June 20, 2005

TO: Interested Parties

SUBJECT: GENERAL GUIDANCE FOR CONDUCTING FUMIGANT FIELD STUDIES

This letter gives general guidance on designing studies to adequately characterize both the flux and off-site air concentrations of fumigants following soil injection, granular spreading, and incorporation or drip applications. Sprinkler applications may involve separate direct-measure flux procedures and need to be individually discussed, though the majority of the material in these guidelines is relevant. Enclosed in this letter is a document outlining the types of studies the Department of Pesticide Regulation (DPR) suggests, and an example study layout. Fumigant field studies can be utilized to develop mitigation measures for off-site air concentrations associated with fumigant applications.

The enclosed documents assist in the development of a study protocol containing elements DPR needs to assess acceptability of the proposed study. The study protocol should include a detailed description of the analytical methods and quality control/quality assurance plan, the application site, application method and rate, and the air-sampling plan. The study should be conducted at the expected maximum-labeled application rate because, while extrapolation to smaller application rates is acceptable, extrapolation to larger rates is not. Since fumigants tend to be hazardous and the application may be large (for example, ten acres at the maximum anticipated application rate), the protocol should also include a discussion covering the basis and plans for worker protection measures and emergency response. A minimum buffer zone of 500 feet is required for applications of one acre or less. Applications larger than one acre will require examination on a case-by-case basis to specify an appropriate buffer zone. Any applicable Occupational Safety and Health Administration guidelines must be followed to insure that persons conducting the study will be adequately protected. If the fumigant is listed as a known human carcinogen under Proposition 65, the Office of Environmental Health Hazard Assessment should be contacted to insure compliance with Proposition 65 notification requirements.

Questions regarding the flux or off-site air concentration studies, may be directed to Dr. Terrell Barry, of my staff, at (916) 324-4140, or tbarry@cdpr.ca.gov , or Dr. Bruce Johnson, of my staff, at (916) 324-4106 or<bjohnson@cdpr.ca.gov >.

Sincerely,

Original signed by

John S. Sanders, Ph.D., Chief
Environmental Monitoring Branch
(916) 324-4039

Enclosures

cc: Dr. Terrell Barry, DPR Senior Environmental Research Scientist (w/Enclosures)
Dr. Bruce Johnson, DPR Senior Environmental Research Scientist (w/Enclosures)

Studies for Fumigant Off-site Mitigation

Date Established

June 20, 2005

Objective

Historically, the Department of Pesticide Regulation (DPR) has used results from scientific studies as a basis to develop mitigation measures to minimize exposure of persons off-site to fumigant vapors. Those scientific studies are discussed in this guidance document.

Definitions

- **Flux** – Physical chemists define flux as mass/area-time. Soil physicists define flux as mass/time (i.e. flow) and flux density as mass/area-time. In this, and other DPR documents, flux and flux density will be used interchangeably and will be defined with units of mass/area-time.
- **Air concentration –** To determine the concentration of a substance in air, a small sample volume is drawn into an appropriate measuring device. The mass of the substance within the sample volume is then determined by the appropriate analysis method. The results are usually expressed as mass/volume (e.g., ug/cm^3) or volume/volume (e.g., ppm) with the sampling time clearly specified. It should be understood that concentration results represent a time weighted average concentration over the entire sampling period.
- **Level of concern (LOC)** – The air concentration below which the margin of safety for exposure is assumed to be acceptable. In order to be meaningful, the LOC must have both air concentration level and duration of exposure specified.
- **Back-calculation technique** – This technique is essentially a calibration procedure where linear regression is used to adjust modeled air concentrations according to the observed patterns of measured air concentrations from a field study. This adjustment provides an estimate of the flux for the sampling period represented by the measured air concentrations. The basis for the back-calculation technique is the proportionality between flux and concentration in the Gaussian plume air concentration equation.
- **Mitigation measures –** Application techniques intended to reduce exposure to air concentrations associated with the loss of fumigants to the environment. Some examples of mitigation measures are tarping, supplemental irrigation, reduced application rate, and buffer zones.

Background

Fumigant use results in some loss of the fumigant from the point of application to the environment. DPR has implemented mitigation measures specific to currently registered fumigants that are intended to minimize both the loss of the fumigant to the environment and the impact of the unavoidable loss of the fumigant to persons off-site. The basis of these mitigation measures for various fumigants is similar. The actual measures vary from fumigant to fumigant, depending upon the LOC and the use practices of each fumigant. For currently registered fumigants, most of these measures are under continual review and improvement as new data is collected. DPR may require registrants of new fumigants, as part of the registration process, to submit studies which adequately characterize expected air concentrations and which can be reliably used together with computer simulation modeling to examine alternative scenarios and mitigation measures designed to keep exposures below the LOC.

Field studies are routinely conducted to measure air concentrations associated with the application of a fumigant. Mitigation measures are based in part on these field studies. However, a major drawback of field monitoring is that it can only determine air concentrations at the specific time and location that the monitoring took place. Extrapolating these data to other locations and times is very difficult due to variability in application size, application rate, weather, and other factors. To generalize results, DPR uses field data in conjunction with a computer simulation model, the Industrial Source Complex model (U.S. EPA 1995).

Once a set of mitigation measures are developed, permit conditions and regulations are among the methods used by DPR to implement those mitigation measures. Permit conditions and regulations are generally applicable statewide. DPR promotes uniformity of approaches between fumigants. This document outlines a uniform approach of developing generally applicable mitigation measures for fumigants. Development of generally applicable mitigation measures is highly desirable. Uniformity of approaches results in transparency of process and easily understood methods. For example, uniformity should be maintained with regard to methods used to estimate flux.

Scope

This document outlines the set of studies to: (1) demonstrate the reliability of measured air concentrations of a given fumigant (recovery study), (2) directly estimate flux (flux study), (3) perform back-calculation estimation of the flux (back-calculation study), and (4) test future modification of fumigant application procedures (follow-up studies).

Initial Studies Description

The initial studies lay the foundation for the development of the mitigation measures. The centerpiece of the initial studies is the flux study because the source strength (flux) will be obtained from the results of this study. A reliable estimate of the flux associated with an application type is necessary before mitigation measures can be developed. However, even before the flux study is conducted it must be demonstrated that the chemical under study can be reliably sampled and that analytical methods exist with proven acceptable performance (recovery) in the concentration range of interest. Therefore the initial studies are: (1) an analytical method development study, and (2) a flux study/back-calculation study. The components of these initial studies are discussed below.

Recovery Study – Before any field studies are conducted it is necessary to demonstrate the ability to both efficiently collect the chemical of interest on sampling media and to successfully analyze the sampling media with acceptable recoveries. This set of abilities is normally demonstrated in a recovery study. For fumigants, the recovery study should employ spiking methods that are similar to the conditions under which the fumigant is collected in the field. Therefore, liquid spikes are not acceptable (Biermann and Barry, 1999). Instead, some type of gaseous spiking should be employed. A protocol describing the recovery study should be submitted to DPR prior to the conduct of the study.

Flux Study – The design of this study should follow techniques to directly measure flux as described in the peer-reviewed literature. Some of the common methods are the Aerodynamic method (Majewski et al. 1993), Eddy Accumulation method (Majewski et al. 1993), and the Integrated Horizontal Flux method (Wilson and Shum 1992). The peer-reviewed literature should be consulted for details on planning and executing a flux study. A protocol describing the flux study should be submitted to DPR prior to the conduct of the study. Consult Segawa (1995) for chemistry laboratory quality control guidelines.

Back-calculation Study – For the initial studies, the back-calculation study should be combined with the Flux Study (described directly above) to both optimize the use of resources and establish the correspondence between the directly measured flux and the back-calculated flux. An example of the basic layout of a back-calculation study is given in Appendix I. The back-calculation technique to obtain an estimate of the flux is described in Johnson et al. (1999). This indirect flux estimation method compares favorably to the direct measurement aerodynamic method (Ross et al. 1996) and is less expensive to conduct. Therefore, once the correspondence between the directly measured flux and the back-calculated flux is established in the initial study, a back-calculation study alone can be employed in further investigations to explore various mitigation measures aimed at minimizing flux (see the “further studies” section below). A protocol describing the back-calculation study should be submitted to DPR prior to the conduct of the study. Consult Segawa (1995) for chemistry laboratory quality control guidelines.

Follow-up Studies

The most prudent approach to developing mitigation measures is to limit the application conditions allowed to those similar to conditions observed in field studies conducted to support registration or re-registration. DPR has considerable experience with methyl bromide demonstrating that assumptions about effectiveness of various mitigation measures are not always born out in field study results. For example, it is commonly assumed that increasing the depth of injection will significantly decrease flux. However, this assumed relationship between depth of injection and flux was not detectable in analysis of many DPR field studies (Barry 1999). Therefore, in order to "give credit" for mitigation measures that are different from those investigated in the initial studies, DPR needs further studies conclusively demonstrating the effectiveness of those mitigation measures. That evidence should consist of adequately designed comparison studies. Where appropriate and feasible, these may be replicated side-by-side comparisons with a control included. The control might be the common application method in practice, and/or the application method used in the initial studies. DPR regards as most convincing results demonstrating a statistically significant reduction in emissions. A protocol describing the study should be submitted prior to the conduct of the study.

Possible Mitigation Measures:

Application type (e.g. broadcast, bedded, drip)
Application rate
Application timing (e.g. day, night)
Application size (acreage limitations)
Tarp use
Depth of injection
Irrigation practices including pre- and post-application
Soil type
Soil Amendments
Season of use
Geographic area limitations
Buffer zones

References

Barry, T.A. 1999. Methyl bromide emission ratio groupings. Memorandum to Randy Segawa dated December 2, 1999. California Environmental Protection Agency, Department of Pesticide Regulation, Environmental Monitoring and Pest Management Branch. Sacramento, California. <http://www.cdpr.ca.gov/docs/empm/pubs/tribal/methbrom%20emiss%20groupings.pdf>.

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Appendix I

Guidelines for off-site field monitoring protocol for soil fumigants

Background. Since 1992, the Department of Pesticide Regulation's (DPR's) staff has designed and reviewed soil fumigant protocols and analyzed data from soil fumigant studies. This experience has led to a basic understanding of elements that increase the success of such studies. A primary objective of off-site studies is to estimate flux using the "back-calculation" procedure. A flux profile (the pattern of flux over time following an application) can be developed using the "back-calculation" procedure. This procedure can be applied to each sampling interval in a field study to estimate flux during that interval. The flux profile together with modeling provides a powerful methodology for investigating off-site fumigant air concentrations (Ross et al. 1986, Johnson et al. 1999).

The "back-calculation" procedure requires three elements: field and monitor geometry, meteorological data during the monitoring periods, and measured concentrations. Each of these elements is presented below. It must be mentioned that there is no guarantee of the success of field studies. Even with the best planning, field studies can fail. We believe that the guidelines presented below greatly increase the probability of a successful field study. In addition, the simulation model, ISCST3, which we have been using for the calculations, may be replaced by the U.S. Environmental Protection Agency with the AERMOD model. We have not used AERMOD for "back-calculation" procedures and anticipate a period of testing when AERMOD is adopted. However, it will be prudent to gather information, which would enable using AERMOD.

Field geometry and air sampler placement. The exact lengths and directions of the field must be accurately measured, as well as the locations of the air samplers relative to the field. Use of Global Positioning System equipment is desirable. The exact directions must also be measured with respect to either magnetic or true north, which must be specified. The directions are critical for properly interpreting the wind direction data.

If a bedded or row application is being studied, a cross section diagram showing the bed/row geometry in relation to the application sites should be provided. The diagram should clearly indicate the bed/row height, sides, furrows, depth of injection or depth of drip application, or location of sprinklers. For chemigation, operating characteristics of the irrigation system should be described (pressure, water rate, concentration, length of time of chemigation injection, watering in after chemigation, etc.).

An essential element of the air sampler placement is that they ring the field. Unsuccessful designs have depended upon a prevailing wind direction, allocating monitors on the downwind side, often to save monitoring costs by reducing the number of samplers. Invariably, wind direction shifts during the study and some sampling intervals are worthless because there are no downwind monitors. In addition, if the only positive measured concentrations are from monitors on the edge of a plume, excessively high flux estimates may result due to the sensitivity of the regression coefficient to variance in those relatively small concentrations.

The example study attached shows a rectangular field ringed by monitors. The monitors are located at different distances in a staggered fashion. A square shaped field is desirable to maximize fetch to the monitors regardless of wind direction. However, rectangular fields may also be used as long as the length to width ratio is not extreme (e.g., greater than five). Proposed use of a rectangular field should be included in the study protocol and discussed with DPR prior to initiating the field study.

Between 8 and 16 air samplers should be used. With eight air samplers, approximately 45-degree sectors can be covered at two distances. When fields are rectangular, instead of square, air samplers should be placed in approximate proportion to the side lengths.

Placement distances of the air samplers should be based on the range of air concentrations expected at the downwind air samplers over the course of the study and the minimum detection limit, which may depend on the length of the sampling interval. Air samplers should generally be close enough to detect positive concentrations when downwind, but not so close as to be adversely affected by low wind speed plume meander or diffusion during calms. Low wind, speed, or calm conditions can produce uniform concentrations at the closest samplers in many or all directions if the air samplers are located too close to the field. This situation leads to difficulty during the “back-calculation” procedure. Sometimes, specific distances are utilized for regulatory purposes; for example, to provide data at a buffer zone distance.

Air samplers should be on a mast at approximately 1.2m height which is close to the human breathing zone.

Enclosed to this draft is a methyl bromide study (Wofford and Segawa 1998) showing a reasonable arrangement for air sampler locations.

Meteorology. Meteorological measurements require on-site sensors. On-site does not mean on the treated field, but within 2-300 meters of the treated area. Wind measurements should be taken at 10m height. These measurements include wind, speed, and direction. Shielded air temperature measurements are also required. These measurements can be instantaneous measurements or averages over time. However, there should be a minimum 12 measurements of each parameter per hour. These measurements must be provided in an electronic format, as either an ascii file or spreadsheet file. Wind direction information must specify whether the frame of reference is truth north or magnetic north in order to properly align wind direction with the geometry of the field and air sampler location design. Degree of cloudiness on an hourly basis is necessary.

Utilize the following categories for cloud information:

0 clear or less than 0.1 coverage
1 thin scattered 0.1 to 0.5 coverage
2 scattered 0.1 to 0.5 coverage
3 thin broken 0.6 to 0.9 coverage
4 thin broken 0.6 to 0.9 coverage
5 broken 0.6 to 0.9 coverage
7 thin overcast 1.0 coverage
8 overcast 1.0 coverage

Ancillary measurements that can assist in interpreting results include soil temperature, soil moisture at injection depth and other depths, soil texture, soil organic carbon, and relative humidity. Site information must be provided including a diagram of the area around the study site showing buildings, berms, roads, towers, structures, trees, adjacent crops, etc. If soil moisture measurements are not provided, then qualitative descriptions must be provided such as dry, moist, wet, general soil type, and condition of field. Locate the meteorological station away from structures, berms, trees or other variations on the surface that might influence the wind measurements.

Sampling Intervals. Sampling intervals may range from 2 to 24 hours. Typical intervals for the first 48 hours in methyl bromide studies have been 6, 6, 12, 12, 12. Other regimes have included eight hour periods. However, there are a number of considerations. If the off-site study is being conducted in conjunction with a flux study, the off-site sampling intervals should correspond closely to the flux sampling intervals. Off-site monitoring should begin with the beginning of the application. The application period should be a separate sampling interval. It is desirable to separate night from day monitoring. In some cases, battery charge duration may determine the length of sampling intervals. Start and stop times, as well as air volumes must be recorded for each sample in a sampling interval. Airflow measurements must be taken on calibrated equipment. A complete sample change out within half-hour is optimal. Shorter sampling intervals (e.g. two to six hours) should be used when the peak flux/air concentrations are expected because when flux changes rapidly concurrent changes in wind direction will make it more difficult to model longer periods. Analytical aspects of the air sampling for field samples must have been validated prior to initiation of the field study.

Total duration of air sampling should be three times longer than the time to achieve peak concentrations, or until the average air concentrations decline to one tenth of the peak concentration. Thus, the air sampling results should clearly demonstrate that the peak concentrations have been captured and the flux has substantially declined. This prescription may be modified if air concentrations during tarp removal are being sampled since tarp removal may require additional sampling beyond the main peak. The study length may be increased if there are requirements to study the material as a volatile organic compound. Study personnel should discuss the proposed length of air sampling intervals and total length of study with personnel from Worker Health and Safety and Medical Toxicology Branches of DPR because health endpoints may affect these time periods, both in terms of the safety of workers conducting the study, as well as obtaining information appropriate for assessment of health endpoints.

Applications Parameters. The method of application must be carefully described, including depth of injection or depth of drip emitters. For injection, shapes and angles, dimension, and locations of implements must be diagramed, photographed, and described in detail. Pressures, valves, and mechanisms for controlling the injection flow must be described. If electronically controlled injection mechanisms are used, the calculated application rate must be compared to the rate obtained by weighing cylinders. The formulation must be clearly specified with regard to the percent of active ingredient.

The quantity of applied material must be accurately measured. This typically requires weighing cylinders before and after application to accurately measure the amount applied to the field. In addition, amounts left in the lines or purged should be noted. Application equipment should be designed and operated so that the injection of the material ceases when shanks are lifted out of the soil at the end of rows, while the tractor turns around.

For tarped applications, the tarping material, thickness, type, and manufacturer must be provided, as well as a physical sample of the tarp. For drip applications, the presence and locations of surface liquid (pooling or puddling) during the application period must be recorded. Pooling of applied material immediately upwind of air samplers can significantly affect the air sampling results.

Enclosure

References

Johnson, Bruce, Terrell Barry, and Pamela Wofford. 1999. Workbook for gaussian modeling analysis of air concentration measurements. EH99-03. California Environmental Protection Agency, Department of Pesticide Regulation, Environmental Monitoring and Pest Management Branch, Environmental Hazards Assessment Program. Sacramento, California 95814-3510 <http://www.cdpr.ca.gov/docs/dprdocs/methbrom/comp_modeling.htm>.

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State of California

Memorandum

To: John S. Sanders, Ph.D., Chief
Environmental Monitoring and
Pest Management Branch

Date: January 28, 1998

From: **Department of Pesticide Regulation** - 1020 N Street, Room 161
Sacramento, California 95814-5624

Subject: MONITORING RESULTS FROM A BEDDED TARPED APPLICATION IN RIVERSIDE COUNTY - METHOD 10

Introduction - Methyl bromide is widely used as a preplant soil fumigant for control of nematodes, fungi, diseases and weeds. The Department of Pesticide Regulation (DPR) and county agricultural commissioners have implemented permit conditions, including buffer zones, to mitigate unacceptable methyl bromide exposure. Buffer zone distances are set so that concentrations measured at this distance do not exceed 0.21 parts per million (ppm; 24-hour time-weighted average). The buffer zone distances for the methods have been determined from data received and evaluated by DPR to date. In some instances, methods which have not been previously monitored have been assigned similar buffer zones based on their similarity to application methods with monitoring data available. Additional monitoring was conducted to test and evaluate the effectiveness of the buffer zone distances for application methods where no or limited monitoring data was available.

Materials and Methods - The sixth application monitored was a 16.2 acre field near Indio (Riverside County) treated with methyl bromide by a tarped bed application method (method 10) on December 17, 1997. A tarped bed application is similar to a shallow tarped broadcast fumigation, where the area to be fumigated is disced and uncovered before application. In this case, tarpaulins were secured over beds formed immediately following injection of methyl bromide; the furrows were left untarped. The methyl bromide is injected into the soil through injectors at a depth of 12-14 inches. The specific equipment for this application method forms the beds and fumigates in one operation. With each pass the application equipment formed three beds with three injectors for each bed - set 5" apart. A second rig followed immediately behind to lay down

SURNAME | | | |

the high barrier tarpaulin. The field had sandy soil. The application rate was 200 pounds per acre of formulated product, 98 percent methyl bromide/2 percent chloropicrin. The applicators were not able to complete the entire 19-acre field application as planned, therefore the remaining 2.6 acres were treated the following day.

Ambient air samples were collected at 16 locations using charcoal tubes and SKC air samplers. Eight samplers were located at the resident buffer zone distance, from each edge. Eight other samplers were located approximately 30 feet from the field, one on each side and corner. Samplers were set up assuming that 19 acres would be fumigated and the buffer zone distance was set at 450 feet from edge of field. Instead, only 16.2 acres were treated so the samplers located at the buffer zone were beyond the actual buffer zone distance. The samplers located on the east side were located even further from the edge of field. Table 1 and Figure 1 indicate the position of each sampler. A series of three samples was collected at each of the 16 locations beginning with start of fumigation at 07:00. Samples were collected for two 6-hour and one 12-hour period, for a total of 24 hours.

The weather was clear with high clouds during daylight and clear at night with temperatures from 43 to 73 degrees Fahrenheit. Wind speeds ranged from very calm to 8 miles per hour with speeds 6 miles per hour or less for 83 percent of the time during monitoring. The wind blew predominantly to the east during the monitoring period.

Results - The buffer zone distance for the actual acreage treated was 420 feet. Ambient methyl bromide 24-hour time weighted average concentrations at the sample locations ranged from no detectable amount to 0.64 ppm. DPR's target level of 0.21 parts per million (24-hour time weighted average) was exceeded outside the buffer zone at samplers located 625 feet downwind from the application. The highest concentrations were detected during the third (12-hour) monitoring interval.

Please feel free to call if you have any questions.

Pamela Wofford — Randy Segawa

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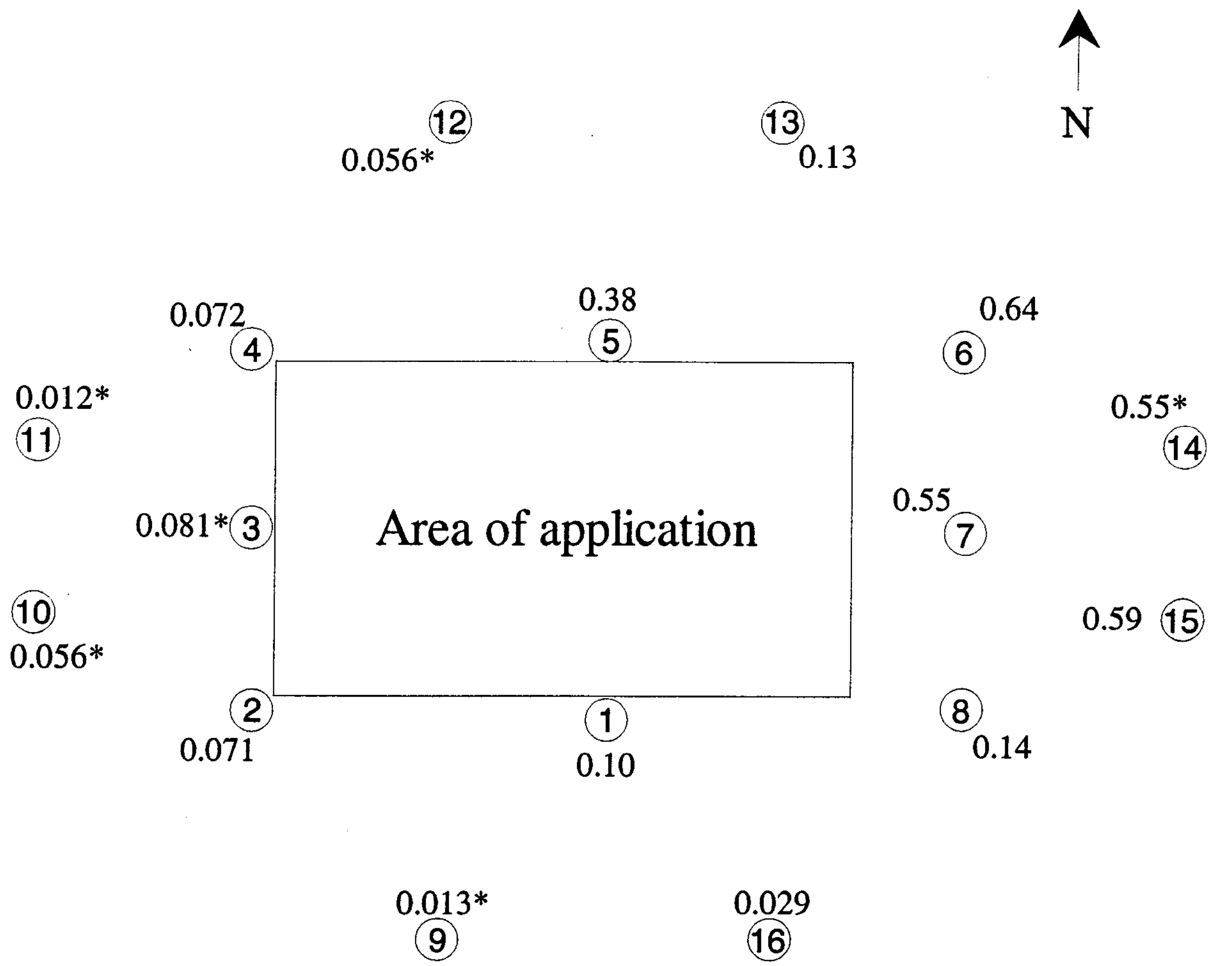
Figure 1. The application site, sampling sites and highest 24-hour time weighted averages (parts per million). (* indicates a period of no detectable amount where ½ the detection limit was used).



Sites 1-5 are located approx. 30 feet from field
Sites 6-8 are located approx. 200 feet from field
Sites 9-13, and 16 are located approx. 450 feet from field
Sites 14 and 15 are located approx. 625 feet from field

Table 1. Ambient methyl bromide air concentrations.

Sampler Location			Methyl Bromide (ppm) for Each Sampling Period			
Site	Direction	Distance (ft)	7:30 - 13:30 (6 hrs)	13:30 - 19:30 (6 hrs)	19:30 - 7:30 (12 hrs)	24-hr Peak[1] (24 hrs)
1	south	30	0.220	0.073	0.060	0.103
2	southwest	35	0.226	0.034	0.011	0.071
3	west	30	0.149	0.171	ND[b]	0.081*
4	northwest	35	0.050	0.225	0.005	0.072
5	north	30	0.085	0.773	0.337	0.383
6	northeast	195	0.023	0.738	0.894	0.637
7	east	205	0.034	0.306	0.922	0.546
8	southeast	205	0.029	0.083	0.226	0.141
9	south	450	0.038	0.015	ND	0.013*
10	west	450	0.013	ND	ND	0.006*
11	west	450	0.011	0.030	ND	0.012*
12	north	450	ND[a]	0.203	0.007	0.056*
13	north	450	0.010	0.350	0.072	0.126
14	east	625	ND	0.730	0.738	0.553*
15	east	625	0.034	0.405	0.966	0.593
16	south	450	0.014	0.024	0.038	0.029

[1] the 24-hour time-weighted average of the concentrations

* indicates a period of no detectable amount where ½ the detection limit was used

ND = No detectable amount; [a] reporting limit = 0.010 ppm, [b] reporting limit = 0.005 ppm