	9V1	45	"
3E-1	15	"	9V2	46	"
3E-2	16	"	9L	47	"
4V	17	"	9BF	48	"
4L	18	"	10E	49	"
4M	19	"	10V1	50	"
4E-1	20	"	10V2	51	"
4E-2	21	"	10L	52	"
5V	23	"	10BF	53	"
5L-1	24	"	11E	54	--§
5L-2	25	"	11V1	55	<MDL
5E	26	"	11V2	56	"
5BF	27	"	11L	57	"
5B	28	"	11BF	58	"
6E	29	"	12E	59	"
6L-1	30	"	12BF	63	"
6L-2	31	"			

*0.5 µg mancozeb (equivalent to ~23 ng/m^3 at 15 liters/min for 24 hours).
§Initial analysis showed mancozeb to be less than the MDL; subsequent analysis showed mancozeb to about 6.5 µg. This was probably due to contamination.

analysis was performed. These standard curves typically spanned the range 0.5-10 μg mancozeb and were described by 2nd- and 3rd-order polynomials, with correlation coefficients (r^2) of 0.99-1.00. From the standard responses of CS_2, as related to standard mancozeb spikes, it was possible to read directly the mass of mancozeb on each filter. The MDL was about 0.5 μg mancozeb (equivalent to about 278 ng/m^3, assuming a flow rate of 15 liters/min for two hours, or about 23 ng/m^3 for a 24 hour sampling period at the same flow rate). As was the case for ziram, the mancozeb chromatograms did not display any peaks other than the ones for CS_2 and iso-octane (Figure 3).

While mancozeb residues were less than the MDL in the pre-application samples, as would be expected, residues greater than the MDL were detected in almost every sampling period thereafter (during and post-application), and residues were consistently detected in the later sampling periods (Table 4). This latter result may have been due to wind erosion of dried, deposited residues. However, no ambient sample showed residues above the MDL, except for one sample (11E, #54) which may have been contaminated (Table 5). Because of this one sample, we spot-checked every 10th sample which again showed no residues above the MDL.

While concentrations declined rapidly during the day of application, measurable residues persisted up to the fourth day (Figure 10). If these data are plotted as Ln (average concentration [detectable residues]) vs sampling period (Figure 11), extrapolation indicated that the minimum detection limit (<25 ng/m^3) would be reached only after about 10-11 sampling periods (6-7 days), assuming field conditions remained the same. These results imply that residues remained suspended and/or deposited residues were re-suspended as a result of wind erosion (wind speed varied

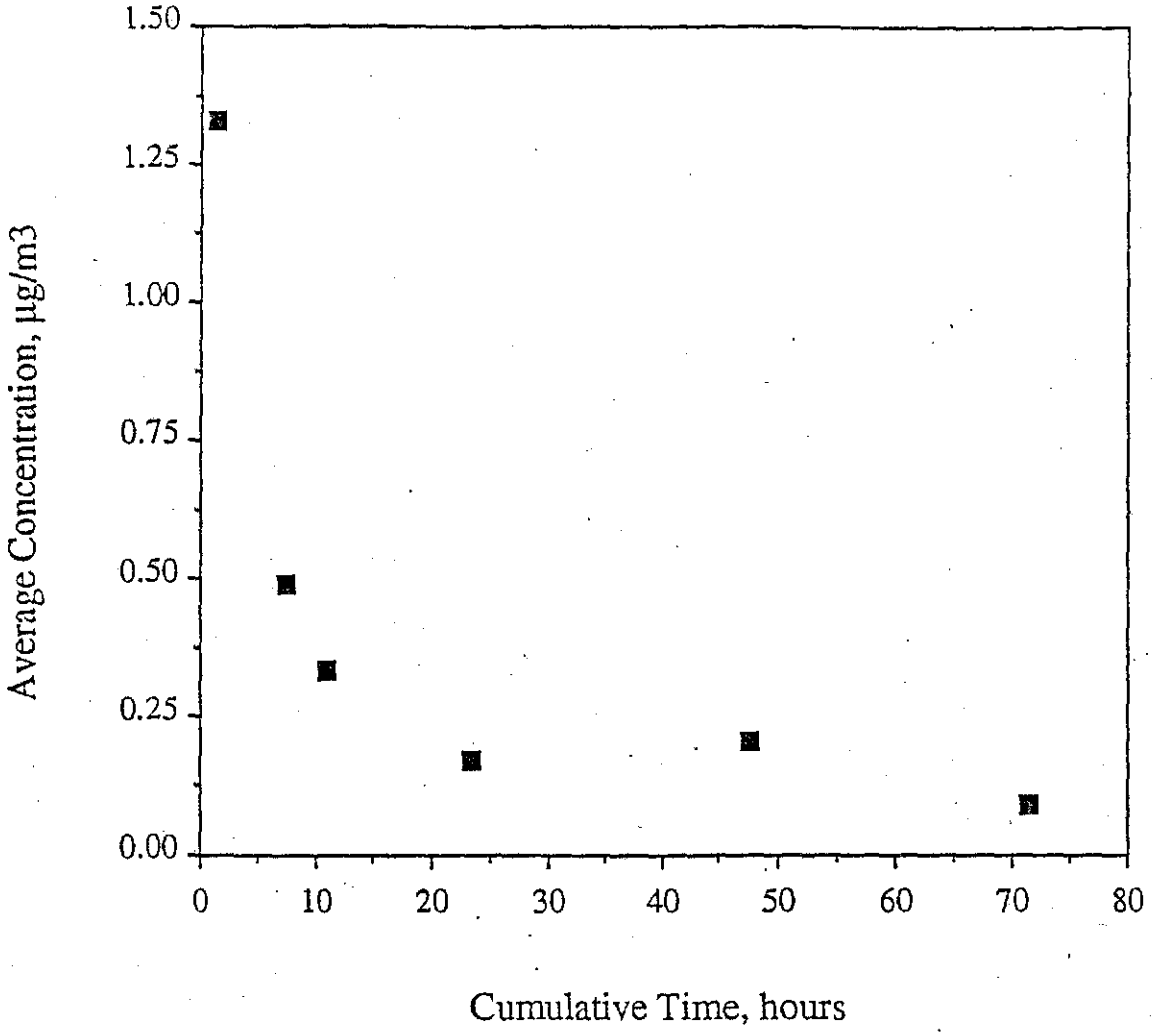


Figure 10. Decline of mancozeb residues in air following application.

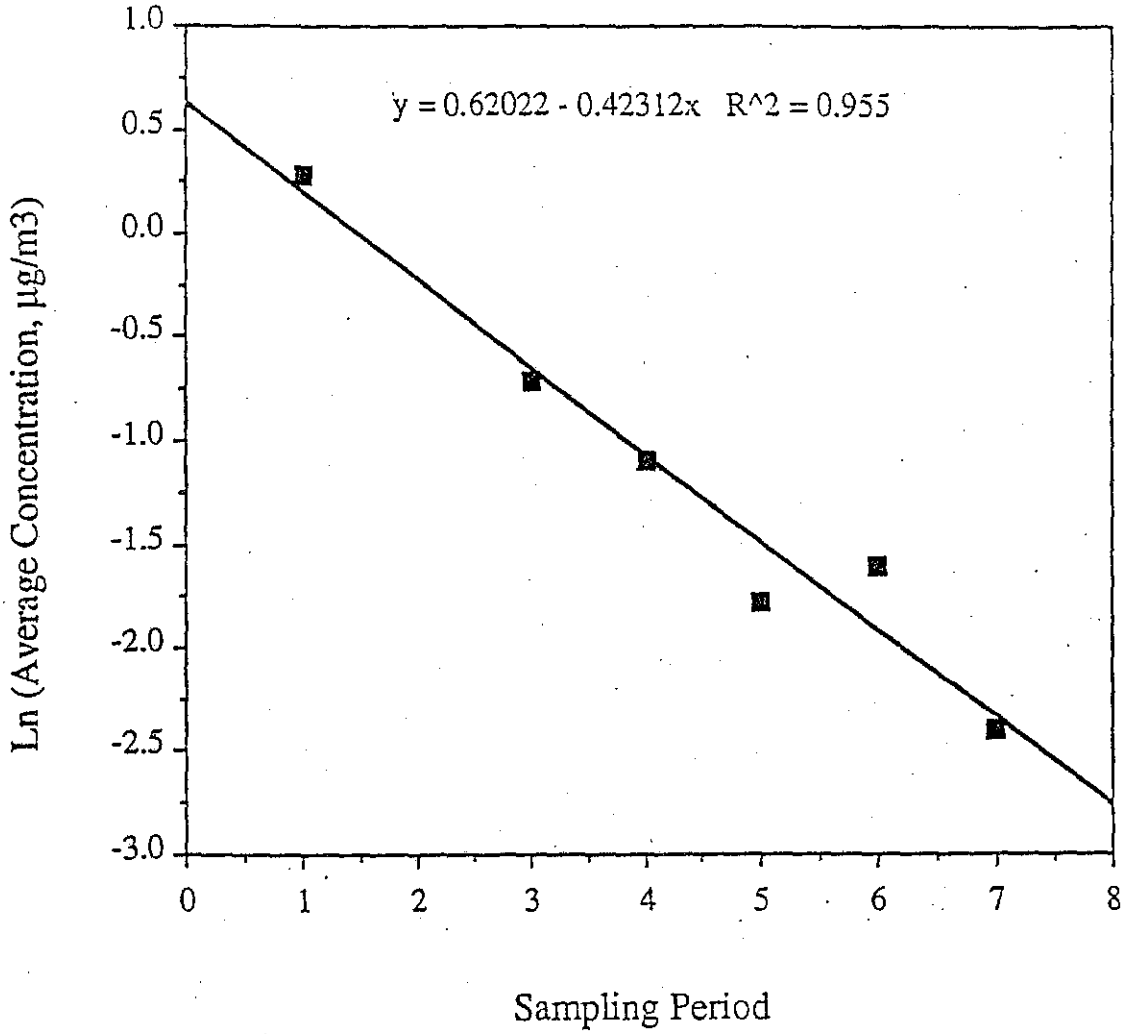


Figure 11. Mancozeb concentration in air vs the sampling period.

between 2-8 mph [0.9-3.5 meters/sec] during the sampling periods). Taking into consideration the settling velocities of particles of varying diameters, residues that could remain suspended in air for a prolonged period of time, or could be re-suspended by wind erosion, would probably have average diameters <1 μm. However, persistent breezes may be capable of suspending particulates of greater average diameters. In any case, mancozeb residues remaining in air would no doubt be respirable and thus be available to workers and residents in a region of use.

Audit spikes. Analytical results for the audit spikes are summarized in Table 6, where quantitation was done using mancozeb standards in 0.1 M EDTA; results are listed as averages (±SD) of at least two determinations. Compared to the intended spikes, analytical results fell in the range 83-101%. A standard curve derived from the standard provided by CARB compared well with a standard curve derived from a UC Davis standard (Figure 12), indicating that either standard would have been suitable for quantitation. The filters arrived still obviously wet from spiking; it is possible that, in some cases, losses to the container walls may have occurred. Immediately after arrival, the containers were opened and the first four samples were folded and inserted into reaction vials. The remaining samples, however, were removed from their containers and suspended to avoid further contact with any surfaces and allowed to air dry; they were then folded and inserted into reaction vials. In the future, this latter technique would probably be a better way to prepare audit spikes, or by spiking filters already inserted into reaction vials.

Table 6. Analysis of glass fiber filters spiked with standard mancozeb in 0.1 M EDTA.

CARB samples	Amount (±SD), µg
MNB-1	9.20±0.16 (92%)†
MNB-2	4.68±0.04 (94%)
MNB-3	<MDL*
MNB-4	5.05±0.03 (101%)
MNB-5	2.54±0.11 (85%)
MNB-6	8.26±0.06 (83%)
MNB-7	<MDL*
MNB-8	2.64±0.11 (88%)

†Recovery relative to intended spike.

*0.5 µg mancozeb.

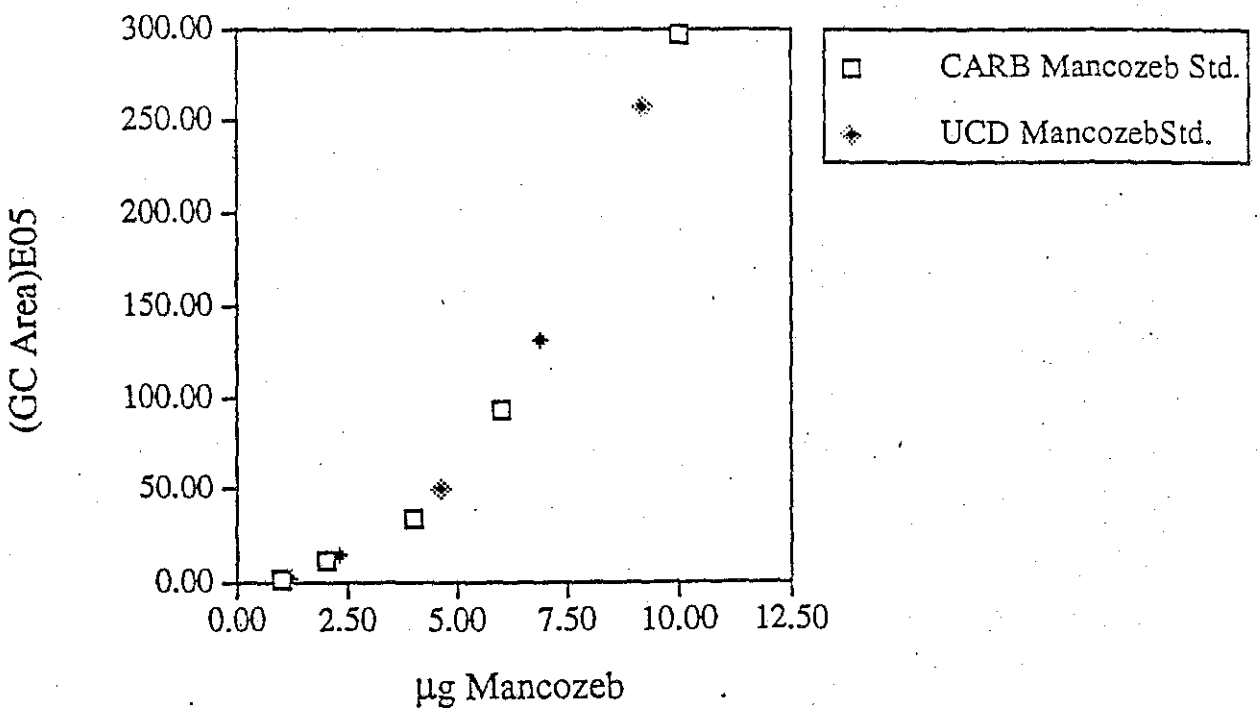


Figure 12. Comparison of standard curves derived from CARB and UCD mancozeb standards.

Ethylenethiourea (ETU)

Freezer stability. Three glass fiber filters were each spiked with 10.7 µg ETU in methyl alcohol, the filters were placed in screw cap sealed glass jars, and the jars were stored in a freezer at -20°C. After at least two months, the samples were removed from the freezer and analyzed; quantitation was done against the standard used to spike the filters. Average recovery was 89.7±5.7%. Samples of clean XAD-4 polymeric adsorbent were also spiked with ETU and placed in the freezer along with the spiked filters. However, the adsorbent samples have not been removed and analyzed because of problems arising from the interaction between ETU and the adsorbent (see below).

Air sampling stability. Glass fiber filters spiked with 8.9 µg ETU and with 10.1 µg EU (oxidation product of ETU) and subjected to an air stream showed a linear disappearance and an exponential disappearance, respectively (Figures 13 and 14). In general, 50% loss for both compounds occurred in 45-50 min under the conditions of the test. For ETU, the linear dissipation curve probably reflected two simultaneous processes: 1) evaporation of ETU and 2) oxidation of ETU to EU. These results emphasized the potential importance of the two-stage sampling train, which consisted of glass fiber filters followed by 30 ml aliquots of XAD-4 adsorbent. However when XAD-4 was spiked with ETU standard and immediately extracted in the usual way (20 min per extraction for a total of one hour), no detectable ETU residue was recovered from the adsorbent. In a follow-up experiment, where ETU was added to solvent and XAD-4 adsorbent was then added and the ETU concentration was determined against time, ETU in the solvent had fallen to below detectable limits after 24 hours, while ETU in pure solvent

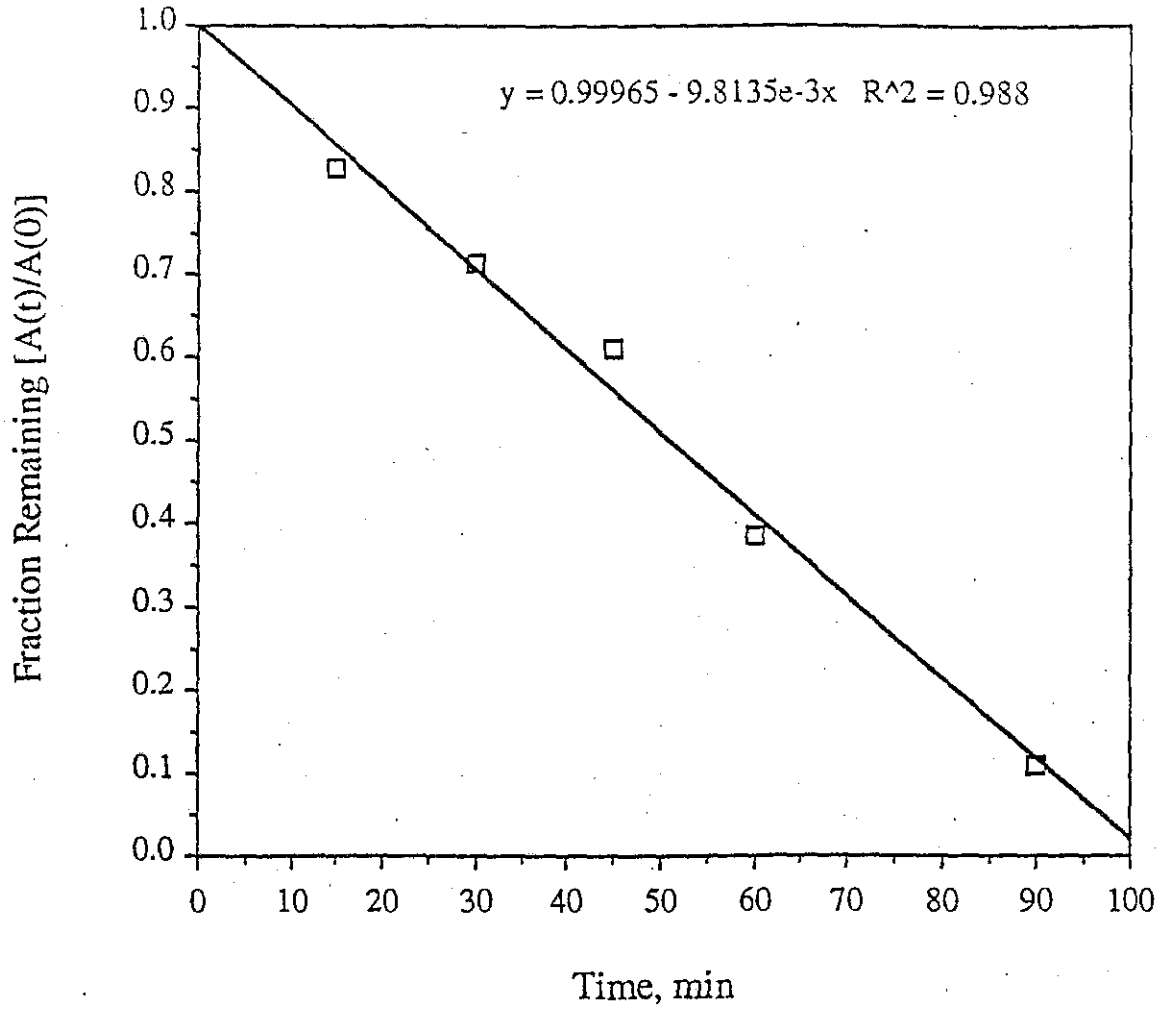


Figure 13. Dissipation of ethylenethiourea from spiked glass fiber filters under dynamic air sampling conditions.

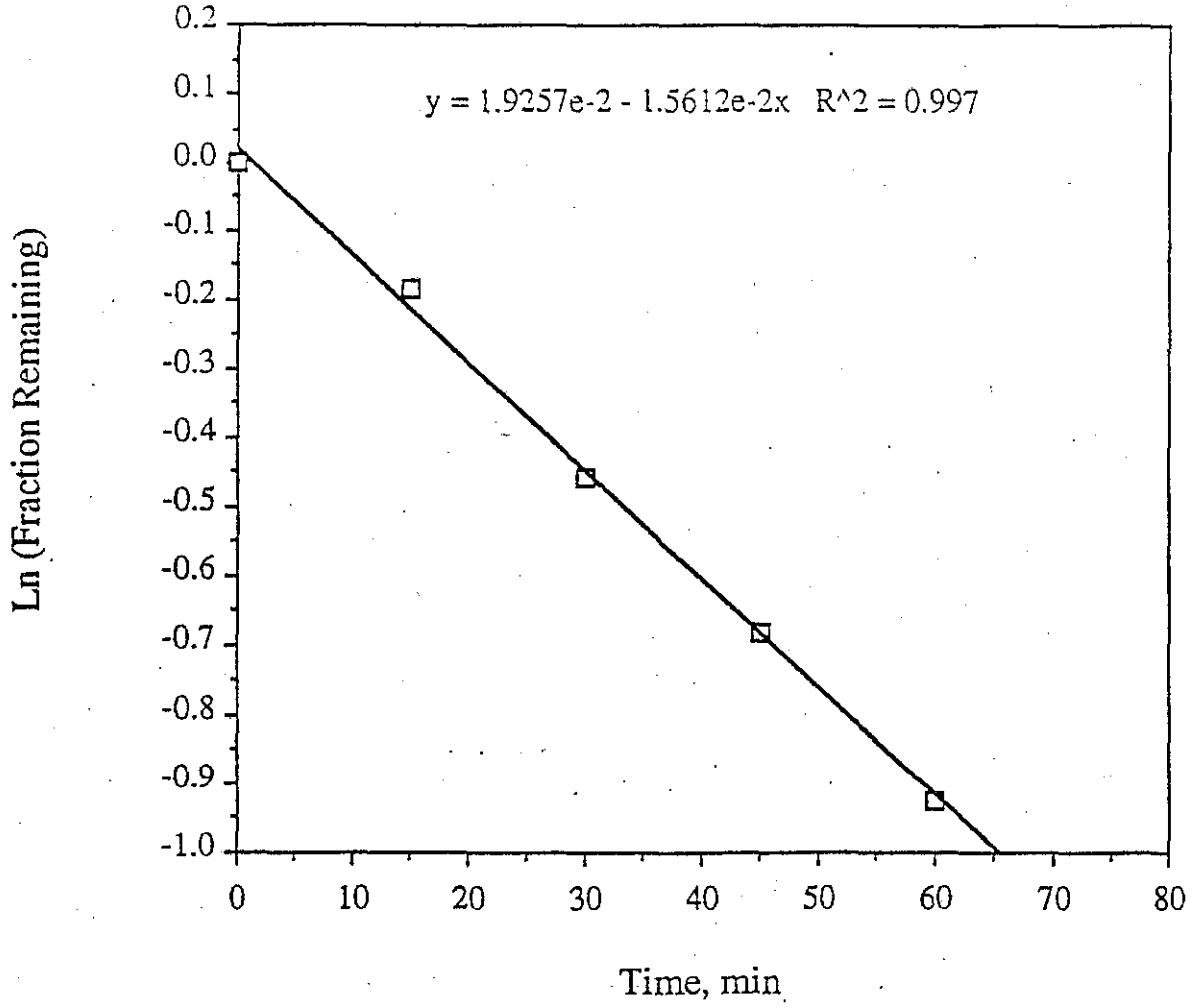


Figure 14. Dissipation of ethyleneurea from spiked glass fiber filters under dynamic air sampling conditions.

remained unchanged (Figure 15). This result is in contrast with the usual observation where organic analytes in an organic solvent will reach equilibrium with XAD-4 adsorbent, with the major portion of the analyte remaining in the solvent. In past studies, extraction of XAD-4 with either methyl alcohol or ethyl acetate usually gave near quantitative recoveries of analytes adsorbed from air.

It was found subsequent to the above adsorption test that some ETU could be removed from XAD-4 regardless of the extraction time if the extraction solvent consisted of methyl alcohol containing 3-4% (v/v) glacial acetic acid. Extractions for 5, 30, and 60 min with this solvent mixture all gave about 19% recovery of ETU spiked to XAD-4; recovery of ETU spiked to just the methyl alcohol/acetic acid mixture (no XAD-4) was about 76%. Replacing the acetic acid with 3-4% conc. hydrochloric acid gave less than half the recovery observed for the acetic acid.

When XAD-4 was spiked with ETU and air was pulled through the adsorbent for 2 hours at 15 liters/min, recovery of ETU was 40-45% (<1% EU was formed), compared to spiked XAD-4 without air (~19-20% absolute recovery). However, no detectable ETU could be extracted from XAD-4 located downstream from spiked glass fiber filters, even though only 30-60% of the original spike was recovered from the filters (about 100% ETU was recovered from spiked filters without air). The PTFE cartridge, used to hold the filter and adsorbent, was also extracted and little (<1%) of the original ETU was detected.

Thinking that ETU in an airstream may not interact well with XAD-4 but mostly pass on through, it was proposed that an impinger be located downstream of the adsorbent trap. Both methyl alcohol and water were considered as possible trapping media for the impinger. In separate tests,

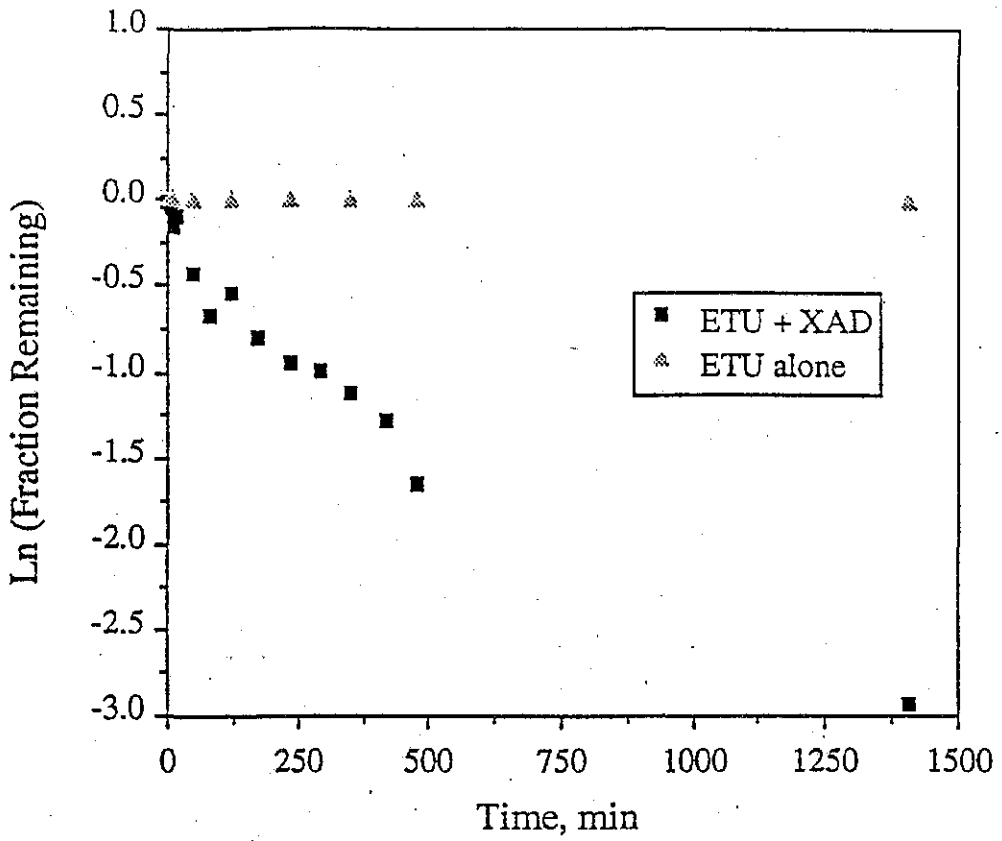


Figure 15: Decline of ethylenethiourea in solvent in the presence of XAD-4 polymeric adsorbent.

where impingers containing 100 ml of methyl alcohol or water were spiked with ETU and air was pulled through the impingers at 15 liters/min for 2 hours, recovery from the methyl alcohol spike was less than 3%, while recovery from the water spike was around 100%, both compared to spiked solvent without air. With the water spike, there was no detectable EU, while with the methyl alcohol spike as much as 20% of the original ETU was converted to EU. These results obviously indicated that methyl alcohol was not a suitable solvent, and in all subsequent tests water was used exclusively.

Using the complete sampling train (glass fiber filter plus XAD-4 plus water-filled impinger), ETU was spiked to the filter and air was pulled through the system at 15 liters/min for 2 hours. While only 15% of the original spike remained on the filter, no detectable ETU was found on the adsorbent and <1% of the original ETU was found in the impinger. Also, the adsorbent and impinger contained some EU, both of which were <1% of the original spike. Taken together, these results indicate that XAD-4 was a poor choice as a trapping medium for ETU/EU. The adsorbent is probably capable of trapping ETU/EU, but because of interaction with the adsorbent leading to irreversible adsorption and/or breakdown, this adsorbent should be omitted from consideration in future field sampling trials.

Based on the appreciable solubility of ETU in water (e.g., 2 g in 100 ml water at 30°C), we considered using water-filled impingers to trap airborne ETU (and possibly EU) and operating them independently of the glass fiber filter system for trapping the fungicides. At a concentration of about 1 ppm ETU in water, the compound could be quantitatively (>90%) extracted from water using a solid-phase extraction cartridge after the

aqueous solution had been saturated with ammonium sulfate. However at a concentration of about 0.3 ppm. extraction efficiency using this technique fell to about 50%. To efficiently remove ETU from water we examined chemical derivatization as a means of lowering its water solubility and to help partition it into an organic phase for subsequent analysis. This was accomplished by using extractive acylation, based on the method of Singh et al. (1979). These investigators claimed that by derivatizing ETU with dichloroacetic anhydride (DCAA, Figure 16), they were able to achieve about 80% recovery from water for concentrations as low as 0.01 ppm. We essentially confirmed this by treating spiked water samples, but we found both the dichloro and cyclized, monochloro derivatives (Figure 16) under our gas chromatographic conditions (confirmed by GC/MS), whereas these investigators observed only the cyclized, monochloro derivative using packed-column gas chromatography.

We soon found that it was necessary to replace water with ethylene glycol (EG), since ETU residues declined significantly under dynamic air sampling conditions. For example, no detectable residues were found for 1.13 μg spikes to water after two hours of room temperature air flow at 10-11 liters/min, compared with almost 50% recovery for similar samples in EG. It turned out that extractive acylation worked just about as well with EG as with water. However, recovery for spiked air samples seemed to vary somewhat: For two hour simulated air sampling runs at room temperature, a 0.28 μg ETU spike (0.014 ppm) gave 60% recovery, a 0.56 μg spike 38%, and a 1.13 μg spike 47%; after nearly 4 hours of air sampling, a 5.65 μg spike gave about 62% recovery. By contrast, spiked EG without air showed variability of as little as 1% between samples, proving the reproducibility of extractive acylation. Variable recovery for

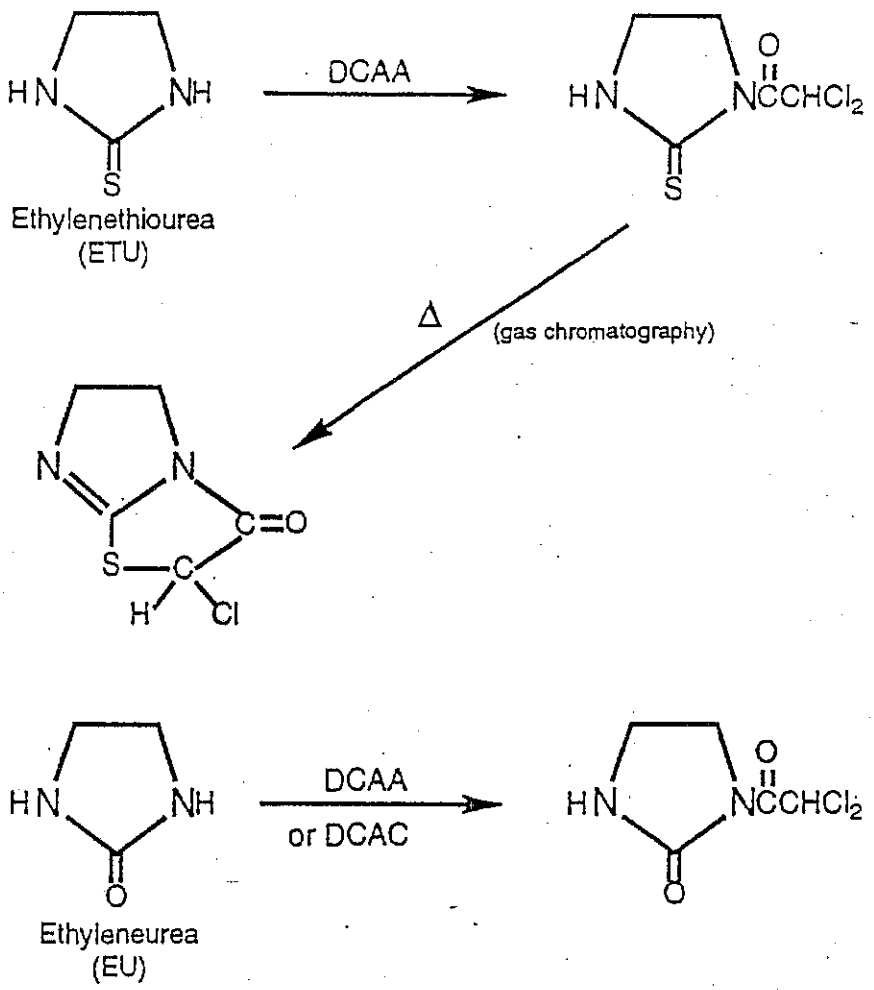


Figure 16. Acylation of ethylenethiourea and ethyleneurea.

the air samples may have been partly due to variable conversion of ETU to the EU oxidation product, and to possibly some volatilization losses and variable losses during sample transfer and workup. However, it was assumed that ETU would primarily oxidize; but, recovery of EU from solution proved to be somewhat difficult, partly because it is less reactive toward the acylating reagents and partly because of its greater solubility in EG. After some manipulation, we were able to obtain derivatives of a 5 μg EU spike (observed by gas chromatography compared to no observable derivative peaks for a reagent blank) by mixing the spiked EG with 1-2 ml methylene chloride containing 20 μl DCAA or DCAC (Figure 16). Recovery of EU failed when the EG was diluted with saturated aqueous sodium sulfate prior to treatment with the acylating reagents.

Thus far, EG-filled impingers coupled with extractive acylation shows the best promise for determining ETU in air. However, much work remains to be done. Trapping and recovery at room and ice temperatures need to be statistically evaluated, and acylation needs to be further validated, especially for a 1-2 order of magnitude lower EU residue level in EG. Once validated, it would be possible to determine total residues in air by assaying for both ETU and EU. However, this method would not be able to differentiate between ETU and EU in air prior to sampling if much of the ETU is oxidized to EU in the impinger.

Field samples. Results of laboratory tests with ETU essentially invalidate the field samples taken with glass fiber filters and XAD-4 adsorbent, because of the reasons discussed above. However, most of the mancozeb filters were analyzed for ETU anyway, and chromatograms of many of the field samples (ambient samples 1-11 and most of the application samples) showed a peak that corresponded in retention time

with ETU (ambient samples 23-63 did not show this peak). However, there was doubt that this peak actually represented ETU because its shape did not exhibit the characteristic tailing of ETU, and the field filter blanks (ambient sample 11 and application sample 13) showed the same peak, which was comparable in size to that for the field air samples. Clean filters under laboratory conditions did not show this peak. However, at some future time, it would be prudent to check these samples using a more definitive analytical method, such as mass spectrometry.

References

Camoni, I.; A.D. Muccio; D. Pontecorvo; and P. Citti. **1988**. Survey of ethylenethiourea (ETU) in ethylenebis(dithiocarbamate) (EBDC) fungicides. Ecotoxicology and Environmental Safety, 16:176-179

Haines, L.D., and I.L. Adler. **1973**. Gas chromatographic determination of ethylene thiourea residues. J. AOAC, 56:333-337.

Keppel, G.E. **1971**. Collaborative study of the determination of dithiocarbamate residues by a modified carbon disulfide evolution method. J. AOAC, 54:528-532.

King, R. **1977**. Derivatization of ethylenethiourea with m-trifluoromethylbenzyl chloride for analysis by electron-capture gas chromatography. J. Agric. Food Chem., 25:73-75.

Lowen, W.K., and H.L. Pease. **1964**. Dithiocarbamates. In: Zweig, G. (ed), Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives, Vol. III (New York: Academic Press), pp. 69-77.

Maini, P., and R. Boni. **1986**. Gas chromatographic determination of dithiocarbamate fungicides in workroom air. Bull. Environ. Contam. Toxicol., 37:931-937.

Mumma, R.O.; G.A. Brandes; and C.F. Gordon. **1985**. Exposure of applicators and mixer-loaders during the application of mancozeb by airplanes, airblast sprayers, and compressed-air backpack sprayers. In: Honeycutt, R.C.; G. Zweig; and N.N. Ragsdale (eds), Dermal Exposure Related to Pesticide Use: Discussion of Risk Assessment, ACS Symposium

Series #273 (Washington, D.C.: American Chemical Society), pp. 201-219.

Savolainen, K.; P. Kurttio; T. Vartiainen; and J. Kangas. 1989. Ethylenethiourea as an indicator of exposure to ethylenebisdithiocarbamate fungicides. Arch. Toxicol., Suppl., 13:120-123.

Singh, J.; W. P. Cochrane; and J. Scott. 1979. Extractive acylation of ethylenethiourea from water. Bull. Environm. Contam. Toxicol., 23:470-474.

APPENDIX IV

QMOSB AUDIT REPORT

STATE OF CALIFORNIA

PETE WILSON, Govern

AIR RESOURCES BOARD
2020 L STREET
P.O. BOX 2815
SACRAMENTO, CA 95812

MEMORANDUM

TO: George Lew, Chief
Engineering Evaluation Branch

THROUGH: Jeff Cook, Chief
Quality Management and Operations Support Branch

FROM: Alice Westerinen, Manager
Quality Assurance Section

DATE: April 5, 1994

SUBJECT: Ziram, Mancozeb, and Ethylenethiourea Monitoring Audit Report

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Please find attached the final quality assurance audit report on the Ziram, Mancozeb, and Ethylenethiourea monitoring project conducted in April and May of 1993 by the Engineering Evaluation Branch of the Air Resources Board, and the University of California, Davis. The report consists of three parts: the results of a flow rate audit of the air samplers, the results of a system audit, and the results of an analytical performance audit. Comments received on the draft report have been incorporated into the final report.

If you have any questions, please contact Ken Bowers of my staff at 332-7317 or ATSS 462-7317.

Attachments

cc: Don Fitzell
Ken Bowers

April 5, 1994

AUDIT REPORT

ZIRAM, MANCOZEB, AND ETHYLENETHIOUREA MONITORING IN KERN COUNTY

SUMMARY

In late April to May of 1993, the Engineering Evaluation Branch of the California Air Resources Board (CARB) conducted ambient air sampling in Kern County, California, to document the airborne emissions of ziram, mancozeb, and ethylenethiourea (ETU, a breakdown product of mancozeb) during the period of peak applications in Kern County. The samples were analyzed by the University of California (UC), Davis, Department of Environmental Toxicology.

On May 23, 1993, staff of the Quality Assurance Section of the CARB conducted an audit of the two rotameters used to set the flow rate of the air samplers used in the monitoring of ziram. The monitoring of ziram was aborted in the field due to rain.

On June 8, 1993, staff of the Quality Assurance Section of the CARB conducted an audit of the two rotameters used to set the flow rate of the air samplers used in the monitoring of mancozeb and ETU. The audits were conducted with a mass flow meter traceable to the National Institute of Standards and Technology (NIST). The difference between the reported and true flow rates averaged -2.0% with a range of -4.9% to 1.3% for one rotameter, and -3.0% with a range of -5.9% to 1.7% for the other.

A system audit of the UC Davis Department of Environmental Toxicology analytical laboratory was conducted to review the sample handling and storage procedures, analytical methodology, and method validation procedures. It was found that these were consistent with good practice.

On May 28, 1993, eight samples spiked with measured amounts of mancozeb were submitted to the laboratory for analysis. The samples were prepared from 74.0% pure mancozeb from AxAct Standards. The difference between the assigned and the reported mass averaged -12.7% with a range of -2.9% to -19.8%.

The only quality control deficiencies noticed in the study were the use of an uncertified mass flow meter in the calibration of the rotameters and the lack of field spikes in the analysis of the samples.

Due to difficulties in the stability of ETU on glass fiber filters under field sampling conditions and irreversible adsorption and/or breakdown of ETU on the XAD-4 adsorbent, the ETU portion of the project was invalidated. More complete method research and development before field monitoring could have avoided these difficulties. If appropriate methods were validated prior to the field testing, valid ETU data may have been collected.

AUDIT REPORT

ZIRAM, MANCOZEB, AND ETHYLENETHIOUREA MONITORING IN KERN COUNTY

INTRODUCTION

In late April to May of 1993, the Engineering Evaluation Branch (EEB) of the California Air Resources Board (CARB) conducted ambient air sampling to document the airborne emissions of ziram, mancozeb, and ethylenethiourea (ETU, a mancozeb breakdown product) during the period of peak applications in Kern County, California. Samples were collected in populated areas of Kern County, and in the vicinity of a treated field during and after the application of the fungicides by drawing ambient air at measured rates through sampling cups containing an adsorbent resin (XAD-4) and/or glass fiber filters. The samples were later analyzed by the University of California, Davis, Department of Environmental Toxicology. Gabriel Ruiz and Ken Bowers of the CARB's Quality Assurance (QA) Section conducted an audit of the rotameters used to set the samplers' flow rate, a system audit of the field and laboratory operations, and a performance audit of the analytical method.

FLOW RATE AUDIT

The air samplers consisted of a sampling cup connected with Teflon tubing to an in-line control valve, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of galvanized steel tube (Figure 1). The samplers' flow rates were set by connecting a calibrated rotameter of low flow resistance to the inlet of the sampler and adjusting the control valve on the sampler so that the actual flow rate, as calculated from the rotameter's calibration, was 16 liters per minute (lpm).

The flow rate of each sampler used for monitoring of mancozeb and ETU was audited individually at the EEB's shop in Sacramento on March 11, 1993, before monitoring was initiated. The audits were conducted with a 30 lpm Matheson mass flow meter (MFM) traceable to the National Institute of Standards and Technology, following the procedures outlined in Attachment I. The difference between the reported and the true flow rates of the original rotameters averaged -0.6% and ranged from -1.2% to 0%.

The rotameter used to set the sampler flow rates was broken just before the mancozeb/ETU monitoring had begun, and was replaced with two rotameters of higher flow resistance. These rotameters were audited on June 8, with the same 30 lpm Matheson MFM used before. Since the indicated flow rates observed in the field actually ranged from 5 to 16 lpm, an attempt was made to cover the entire range in the audit; however, only indicated flow rates up to 13 lpm could be verified, because the capacity of the sampler's pump was not sufficient to overcome the combined flow resistance of the audit device and the rotameter.

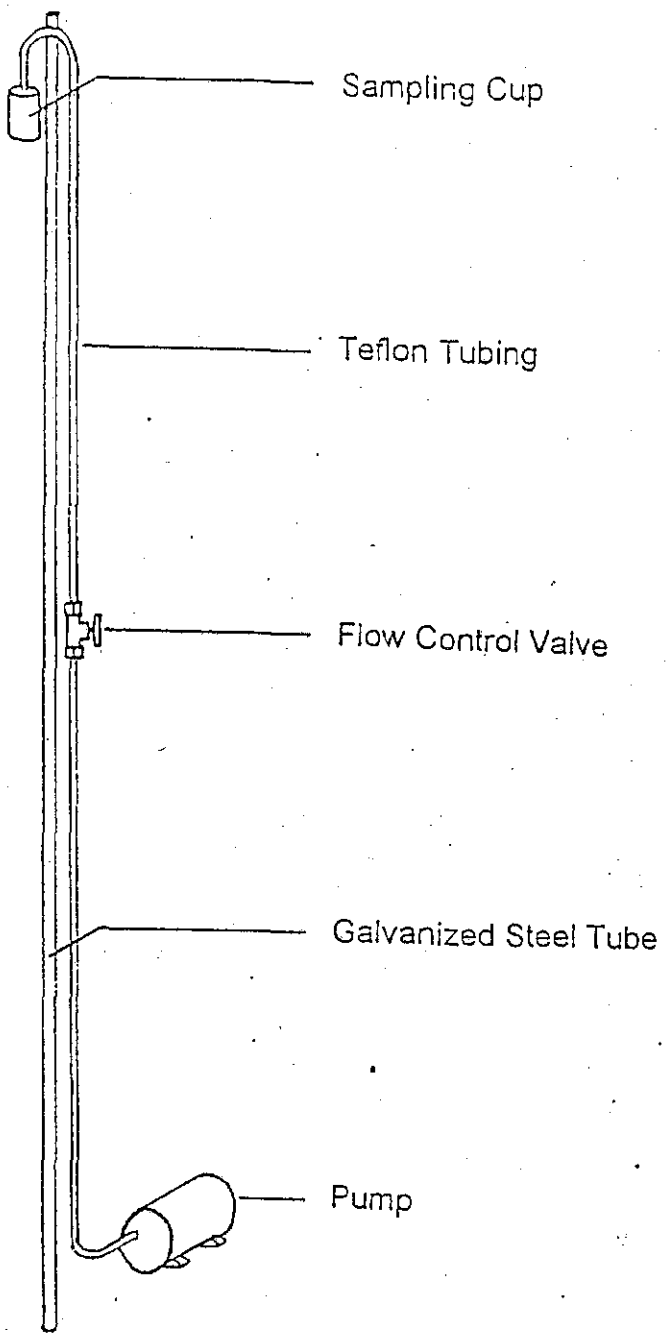

Figure 1. Air sampler used in the monitoring of ziram, mancozeb, and ethylenethiourea

While the accuracy of the rotameters at flow rates greater than 13 lpm could not be ascertained, the pumps proved capable of sustaining flow rates of 16 lpm in the field.

The difference between the reported and true flow rates averaged -2.0% with a range of -4.9% to 1.3% for the rotameter used in the ambient monitoring (Table 1), and -3.0% with a range of -5.9% to 1.7% for the rotameter used in the application monitoring (Table 2). The reported flow rates were fairly accurate, but an increasingly negative bias was noticed as the flow rates increased from 5 to 13 lpm. The bias was probably caused by the lack of a correction factor for the MFM used in the calibration of the rotameters, since it was uncertified.

The flow rate of each sampler used for monitoring of ziram was audited on April 23, 1993. These samplers were not used in the field since the monitoring project was cancelled due to rain, and therefore the audit results are not reported.

Table 1. Results of the audit of the rotameter used to set the sampler flow rates in the ambient monitoring of mancozeb and ethylenethiourea.

Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
5.0	5.40	5.33	1.3
6.0	6.54	6.46	1.2
7.0	7.44	7.39	0.7
8.0	8.28	8.41	-1.5
9.0	9.18	9.40	-2.3
10.0	10.08	10.41	-3.2
11.0	10.92	11.43	-4.5
12.0	11.84	12.45	-4.9
13.0	12.87	13.52	-4.8

Table 2. Results of the audit of the rotameter used to set the sampler flow rates in the mancozeb application monitoring.

Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
5.0	5.25	5.36	-2.1
6.0	6.66	6.55	1.7
7.0	7.41	7.60	-2.5
8.0	8.52	8.50	0.2
9.0	9.24	9.48	-2.5
10.0	9.93	10.44	-4.9
11.0	10.86	11.49	-5.5
12.0	11.94	12.62	-5.4
13.0	12.69	13.49	-5.9

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

SYSTEM AUDIT

A system audit of the field and laboratory operations was conducted to evaluate the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation. The audit was conducted by reviewing the method validation data sent to the CARB and telephone conversations with Jim Woodrow of UCD. The following is a discussion of the audit findings.

Sample Handling and Storage

Sampling was conducted by staff of the CARB's EEB, following the schedule specified in the sampling protocol. After sampling, the exposed glass fiber filters and XAD-4 resin were collected into clean four fluid-ounce glass jars with teflon-lined lids. The jars were then placed inside cardboard boxes and stored over dry ice in an ice chest until they were delivered to the laboratory on Friday of each week.

Upon receipt at the laboratory, the samples were logged in and stored in a freezer at -20°C. Extraction and analysis of the samples were carried out within one week of receipt.

Sample Analysis

The analytical method was developed by laboratory staff based on published methods. To analyze dithiocarbamates (ziram and mancozeb) the fungicides were decomposed to carbon disulfide (CS_2), which was quantified by gas chromatography (GC). The method entails extraction of the glass fiber filter in 2 ml iso-octane and 10 ml 37%HCl/3%$SnCl_2$ in 22 ml glass headspace vials sealed with teflon lined crimp caps. After heating to 80°C for one hour and cooling, the iso-octane layer was pipetted into a 4 ml vial and 2 ml distilled water was added. The iso-octane layer was chromatographed on a 30 m by 0.53 mm DB-1 megabore fused silica column with helium as the carrier gas. The gas chromatograph used was a Hewlett-Packard (HP) 5890 Series II with a flame photometric detector in the sulfur mode.

Ethylenethiourea was solvent extracted from glass fiber filters using ethyl acetate and analyzed on the HP 5890 GC with a 30 m by 0.53 mm DB-5 FSOT column and a nitrogen-phosphorus thermoionic detector (NPD). The original method to determine ETU from the XAD-4 adsorbent was unable to extract the ETU. Originally the adsorbent was extracted with three 50 ml aliquots of methyl alcohol. When no ETU was found to be extractable from spiked XAD-4, 3-4% glacial acetic acid was added to the methanol resulting in consistent, but low, recovery (about 19%) of the spiked ETU. The methanol extracts were combined and reduced to 2-3 ml and neutralized with sodium carbonate and the mixture extracted with 4 ml ethyl acetate. The ethyl acetate extract was analyzed on the HP 5890 GC/NPD.

A matrix standard curve was used for ziram and mancozeb rather than pure CS_2. Varying amounts of ziram and mancozeb were spiked onto glass fiber filters and the filters were treated with 37%HCl/3%$SnCl_2$ to produce CS_2. For ziram the spiking levels were 1.3-19.5 ug, and for mancozeb the spiking levels were 0.47-20.5 ug.

The calibration standards were prepared within three weeks of analyses. Their stability was monitored by periodic laboratory spikes. The total CS_2 and ETU mass was calculated from the area of the peaks on the chromatogram. The mass of ziram and mancozeb were calculated from the mass of CS_2 recovered.

Quality control activities performed to monitor and document the quality of the data included analyses of a set of eight mancozeb spiked filters from the ARB, analysis of laboratory spikes and laboratory blanks, one field blank per shipment of samples, and one duplicate sample per sampling day. For each set of field samples received, clean filters and adsorbent were spiked and stored in the freezer along with the samples. The results of these laboratory spikes were not presented in the report. The response factors of the calibration standards were monitored by the analyst to confirm the instrument's stability. The stability results were plotted on a control chart. The study did not include field spikes.

Method Validation

The limit of detection (LOD) was determined as the lowest amount consistently detectable by the method (2 to 3% full scale response for a 4-5 ul injection). This method gave detection limits comparable to the U.S. EPA criteria for detection limits. The laboratory set the limits of quantification at 0.5 ug ziram, 0.5 ug mancozeb, and 0.2 ug ETU.

For each analyte the stability under air sampling conditions and freezer storage conditions was determined in addition to the analysis of the field samples.

Ziram on glass fiber filters was stable in the -20°C freezer for at least 60 days. After 60 days ziram recovery was 92.4 ±8.4%.

After two weeks in the -20°C freezer the recovery of mancozeb chelated with 0.1 M EDTA spiked on glass fiber filters fell to 15-20%, indicating the chelated fungicide was not stable in cold storage. Analysis of non-chelated mancozeb on glass fiber filters was 97.0 ±2.7% after two weeks, indicating that the non-chelated fungicide was stable in cold storage. The actual samples were in the non-chelated form.

Analysis of glass fiber filters spiked with ETU and stored in the freezer for 60 days indicated good stability in cold storage. After 60 days the average recovery was 89.7 ±5.7%. ETU samples spiked onto XAD-4 adsorbent and stored in the freezer were not analyzed due to the apparent irrecoverable adsorption and/or breakdown of ETU on XAD-4.

Glass fiber filters spiked with ziram in acetone resulted in the disappearance of the fungicide under field sampling conditions due to the instability of the solution. Spikes of a crystalline form of ziram or a suspension of ziram, rather than a solution, would have been more appropriate and better mimicked the situation being monitored. In tests following the field sampling, using ziram suspended in iso-octane, the average recovery was 88.2 ± 19.4%. The large uncertainty is due to the iso-octane spikes being a suspension rather than a true solution.

Spikes of non-chelated mancozeb on clean glass fiber filters were stable under air sampling conditions (15 liters/min, 23°C). Recovery after 24 hours of air flow was 100.9 ±5.4%.

Glass fiber filters spiked with ETU showed a linear disappearance of ETU, with a 50% loss in 45 to 50 minutes. The loss of ETU represented two simultaneous processes: 1) evaporation of ETU and 2) oxidation of ETU to ethyleneurea (EU). The EU further disappears at an exponential rate. XAD-4 adsorbent was used following the glass fiber filter to capture the ETU/EU lost from the filter. However, ETU and EU irreversibly adsorb and/or breaksdown on XAD-4 adsorbent.

If the ETU method had been fully researched and developed before the monitoring activities, the above problems would have been found and could have been corrected. There was no way found to accurately determine ETU from the filters and adsorbent used. In post monitoring experimentation it was found that a water filled impinger can be used to collect ETU and EU. Since the glass fiber filter/XAD-4 sampling train was used in the project, ETU results were inconclusive and the ETU portion of the project was considered invalid.

Documentation

All the samples received at the laboratory were accompanied by ARB's chain-of-custody records. Upon receipt, the samples were inspected and logged into an electronic file. The field sample number of each sample was recorded and used as the laboratory analysis number.

Field data sheets containing the sample collection information were retained by the EEB staff. The information included sampler location, date, start and stop times, initial and final flow rates, and comments about unusual conditions.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date of analysis, results, and analyst. The raw analytical data and the results of the analyses were stored in an electronic spreadsheet. Hard copies of the run data and the chromatograms were saved in an accessible form.

LABORATORY PERFORMANCE AUDIT

The accuracy of the UCD's analytical method was evaluated by submitting for analysis a set of eight audit samples spiked with measured amounts of mancozeb. The samples were prepared on May 28, 1993, following the procedures outlined in Attachment II. The samples were delivered to the laboratory on the same day, and they were extracted and analyzed immediately.

Ziram samples for a laboratory performance audit were not submitted since the field monitoring was cancelled. Ethylenethiourea samples were also not submitted for a laboratory performance audit due to the instability problems encountered in the monitoring method.

The difference between the assigned and the reported mass of mancozeb averaged -12.7% with a range of -19.8% to -2.9% (Table 3). The results are consistent with the reported method recoveries.

Table 3. Results of UCD's analyses of the mancozeb audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
MNB-1	10.30	9.20	-10.7
MNB-2	5.20	4.68	-10.0
MNB-3	0	<0.5	N/A
MNB-4	5.20	5.05	-2.9
MNB-5	3.10	2.54	-18.1
MNB-6	10.30	8.26	-19.8
MNB-7	0	<0.5	N/A
MNB-8	3.10	2.64	-14.8

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

CONCLUSIONS

In general, good quality control practices were observed during the study. The records for field operations were appropriate; the flow rates reported were in good agreement with the actual flow rates measured by the QA staff; the sample handling and storage procedures and the validation methods were consistent with good laboratory practices; and the results of the analytical performance audit were in agreement with the expected values.

The only quality control deficiencies noticed were the use of an uncertified MFM in the calibration of the rotameters, the omission of field spikes, and the use of insufficiently developed methods.

While the reported sample collection flow rates were fairly accurate, the rotameters should have been calibrated with a certified flow measurement device. Field spikes should be included with each batch of samples submitted to the laboratory to monitor sample recovery.

All method and quality assurance/quality control procedure development should be completed and demonstrated before the beginning of monitoring. Field sampling and analytical methodology for ziram and mancozeb were appropriate. However, the spiking methodology whereby filters spiked with ziram in acetone resulted in the disappearance of the fungicide due to the instability of the solution was not properly developed methodology. Spikes of a crystalline form of ziram or a suspension of ziram, rather than a solution, would have been more appropriate and better mimicked the situation being monitored. Glass fiber filters with an XAD-4 second stage adsorbent was an inappropriate sampling configuration for ETU. The ETU dissipates from the filter by evaporation and oxidation to EU and the XAD-4 then fails as a second stage since ETU and EU interact with the adsorbent leading to irreversible adsorption and/or breakdown.

ATTACHMENT I

Flow Audit Procedure for Air Samplers Used in Pesticide Monitoring

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable Brooks automatic flow calibrator. The audit device is connected in series with the sampler's flow meter, and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

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

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 V AC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a 5 ft. section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

ATTACHMENT II

Performance Audit Procedure for the Laboratory Analysis of Mancozeb

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of mancozeb. The audit is conducted by submitting audit samples spiked with known concentrations of mancozeb. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Mancozeb 74.0% pure, AxAct Standards
2. Tetrasodium EDTA, tetrahydrate
3. Deionized water
4. Glass fiber filters
5. Petri dishes (47 mm diameter)
6. 50 ul Microsyringe.

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Sample Preparation

0.1 M EDTA Solution: Weigh about 4.52 g of tetrasodium EDTA (MW 452.2) into a 100 ml volumetric flask. Dissolve with deionized water and dilute to the mark. Record the concentration.

4 mg/ml (nominal concentration) Mancozeb Solution: Weigh about 135 mg of mancozeb onto a 25 ml volumetric flask. Add about 20 ml of 0.1 M EDTA and allow to sit overnight to dissolve. Dilute to the mark with 0.1 M EDTA. Record the concentration.

0.2 mg/ml (nominal concentration) Mancozeb Spiking Solution: Transfer 500 ul of the 4 mg/ml mancozeb stock solution to a clean 10 ml volumetric flask. Dilute with 0.1 M EDTA to the mark and record the concentration.

Prepare eight audit samples from the 0.2 mg/ml mancozeb spiking solution using a 50 ul syringe to transfer mancozeb spiking solution to glass fiber filters according to the following table:

Sample	0.2 mg/ml Mancozeb Volume (ul)
MNB-1	50
MNB-2	25
MNB-3	0
MNB-4	25
MNB-5	15
MNB-6	50
MNB-7	0
MNB-8	15

Also, spike filter MNB-7 with 25 ul of 0.1 M EDTA. Place the filters in 47 mm petri dishes for delivery to the analysis laboratory.