

APPENDIX III
QMOSB AUDIT REPORT

STATE OF CALIFORNIA

AIR RESOURCES BOARD

AUDIT REPORT

CARBOFURAN MONITORING IN IMPERIAL COUNTY

MONITORING AND LABORATORY DIVISION

QUALITY ASSURANCE SECTION

JUNE 1995

AUDIT REPORT
CARBOFURAN MONITORING IN IMPERIAL COUNTY

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1. Air Sampler Used in the Monitoring of Carbofuran

I. EXECUTIVE SUMMARY

In February of 1995, the Engineering and Laboratory Branch of the California Air Resources Board conducted ambient air sampling in Imperial County, California, to document the airborne emissions of carbofuran in the vicinity of a treated field during and after an application. The samples were collected by the Engineering and Laboratory Branch and analyzed by the Trace Analytical Laboratory of the UC Davis Department of Environmental Toxicology.

The California Air Resources Board Monitoring and Laboratory Division's Quality Assurance Section staff conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. It was found that laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (California Air Resources Board, February 4, 1994).

Additionally, Quality Assurance Section staff conducted performance audits of the air monitoring samplers. The performance audits of the air monitoring samplers were conducted to evaluate the flow rate accuracy. The difference between the reported and assigned flow rates averaged -1.0% with a range of -2.0% to 0.7%. In order to determine the effectiveness of the analytical procedure, laboratory performance audits were also conducted. On March 10, 1995, seven samples spiked with measured amounts of carbofuran were submitted to the laboratory for analysis. The samples were prepared from a carbofuran standard solution obtained from Chem Service. The difference between the assigned and the reported total mass averaged -10.2% with a range of -21.1% to 0.0%.

II. CONCLUSIONS

The records for field operations, sample handling and storage procedures, analytical methodology, and method validation were in agreement with the Quality Assurance Plan for Pesticide Monitoring. The results of the reported flow rates were in good agreement with the actual flow rates measured by Quality Assurance Section staff. The results of the analytical performance audit showed an average of -10.2% difference. This is within acceptable parameters.

III. RECOMMENDATIONS

There are no recommendations at this time.

IV. INTRODUCTION

In February of 1995, the Engineering and Laboratory Branch (ELB) of the California Air Resources Board (CARB) conducted ambient air sampling in Imperial County, California, to document the airborne emissions of carbofuran in the vicinity of a treated field during and after an application. The samples were collected by the ELB and analyzed by the Trace Analytical Laboratory (TAL) of the UC Davis Department of Environmental Toxicology. The CARB Monitoring and Laboratory Division (MLD) Quality Assurance Section (QAS) staff conducted a system audit of the field and laboratory operations, and performance audits of the air samplers' flow rates and of the analytical method.

V. AUDIT OBJECTIVE

The system audit was conducted to determine whether the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation were consistent with the Quality Assurance Plan for Pesticide Monitoring (CARB, February 4, 1994). Performance audits were conducted to evaluate the accuracy of the air samplers' flow rate and the analytical method.

VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated in February 1995 through a questionnaire submitted to TAL staff. Also, the protocol for ambient air monitoring of carbofuran and the laboratory sampling methodology for the analysis of carbofuran were reviewed. The following is a discussion of the audit findings.

Sample Handling and Storage

Samples were collected by drawing ambient air at measured rates through a Teflon holder containing 30 ml of cleaned XAD-4 resin. The air samplers consisted of one sample holder, connected with Teflon tubing to an in-line rotameter, 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' rotameters were set to an indicated flow rate of 15 liters per minute (lpm) by adjusting the control valve on the rotameter.

Sampling was conducted following the schedule specified in the sampling protocol. After sampling, the XAD-4 resin was removed from the Teflon holder and transferred into a glass jar with a Teflon-lined lid. The jars were stored in an ice chest containing dry ice. Samples were shipped, in an insulated container containing dry ice, to the lab at the end of each week.

Upon receipt at the laboratory, the samples were stored in a freezer until extraction and analyses were conducted.

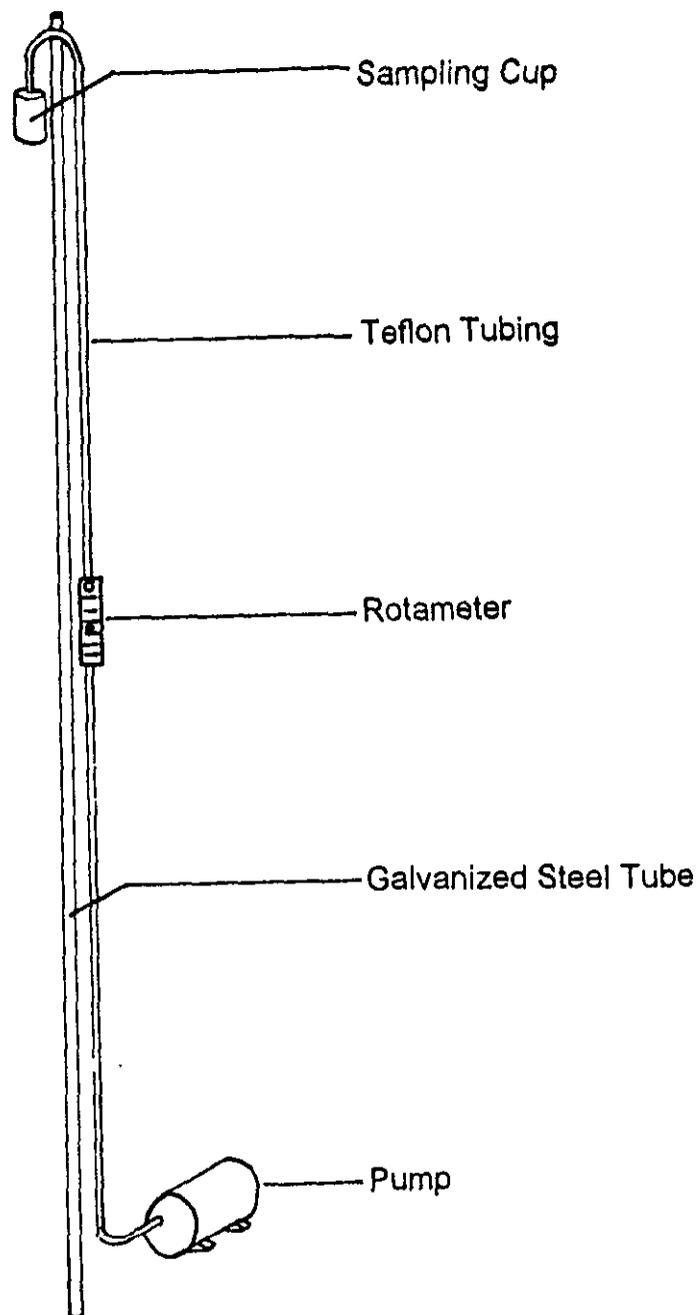


Figure 1. Air sampler used in the monitoring of carbofuran.

Sample Analysis

The analytical method was developed by the TAL, and is described in a document entitled "Sampling Methodology for Carbofuran". The method calls for the glass jars to be frozen until extracted with 75 ml of ethyl acetate. One half of the samples are then concentrated on a rotary evaporator and re-dissolved in 2 ml of ethyl acetate. The analyses are performed on a Perkin-Elmer Autosystem Gas Chromatograph (GC) with a built-in automatic injector, and a Hewlett Packard 5890 GC.

Quality control activities performed to monitor and document the quality of the data included analysis of a field control blank with every sample set, laboratory spikes of three replicates per set of samples with 100% \pm 0.09% recovery, and field duplicates from collocated sites once each sampling day. A portion of the samples were analyzed by GC/Mass Spectroscopy Selective Ion monitoring to confirm the identity of the analyte.

Method Validation

The limit of detection (LOD) was determined by injecting known quantities of external standards on a GC. The LOD was calculated as 0.25 ug per sample. Trapping efficiency was determined as 96%. Sample stability studies were conducted and verified the integrity of the sample for at least 12 days when stored in the freezer. Breakthrough mass load was 100 ug over 24 hours at a flow rate of 50 lpm.

Documentation

All the samples received at the laboratory were accompanied by chain-of-custody records. Field data sheets containing the sample collection information were received by the TAL. The information recorded in the field data sheets included sampler location, sampling date, start and stop times, log number, identification number, description, job name, date, job number, and initials of the field technician.

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 sample was received, date of analysis, results of analysis, and analyst.

The raw data are available for review and electronic files are kept for four years.

VII. PERFORMANCE AUDITS

Flow Rate Audit

The flow rate of each sampler used for the monitoring was audited on February 1, 1995, following the procedures outlined in Attachment I. The audit was conducted with a 0 to 30 lpm mass flow meter traceable to the National Institute of Standards and Technology (NIST). The difference between the reported and true flow rates averaged -1.0% and ranged from -2.0% to 0.7% (Table 1).

Table 1. Results of the flow rate audit of the samplers used in the monitoring of carbofuran.

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
1	14.6	14.5	0.7
2	14.6	14.7	-0.7
3	14.6	14.9	-2.0
4	14.6	14.8	-1.4
5	14.6	14.8	-1.4
6	14.6	14.8	-1.4

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

Laboratory Performance Audit

The accuracy of the analytical method was evaluated by submitting for analysis a set of seven audit samples spiked with measured amounts of carbofuran. The samples were prepared by QAS staff on March 10, 1995, following the procedures outlined in Attachment II. The audit samples were also extracted and analyzed on March 11. The difference between the assigned and the reported total mass of carbofuran averaged -10.2% with a range of -21.1% to 0.0% (Table 2).

Table 2. Results of analyses of the carbofuran audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
CARBO 1	6.25	5.39	-13.8
CARBO 2	3.75	2.96	-21.1
CARBO 3	8.75	7.75	-11.4
CARBO 4	3.75	3.16	-15.7
CARBO 5	6.25	5.67	- 9.3
CARBO 6	0.00	<0.25	0.0
CARBO 7	8.75	8.72	- 0.3

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

ATTACHMENT I

Flow Rate Audit Procedures for Air Samplers
Used in Pesticide MonitoringIntroduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST-traceable 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 VAC 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 Procedures
for the Laboratory Analysis of CarbofuranIntroduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory to measure the ambient concentrations of carbofuran. The audit is conducted by submitting audit samples spiked with known concentrations of carbofuran. 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. Carbofuran, 0.25 ug/ul in ethyl acetate, Chem Service, Lot # 151-50A
2. Glass jars with Teflon-lined lids, 30 ml XAD-4 resin

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.

Preparation of Audit Samples

Prepare seven audit samples by spiking the XAD-4 resin contained in the glass jars with the volume of carbofuran solution indicated in the table below. Using a microsyringe, slowly expel the solution into the glass jar, move the syringe so that the solution is not landing in the same place on the resin. Touch the tip of the syringe to the side of the glass jar to expel the last bit of solution.

Sample ID	Total Spiking Solution Volume (ul)
CARBO 1	25
CARBO 2	15
CARBO 3	35
CARBO 4	15
CARBO 5	25
CARBO 6	0
CARBO 7	35