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**Study 212: Protocol for**
**Evaluation of Buffer Zones and Relative Emission Rates for Fumigants**
**April 5, 2004, revised July 30, 2004**

## I. INTRODUCTION

DPR has implemented or is considering buffer zones for four major fumigants: methyl bromide, methyl isothiocyanate, 1,3-dichloropropene, and chloropicrin. In some cases, the buffer zones are based on limited or no monitoring data, and all are based on monitoring for individual fumigants. This study will measure air concentrations and back-calculate emission rates for fumigants used individually and in various combinations to determine the effectiveness of current or proposed buffer zones. Monitoring applications of fumigant combinations will provide relative emission rates between fumigants. If a consistent relationship in relative emission rates can be established, monitoring data for one fumigant may be used as surrogate data for another fumigant. If the data can be leveraged in this manner, DPR may be able to detect flux variation with soil type, cultural practices, or other factors that are not detectable with the current data. This could provide more flexibility and buffer zone adjustments for local conditions than currently possible. This may also provide information and other options (e.g., irrigation practices) for decreasing emissions (as both active ingredients and volatile organic compounds), and decreasing buffer zones. Determining the relative emission rates will also confirm the appropriate relative sizes of the buffer zones. This study will take at least two years to complete.

## II. OBJECTIVES

This study will determine back-calculated fluxes for fumigants not monitored previously and/or for fumigations using more than one fumigant. Higher priority will be given to application methods for which DPR has little or no monitoring data. Within these guidelines opportunities for monitoring will arise. The particular fumigants which will be monitored are not known at this time. Specific protocols referencing this template protocol will be used to guide specific monitoring opportunities as they arise. As more fumigations are monitored, a database of monitoring studies and corresponding modeling analyses will accrue. The nature of more general conclusions and the certainty of those conclusions will depend in large measure on the composition of the database. Basic information from each of these studies will include

1. flux estimate of each constituent fumigant (using back-calculation)
2. when buffer zones are known, an estimate of the adequacy of the buffer zones for this particular application, including what buffer zone would have been required for the application
3. flux profile during the monitoring period
4. fractional mass loss during the first 24 and 48 hours

In addition, more general analyses may be possible. Such analyses may include testing for consistency of relative flux between two simultaneously applied fumigants, comparison of flux when applied in combination to flux when applied individually, and exploratory data analysis to look for correlations between flux and application method, season, soil or other environmental factors.

This study will initially focus on the following fumigants and application methods (in no particular order):

1) methyl bromide/chloropicrin bed fumigations
2) methyl bromide/chloropicrin strip fumigations
3) methyl bromide/chloropicrin deep-tarp fumigations
4) 1,3-dichloropropene/chloropicrin drip fumigations
5) dazomet fumigations
6) metam drip fumigations
7) metam rototill fumigations
8) metam flood fumigations
9) metam non-ag fumigations

This general protocol discusses the broad outlines of the study. This protocol will be amended as necessary to address specific fumigants and application methods.

## III. PERSONNEL

The Environmental Monitoring Branch will conduct this study, under the overall supervision of Randy Segawa. Other key personnel include:

Project Leader: to be determined
Field Coordinator: to be determined
Quality Assurance/Lab Liaison: Carissa Ganapathy
Laboratory: Department of Food and Agriculture, Center for Analytical Chemistry
Senior Staff Scientist: to be determined

Personnel to be determined will differ depending on the fumigant, method of application, and date of monitoring. Responsibilities of the key personnel are described in Standard Operating Procedure (SOP) ADMN002.1. Questions concerning this study should be directed to Randy Segawa at 916-324-4137, rsegawa@cdpr.ca.gov.

## IV. STUDY PLAN

For each application monitored, DPR will establish 8 - 16 monitoring stations surrounding the application site. DPR will monitor each application for 48 - 96 hours beginning with the start of application. In addition, background samples will be collected for 12 to 24 hours prior to start of application

Minimum number of samples for each application:

8 stations x 3 sample intervals = 24 samples + 1 background sample

Maximum number of samples for each application:

16 stations x 9 sample intervals = 144 samples + 4 background sample

Quality control samples = 10 percent of sample total

## V. SAMPLING METHODS

Air monitoring will be conducted using SKC personal air sampling pump. Each air sampler will be positioned approximately four feet above ground level and will be fitted with sorbent collection tubes. The use, operation, calibration and maintenance of air sampling pumps are described in DPR's SOP EQAI001.00. The collection tubes and flow rates used for sampling will be determined by the fumigant monitored. Sorbent tube samples will be collected according to procedures listed in DPR'S SOP EQAI001.00. Once samples are collected, each tube opening will be tightly capped and samples will be placed on dry ice and remain frozen until analysis. Samples will follow the tracking procedures outlined in DPR's SOP QAQC003.01. If the possibility of breakthrough is anticipated, a second tube will be added in tandem to form a sampling chain.

A weather station will be set up next to the treatment area to measure wind speed, wind direction, ambient air temperature, and relative humidity. The meteorological data will be recorded on a Campbell Scientific CR 21X Datalogger as a 5-minute average of one-second readings, except for wind direction which is an instantaneous reading. The meteorological station will be set up according to DPR's SOP EQWE001.00.

The project leader will conduct and record accurate measurements of the field and sampling locations will be made so that an accurate map of the field, correctly oriented with respect to compass directions and including size and dimensions of applied area, orchards, chemical monitor and meteorological monitor locations, buildings, roads, berms, water, or any other land feature which could affect wind direction, wind speed, temperature, or humidity will be included. Field description information such as furrow and bed widths and soil conditions will be recorded. Application information, including application time, method, equipment, dosage (rate), fumigation duration, aeration method and duration, etc will be recorded. Equipment information may include photographs of the application equipment and general type and operation including shank spacing, number of shanks, depth of application, or in the case of drip application, number of emitters per area or linear bed distance, and water volumes and application rates (by time and area). Record the real application rate and how it was determined, such as the weights of fumigant containers prior to and following application and the flow rate of the injection system.

## VI. CHEMICAL ANALYSIS

Chemical analysis will be performed by the California Department of Food and Agriculture Center for Analytical Chemistry (CDFA). Analytical methods for 1,3-dichloropropene from sorbent tubes will be performed in accordance with CDFA laboratory method number EM 59.6 (CDFA, 1999b). Analytical methods for chloropicrin from sorbent tubes will be performed in accordance with CDFA laboratory method number EM16.0 (CDFA, 1999a). Analytical methods for MITC from sorbent tubes will be performed in accordance with CDFA laboratory method EM 41.9 (CDFA, 1993). Analytical methods for methyl bromide from sorbent tubes will be performed in accordance

with CDFA laboratory method number 39.0 (CDFA, 1998). All laboratory quality control methods will follow procedures presented in DPR's SOP QAQC001.00. Matrix blanks and spikes will be analyzed as a quality control measure. Concentrations for primary and secondary tubes will be reported separately to document any breakthrough in the primary tube.

## VII. DATA ANALYSIS

Air concentrations will be presented as micrograms per cubic meter ($ug/m^3$). In addition, the weather data and measured concentrations will be entered into the Industrial Source Complex-Short Term 3 (ISCST3) computer model (U.S. EPA, 1995). The ISCST3 model uses the flux, field size, weather, and terrain to simulate air concentrations. These studies will provide data on the field size, weather, terrain, and air concentrations, but not the flux. DPR will use the ISCST3 model to "back-calculate" an estimate of flux.

DPR will back-calculate fluxes by inputting the specific field dimensions, weather, and terrain data into the ISCST3 model, as well as an assumed flux value. The air concentrations simulated by the ISCST3 model (using the assumed flux value) will be regressed on the measured air concentrations (Johnson, et al. 1999). The slope of the regression line yields an adjustment or calibration factor for the assumed flux value used in the ISCST3 model. Using the calibrated flux value in the ISCST3 model gives the best match to the measured air concentrations. This flux calibration factor represents the flux for modeling purposes.

For each study, DPR will utilize the estimated flux to (1) test adequacy of buffer zones when they are known (2) determine the flux profile during the monitoring period and (3) compute the fractional mass loss for 24 and 48 hours. In addition, more general analyses will be conducted, if the database of monitoring studies will support it.

If there are multiple studies of the same fumigant mix, then a simple t-test will be utilized to determine if the ratio of the two fumigants' 24 and 48 hour emission ratios is significantly different from 1. The purpose of this is to assist in the development of buffer zones, increase our understanding of fumigants, and provide the basis for estimating flux in novel situations. In addition, if there are multiple studies of the same fumigant mix, the coefficient of variation of the emission factors for 24 and 48 hours will be computed. This information is important in assessing field-to-field variability in flux.

If flux studies have been conducted on the fumigant used in isolation and if such studies were conducted under conditions similar to those monitored in the DPR study, then the flux will be compared to determine if application in a mixture affects the flux. There is laboratory evidence that such interactions occur (Zheng et al. 2004).

Depending on the size and nature of the database, exploratory data analysis may be used to look for patterns in flux relating to application method, season, soil or other environmental factors.

## VIII. TIMETABLE

This study will take at least two years to complete. Most sampling will occur in summer and fall, but some monitoring may occur in other seasons. The number of fumigations monitored and time of monitoring will depend on availability of field and laboratory resources.

## IX. REFERENCES


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**Study 212: Protocol Amendment 1**
**April 5, 2004**

**Personnel** (for this phase of the protocol)

Johanna Walters - project leader
Dave Kim - field coordinator

**Study Plan**

The field is approximately 10.5 acres and is bordered to the north with railroad tracks (far side approximately 75 feet) followed by Hwy 99; a county owned labor camp and a single residence to the east side; Westside Dr. (approximately 30 feet) a peach orchard (approximately 80 feet) to the south; and thirteen rows of hotbeds to the west. Twelve samplers will be set up: four at the corners and two along each side equidistant from the corners and each other. Samples along the east side will be set up along the property line between the application field and the labor camp/residence. The other ten samplers will be set up at a distance ranging from edge of field to approximately 60 feet; all samplers will be approximately the same distance away from the field. Two background samples will run for a minimum of 12 hours prior to the application starting. Samples will be collected every four hours for the first 24 hours and then every 6 hours for the following 48 hours for a total of 14 sampling intervals.

Number of samples:

2 applications x 12 stations x 14 sample intervals = 336 samples + 4 background samples

**Application Method**

The application is an untarped, bedded drip application of metam sodium (Sectagon 42) at a rate of 32 pounds AI per acre. Beds are three-foot beds running in a north south direction with the drip tape laid on top. There will be 3 or 4 applications to the one field approximately 1 week apart; two applications will be monitored. The drip tape is moved between applications (from the sides to the center of the bed) to get full coverage with the chemical. Each application is expected to take approximately 5-6 hours with an additional hour of flushing the irrigation system with water. The second application monitored will include additional irrigation: length and timing of irrigation to be determined.

**Study 212: Protocol Amendment II**
**June 30, 2004**

## Introduction

Over 95% of all Easter Lily bulbs are produced in a narrow coastal region along the Northern California/Oregon borders from Smith River, California to Brookings, Oregon. In 2002, 438 acres in Del Norte County were planted for Easter lily bulb production, with a value of approximately $6.4 million dollars (Annual Crop Report for Del Norte County for 2002). Bulbs are sold to greenhouse operations to produce flowering plants. Soil fumigants are commonly used to control nematodes and fungi which are a serious threat to Easter lily production. The soil fumigants are applied in mid-July through mid-August just prior to planting. Fumigants used include, methyl bromide, 1,3-dichloropropene (Telone ®), and metam sodium.

A common method used in the Smith River Valley is to inject 1,3-dichloropropene and follow with a metam sodium application incorporated with a rototiller and roller. Both chemicals are applied at a rate of approximately 300 – 330 pounds active ingredient (ai.) per acre. The method involves separate application rigs for each chemical. The Department of Pesticide Regulation does not have any previous monitoring data for this method. This study will measure air concentrations and back-calculate emission rates to determine if the current buffer zones for metam sodium and 1,3-dichloropropene are appropriate, too restrictive, or inadequate for this method of application.

**Personnel** (for this phase of the protocol)

- Project leader, Pam Wofford
- Field coordinator, to be determined

## Study Plan

A field will be selected which is located at least 1 mile from any other application being made within 3 days prior to date of application. Two sets of twelve to sixteen samplers will be set up around the field in concentric circles at distance of approximately 50 and 150 feet from the edge of the field, one set for each chemical. The sampler pumps will be equipped with 200/400 mg coconut charcoal tubes set at an air flow rate of 1.5 liters per minute (L/min).

One set of background samples for both chemicals will be collected for a minimum of 12 hours prior to the start of application. Application monitoring will begin with the start of the 1,3-dichloropropene application. Samples will be collected every four hours for the first 24 hours, every 6 hours for the following 24 hours, and every 12 hours for the third, fourth and fifth 24-hour periods, for a total of sixteen sampling periods.

Number of samples:

Minimum – 2 chemicals x 12 sampling sites x 16 sampling intervals =
384 samples + 4 background samples.

Maximum – 2 chemicals x 16 sampling sites x 16 sampling intervals =
512 samples + 4 background samples.

Quality Control samples = 10 percent of sample total.

In addition, soil samples will be collected at 4 to 8 sites prior to application to measure texture, bulk density and soil moisture at the depth of application.

A meteorological station will be set up as close to the study field as possible.

The monitoring study may be repeated with a second field if another appropriate field is located.

**Study 212: Protocol Amendment 3**
**To the "Study 212: Protocol for Evaluation of Buffer Zones and Relative Emission Rates for Fumigants" April 5, 2004, revised July 30, 2004**
**http://www.cdpr.ca.gov/docs/empm/pubs/protocol/prot212a.pdf**

**April 29, 2005**

**Personnel** (for this phase of the protocol)
Shifang Fan - project leader
Dave Kim - field coordinator
Bruce Johnson - senior scientist

**Study Plan**
DPR will conduct a monitoring study of methyl isothiocyanate (MITC) and methyl bromide at a strawberry nursery in Manteca (San Joaquin County) involving multiple applications of Basamid, Telone C35, and methyl bromide/chloropicrin during May 2005.

In an approximately five acres (ac) field, the fumigation will consist of 12 experimental plots, each 100 x 22 feet (0.05 ac). There will be 3 different treatments: Basamid (200 lbs/ac) + Telone C35 (48 gals/ac), Telone C35 (48 gals/ac) only, and methyl bromide/chloropicrin (67/33, 350 lbs/ac). Each of the treatments will be replicated 4 times, for a total of 12 plots.

Twelve sampling stations will be arranged around the plots at approximately 30 to 50 feet from the edge of the plots. At each sampling station, two samplers will be placed to collect air samples, one for MITC using a coconut charcoal tube and the other for methyl bromide using a petroleum charcoal tube.

Monitoring will continue over a 5-day period. Air samples will be collected prior to, during, and after the fumigant applications. Prior to application, duplicate 12-hour air samples will be collected from the prevailing downwind direction to determine background levels of MITC and methyl bromide. Application samples will be collected from start of the first treatment to approximately 7:00 pm on the application day. Post application samples will be collected at approximately 7:00 pm/am rotations for the following 4 days. The number of samples to be collected is

12 stations x 2 chemicals (tubes)/station x 10 sampling intervals + 4 background samples
= 244 samples

Quality control will consist of approximately 5 samples for each of the two chemicals (one colocated sample for the application sampling interval at the downwind site, two field spikes at low and high spike dosages, 1 trip spike, and 1 trip blank).

In addition, duplicate soil samples will be taken for bulk density, moisture content, organic matter content, and texture information

**Application Method**

Methyl bromide/chloropicrin and Telone C35 will be applied using a standard broadcast soil fumigation rig. The methyl bromide/chloropicrin treatment will be tarped. Following the Telone C35 application, the Basamid will be broadcast-applied using a commercial tractor-mounted Gandy applicator (or an alternative piece of equipment) and then water-incorporated via sprinkler irrigation.