State of **California**

Memorandum

TO John S. Sanders
Branch Chief

Dale : December 2, 1994

Place : Sacramento

Phone : 324-4100

From : **Department of Pesticide Regulation** - Randy Segawa, Terri Barry, Pam Wofford and Clarice Ando

Subject : Methyl Bromide Monitoring: Building Fumigation, Madera County

This study measured the air concentrations associated with a methyl bromide fumigation of a warehouse, estimated the size of buffer zones required for this fumigation and how the measured concentrations compared to those predicted by a computer simulation model.

A total of 700 pounds of methyl bromide were used to treat the 320,000 cubic foot building. The treatment period was approximately 90 hours. At the end of the treatment period, all doors were opened to passively aerate the warehouse. Ambient air samples were collected at 16 locations using charcoal tubes and SKC air samplers. During the treatment period, leakage of methyl bromide from the fumigated building caused ambient concentrations to exceed the 0.21 ppm (24-hr time weighted average, TWA) target level. As much as 70% of the applied methyl bromide leaked out of the building during the first 24 hours of fumigation. During the treatment period, the highest 20-hour TWA detected **was** 0.96 ppm. Downwind air concentrations measured during the 2-hour aeration period were less than the 2.5 ppm (2-hr TWA) target level. It was estimated that a buffer zone of 308 feet would have been required during the treatment period.

The ISCST2 computer model generally performed well. Using the site specific data, the model did not display any bias, overestimating nine measured values and underestimating 13 measured values.

A complete description of the monitoring and modeling follows.

Approved: John S. Sanders Date: 12/5/94
Branch Chief

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Introduction - The objective of this monitoring was to measure the air concentrations associated with a methyl bromide fumigation of a building and to estimate the size of buffer zones required for this type of fumigation. This was one of several building fumigations which have been monitored to date. Data are needed for this type of fumigation because large amounts of methyl bromide are used and the buildings leak an unknown fraction of the applied methyl bromide.

Materials and Methods - The building fumigated was a corrugated metal warehouse, 80 by 160 feet and 25 feet tall used to process nuts. Prior to fumigation, all doors and other openings were sealed with plastic tarp. Methyl bromide was introduced into the structure on May 28, 1993, 12: 15 PM. A total of 700 pounds of methyl bromide were used to treat the 320,000 cubic foot building (application rate 2.2 lbs/1000 ft^3, 9000 ppm). The treatment period was approximately 90 hours. At the end of the treatment period, all doors were opened to passively aerate the warehouse. The aeration period was an additional 2 hours.

Ambient air samples were collected at 16 locations using charcoal tubes and SKC air samplers. Eight of the sampling locations were 30 feet from building, four were approximately 300 feet and four were 500 feet (Figure 2). A series of seven samples were collected at each of the 16 locations during treatment. Sampling periods varied between 8 and 24 hours. During the aeration period, a single 2-hour sample was collected at each of 8 locations (Figure 3). The California Department of Food and Agriculture's Chemistry Laboratory Services determined the amount of methyl bromide in the charcoal tube samples by extracting with ethyl acetate and analyzing with a gas chromatograph/electron capture detector. Wind speed, wind direction, temperature and humidity were recorded at five minute intervals with a Met-1® weather station located at the site. Heavy rainfall on May 31 prevented a scheduled sampling tube change and may have affected the results for that date.

Methyl bromide concentrations inside the building were measured during the treatment period with a fumiscope and charcoal tubes.

Results - During the treatment period, leakage of methyl bromide from the fumigated building caused ambient concentrations to exceed the 0.21 ppm (24-hr time weighted average, TWA) target level. The leakage or dissipation of methyl bromide from inside the warehouse followed an exponential decay, with an assumed form of:

$$y = A_0 e^{rt} \text{ or}$$

$$\ln(y) = \ln(A_0) + rt$$

where: A_0 = concentration at time 0
t = time in hours
r = exponential coefficient
y = concentration at time t

Using the concentration measurements from inside the warehouse (Table 1, Figure 1) to estimate the exponential coefficient, the linear regression fit is:

$$y = 7727 \text{ ppm} \times e^{-0.05t} \qquad R^2 = 99.4\% \qquad p = 0.000$$

This equation indicates that at least 30% of the applied methyl bromide was retained within the structure during the first 24 hours of fumigation. Absorption of methyl bromide during this period was probably minimal, since most of the building was empty. Therefore, up to 70% of the applied methyl bromide leaked out of the building during the first 24 hours of fumigation. This leakage lead to methyl bromide being detected downwind from the building. During the treatment period, the highest 20-hour TWA detected was 0.96 ppm with a peak concentration of 1.04 ppm-8 hour average (Table 2, Figure 2). Figure 2 shows the measured geographic pattern of air concentrations. As expected, the highest methyl bromide concentrations were detected in the predominant wind direction, with concentrations decreasing with increasing distance from the source. The exception to this pattern were the concentrations detected to the east, where the closer sampling site (300 ft east, 0.018 ppm) had a lower concentration than the site located further away (500 ft east, 0.141 ppm). There is no explanation for this discrepancy.

Downwind air concentrations measured during the 2-hour aeration period were less than 2.5 ppm (2-hr TWA) target level. The highest concentration detected was 0.26 ppm (Table 3, Figure 3). The low downwind concentrations were due to the relatively small amount of methyl bromide remaining within the warehouse at the end of the 90 hour treatment period. Just prior to aeration, the methyl bromide concentration within the warehouse was 79 ppm.

The measured concentrations were compared to the concentrations predicted by the Industrial Source Complex-Short Term 2 (ISCST2) model (Table 4). Only the treatment period was modeled because the aeration period had too few positive samples. For the treatment period, the fumigation was modeled as an area source, with an emission rate determined from the air concentrations measured inside the building.

The treatment period was first modeled as a single area source. However, this resulted in poor agreement between the measured downwind concentrations and the ISCST2 model. The building, or emission source, was then modeled as a “stacked” area source. Five sources were arrayed at various heights from three to thirty feet above ground level. Regression of the predicted and measured values showed that the model estimated the measured concentrations fairly well:

1 st sampling period: measured = 0.897(modeled) + 0.079 $\qquad R^2 = 53.3\% \qquad p = 0.003$

2nd sampling period: measured = 1.03(modeled) + 0.032 $\qquad R^2 = 48.1\% \qquad p = 0.001$

Conclusions - Both the methyl bromide concentrations measured inside the fumigated warehouse, as well as the ambient concentrations measured downwind from the warehouse gave supporting evidence that significant methyl bromide leakage occurred. This warehouse lost as much as 70% of the applied methyl bromide during the first 24 hours of fumigation. As with other building fumigations, all large seepage areas such as doors and vents were tarped and sealed before fumigation. However, this warehouse had more leakage than the others that have been monitored. The difference in leakage may be due to the construction materials. This warehouse was constructed of corrugated metal, while the others were constructed of concrete. Downwind air concentrations reflected the high leakage during treatment. High concentrations were detected during the treatment period, and low concentrations were detected during aeration.

The ISCST2 model generally performed well. Using the site specific data (emission rate, emission source dimensions, weather), the model did not display any bias, overestimating nine measured values and underestimating 13 measured values. However, in order to calculate generalized buffer zones that encompass all types of facilities, all of the site specific information cannot be used. In particular, default assumptions must be made regarding weather conditions and source dimensions, two factors which significantly influence the size of the buffer zone. Depending upon the default assumptions used, the resulting generalized buffer zones may be much larger than needed for the great majority of fumigations. Some flexibility in the size of the buffer zones can be provided by using site specific application rates, size of volumes fumigated, and proportion of methyl bromide retained.

Table 1. Methyl bromide concentrations inside building during the treatment period. Treatment started on 5/28/93, 12: 15 PM.

Date/Time Sampled	Elapsed Time (hrs)	Methyl Bromide (ppm)
5/28/93/1315	1.0	9159
5/28/93/1935	7.3	5031
5/29/93/0835	20.3	2580
5/29/93/2010	31.9	1354
5/30/93/0820	44.1	774
5/30/93/2010	56.1	379
5/31/93/2010	80.1	149
6/1/93/0550	*89.8*	*79*

Figure 1. Methyl bromide concentrations inside building

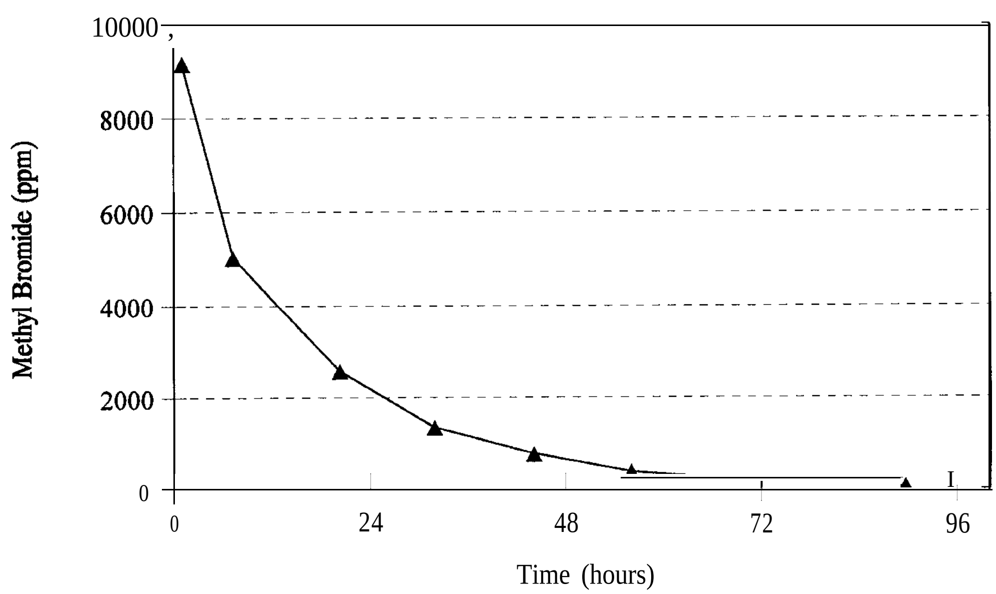

Table 2. Ambient methyl bromide concentrations during the treatment period

Sample Location		Methyl Bromide Concentration (ppm) for Each Time Period						
		5/28/94	5/28-29/94	5/29/94	5/29-30/94	5/30/94	5/30-31/94	5/31-6/1/94
		1215-1935	1935-0835	0835-2010	2010-0820	0820-2010	2010-2010	2010-0550
Transect	Distance (ft)	(7 hrs)	(13 hrs)	(12 hrs)	(12 hrs)	(12 hrs)	(24 hrs)*	(10 hrs)
North	30	0.132	0.057	0.086	ND**	not sampled	not sampled	not sampled
Northwest	30	0.008	ND	0.063	ND	not sampled	not sampled	not sampled
West	30	0.119	0.022	0.048	ND	not sampled	not sampled	not sampled
Southwest	30	0.037	ND	0.039	ND	ND	0.007	ND
Southwest	200	ND	ND	0.007	ND	ND	ND	sample lost
Southwest	400	ND	ND	ND	ND	not sampled	not sampled	not sampled
South	30	0.639	0.771	0.127	0.238	0.073	0.075	0.056
South	300	ND	0.010	0.006	ND	ND	sample lost	ND
South	500	ND	ND	ND	ND	not sampled	not sampled	not sampled
Southeast	30	0.384	0.397	0.033	0.155	0.049	0.032	0.039
Southeast	300	0.054	0.059	ND	0.040	0.009	0.003	0.013
Southeast	500	0.028	0.030	ND	0.014	not sampled	not sampled	not sampled
East	30	1.041	0.907	0.096	0.254	0.121	0.048	0.076
East	300	0.035	ND	ND	0.009	ND	ND	ND
East	500	0.301	0.040	ND	0.005	not sampled	not sampled	not sampled
Northeast	30	0.241	0.178	0.042	0.029	not sampled	not sampled	not sampled

* Significant breakthrough in these samples

** None Detected, detection limit approximately 0.006 ppm

Figure 2. Methyl bromide concentrations (ppm, time weighted average) during the first 20 hours

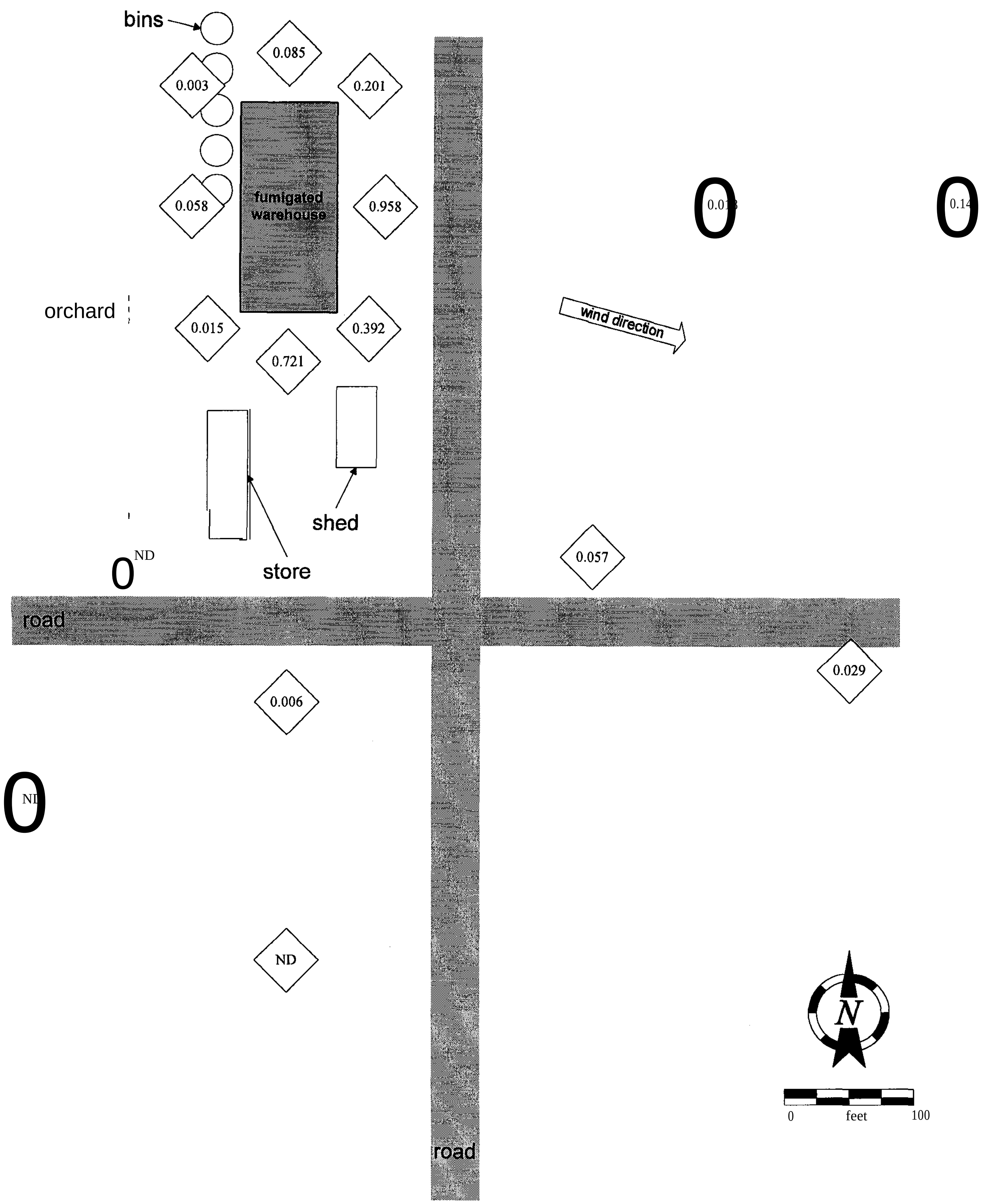

Table 3. Ambient methyl bromide concentrations (2-hour average) during the aeration. Aeration and samplers started simultaneously on 6/1/93, 6:37 AM.

Sample Location		Methyl Bromide
Transect	Distance (ft)	(ppm)
Southwest	30	0.030
Southwest	200	ND*
South	30	0.261
South	300	ND
Southeast	30	0.034
Southeast	300	ND
East	30	ND
East	300	ND

* None Detected, detection limit approximately 0.03 ppm

Figure 3. Methyl bromide concentrations (ppm) during the first 2 hours of aeration

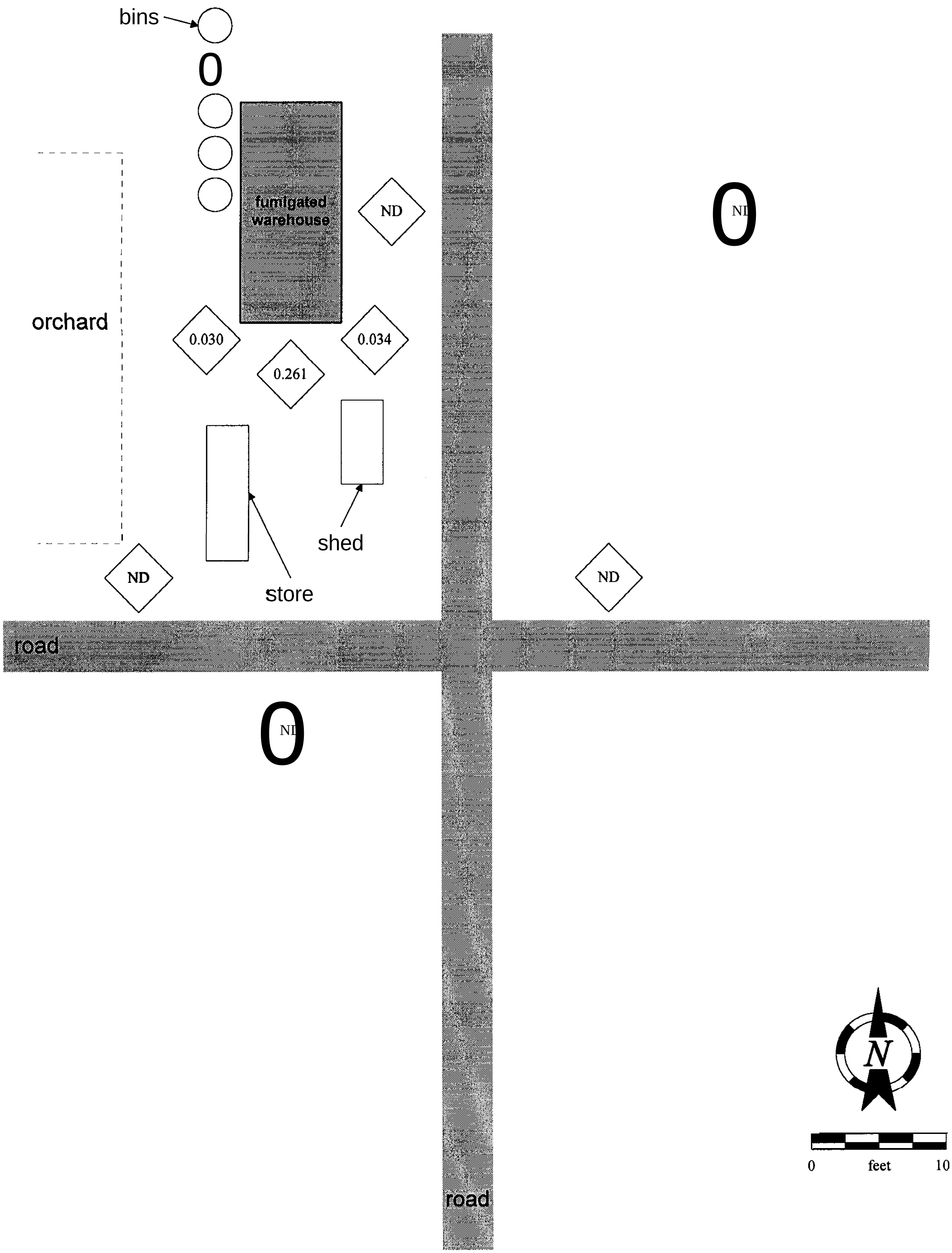

Table 4. Comparison of methyl bromide concentrations measured in the field to those predicted by the ISCST2 model.

Sample Location		Methyl Bromide (ppm)			
		5/28/94 12:15-19:35		5/28-29/94 19:35-08:35	
Transect	Distance (ft)	measured	modeled	measured	modeled
North	30	0.132	0.000	0.057	0.000
Northwest	30	0.008	0.000	ND	0.000
West	30	0.119	0.000	0.022	0.000
Southwest	30	0.037	0.000	ND	0.000
Southwest	200	ND	0.000	ND	0.000
Southwest	400	ND	0.000	ND	0.000
South	30	0.639	0.046	0.771	0.145
south	300	ND	0.000	0.010	0.000
South	500	ND	0.000	ND	0.000
Southeast	30	0.384	0.617	0.397	0.603
Southeast	300	0.054	0.234	0.059	0.205
Southeast	500	0.028	0.111	0.030	0.143
East	30	1.041	0.779	0.907	0.547
East	300	0.035	0.102	ND	0.154
East	500	0.301	0.045	0.040	0.099
Northeast	30	0.241	0.018	0.178	0.000