State of California

Memorandum

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

Date: June 16, 1994

Place: Sacramento

Phone: 324-4248

From: Department of Pesticide Regulation - Randy Segawa, Terri Barry, Heinz Biermann, and Pam Wofford
Environmental Hazards Assessment Program (EHAP)

Subject: Methyl Bromide Monitoring: Building Fumigations, Sutter County

Ambient concentrations associated with two large building fumigations were monitored. The two buildings were both concrete warehouses, one 6,800,000 cubic feet and the second 3,100,000 cubic feet. The fumigations occurred one week apart. The highest concentration detected during the treatment periods was 0.131 parts per million (ppm) as a 23-hour time weighted average. The highest concentration detected during the aeration periods was 3.2 ppm as a 4.3-hour time-weighted average (0.55 ppm, 24-hour time-weighted average). During aeration, concentrations exceeding the 0.21 ppm (24-hour time-weighted average) were detected as far as 860 feet from the source. Comparison of the measured concentrations to those predicted by the Industrial Source Complex-Short Term 2 model showed inconsistent results. The modeling results were marginal for the treatment periods because of low wind speeds. However, during aeration modeled concentrations generally matched those measured at the sampling sites. A detailed description of the monitoring and modeling is attached.

Attachments

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Introduction - The objectives of this monitoring were to measure the air concentrations associated with a methyl bromide fumigation of a building, estimate the size of buffer zones required for this type of fumigation, and compare the measured concentrations with those predicted by a computer simulation model . This is one of several building fumigations monitored. Data are needed for this type of fumigation because they typically require a large amount of methyl bromide and leak an unknown fraction.

Materials and Methods - Two separate fumigations were monitored, both buildings were concrete warehouses used to process dried fruit. The first fumigation monitored was a single building that contained two adjacent warehouses (Warehouses 1 and 2) fumigated at the same time. Warehouses 1 and 2 combined were 400 by 680 feet and 25 feet tall. Warehouse 4 was fumigated separately and was 300 by 350 feet and 30 feet tall. Prior to fumigation, all doors and other openings were sealed with plastic tarps. Warehouses 1 and 2 were fumigated beginning on October 15, 1993, 7:50 AM. A total of 7350 pounds of methyl bromide were used to treat the 6,800,000 cubic foot building (application rate 1.1 lbs/1000 ft^3, 4500 ppm). The treatment period was approximately 24 hours. At the end of the treatment period, several doors were opened and roof fans forced air out of the ground-level doors to aerate the warehouse. The aeration period was an additional 48 hours. Warehouse 4 was fumigated beginning October 20, 1993, 9:00 AM. A total of 2975 pounds of methyl bromide were used to treat the 3,100,000 cubic foot building (application rate 1.0 lbs/1000 ft^3, 4000 ppm). The treatment period was approximately 24 hours. At the end of the treatment period, several doors were opened and four fans forced air out of roof vents to aerate the warehouse. The stack for each fan was 30 inches in diameter, with a height of six feet above the roof. The rated fan capacity was 27,000 cubic feet per minute. The aeration period was an additional 24 hours.

Ambient air samples were collected at 14 to 21 locations using charcoal tubes. Most of the sampling locations were along the property perimeter, 100 to 1460 feet from the fumigated building (Figures 1 - 4). A series of two, 12-hour samples were collected at each of the designated sampling locations during treatment. During aeration, either one or two, 2-hour samples were collected at each of the designated sampling locations. 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 live minute intervals with a Met-1® station located at the site.

The measured concentrations were compared to the concentrations predicted by the Industrial Source Complex-Short Term 2 (ISCST2) model. This model uses the emission rate, emission characteristics (dimensions, emission height), weather conditions (wind direction, wind speed, atmospheric stability), and terrain characteristics (urban or rural) to estimate the downwind air concentrations.

Air concentrations inside the building were measured during the treatment period and after the aeration was completed. During the treatment period, concentrations were measured with a Fumiscope. After aeration, concentrations were measured with a Fourier Transform Infrared Spectrometer (FTIR). The spectra were averaged and recorded at 15 minute intervals.

Results (Warehouses 1 and 2) - Fumiscope readings and ambient samples indicated minimal leakage of methyl bromide from the building occurred during the treatment period. The initial air concentration inside the building was 71% of the theoretical application rate, with no significant decrease during the entire treatment period (Table 1). During the treatment period, ambient concentrations did not exceed the 0.2 1 ppm (24-hr time weighted average, TWA) target level at any of the sampling sites. The highest 22-hour TWA detected was 0.093 ppm (Table 2). Figure 1 shows the geographic pattern of air concentrations. As expected, the highest concentrations are located along the predominant wind direction.

Two unusual events apparently had minimal effect on the concentrations detected. The first was a leak in one of the fumigation lines. This leak caused an unknown amount of liquid methyl bromide to be released outside the building. The second event was heavy rainfall for approximately one hour at the beginning of the treatment period.

Since minimal leakage and low ambient concentrations of methyl bromide were detected during the treatment period, it was anticipated that most of the applied methyl bromide would be released during aeration and higher concentrations would be detected. As expected, air concentrations during aeration exceeded the target level. Concentrations exceeding the target level were detected as far as 860 feet from the fumigation (Table 3). Monitoring during this period also showed the highest concentrations along the predominant wind direction (Figure 2, Figure 3). Since methyl bromide was still found during the last sampling period, detectable concentrations would be expected to continue past the 4-hour monitoring period and the 24-hour TWA concentrations would be higher than those documented here.

The ISCST2 model was unable to predict the downwind air concentrations from this fumigation because the predominant wind direction was from the south and into the building. The ISCST2 model is unable to predict the concentrations associated with a plume blowing into the wall of a structure.

Methyl bromide was measured inside the building after the completion of aeration. While the S-hour target concentration of 0.63 ppm was not exceeded, two “spikes” were detected (Figure 4). It is possible the spikes were associated with turning off the ventilation fans. When the fans are off, methyl bromide off-gassing from the treated commodity accumulates within the building.

Results (Warehouse 4) - During the treatment period, again minimal leakage of methyl bromide from the building was detected. The initial air concentration inside the building was

65% of the theoretical application rate, with no significant decrease during the entire treatment period (Table 5). During the treatment period, ambient concentrations did not exceed the 0.21 ppm (24-hr time weighted average, TWA) target level at any of the sampling sites. The highest 23-hour TWA detected was 0.13 1 ppm (Table 6). Figure 5 shows no geographic pattern of high and low air concentrations. This is probably due to very low wind speeds and lack of a predominant direction during this period.

Air concentrations during aeration also exceeded the target level for this fumigation. Concentrations exceeding the target level were detected as far as 330 feet from the fumigation (Table 6). Monitoring during this period showed a more diffuse pattern than observed during the fumigation of Warehouses 1 and 2 (Figure 6). This is because of a sudden change in wind direction 30 minutes into the aeration (Figure 7). Had there been no wind shift, downwind concentrations would have been higher. High concentrations, relative to the other sites, at the sampler located 100 feet south of the warehouse indicates that building downwash occurred. Had the exhaust stacks been high enough to escape the building downwash, this sampler would have shown low concentrations.

The measured concentrations were compared to the concentrations predicted by the ISCST2 model. For the treatment period, this facility was modeled as an area source. Since a reliable estimate of the emission rate was not obtained from the monitoring, it was "back-calculated" from the monitoring data. This was done by adjusting the emission rate input into the model until modeled concentrations approximately matched the measured concentrations. The "back-calculated" emission rate for the treatment period resulted in an estimated leakage rate of 154 lbs or 5% of the applied amount. To obtain this estimate, one value (the second interval for site 21) was considered an outlier and removed. The modeled concentrations did not match the measured values well, probably because of the low wind speeds during the treatment period (Table 7). The model does not predict well at low wind speeds, particularly when there is no wind for extended periods. The linear regressions of the modeled concentration as predicted by the measured concentration had R^2 values of 32% and 49.5% for the first and second sampling periods, respectively. However, the slopes were significant at the $p = 0.05$ and 0.001 levels for the two periods.

For the aeration period, this facility was modeled as a single stack located at the center of the configuration of the four stacks. The emission rate was estimated at one minute intervals using the following equation:

$$C_t = C_0 e^{-(xt/v)}$$

where: v = volume of the building (3,100,000 cubic feet)
x = air flow rate (varied until modeled matched measured concentrations)
C_0 = building concentration at the end of treatment (2850 ppm)
t = time after the start of aeration in minutes

The modeled concentrations for the aeration more closely matched the measured concentrations than the treatment period (Table 8). A regression of measured on modeled concentrations gave an R^2 of 63.3% and a slope of 0.56. The slope was significant at the p = 0.001 level. The slope indicates that the model generally underestimated the measured concentrations.

Based on measured and modeled concentrations, the furthest distance at which 0.21 ppm (24-hr TWA) occurred during aeration was estimated to be 330 feet from the source exhaust stack. The furthest distance at which 0.21 ppm occurred for the treatment period could not be estimated, but was closer than 50 feet.

Concentrations inside Warehouse 4 were measured with the FTIR starting 5 hours after the initiation of aeration. Concentrations declined exponentially during the monitoring period, but still exceeded the 0.63 ppm, S-hour target level at the end of the monitoring, 28 hours after the start of aeration (Figure 8).

Conclusions - This structure is a concrete building with all large leakage areas such as doors and vents tarped and sealed before fumigation. Therefore, this building could be expected to retain more methyl bromide than some other building types, for example those constructed of corrugated metal. In addition, Warehouses 1 and 2 had only two exterior walls and during the fumigation of Warehouse 4 wind speeds were low (less than 5 mph). As a result, these buildings retained a high proportion of the applied methyl bromide and the target level was not exceeded along the property perimeter.

Conversely, a large amount of methyl bromide was released during aeration. During the aeration, measured concentrations exceeded the target concentration at distances of 860 and 330 feet from the source for Warehouses 1/2 and 4, respectively. For some areas just outside the property boundaries, exposure exceeding the target level could have occurred in less than one hour after the start of aeration, In addition, detectable concentrations within the buildings and/or downwind were measured at the end of monitoring period (120 minutes after the start of aeration). Therefore, the actual 24-hour TWA concentrations and required buffer zone size would be higher than those estimated here.

The ISCST2 model performed inconsistently. It is believed that this was mainly due to the unusual weather conditions at the time of the monitoring. During the treatment period, wind speeds were less than 5 mph and sometimes zero. The ISCST2 model is unable to predict concentrations when wind speeds are less than 2 mph. Therefore, extended periods of low wind speeds are difficult to model. During aeration, the wind direction changed suddenly. In addition, the emission rate changed by several orders of magnitude during this period. These conditions made precise modeling problematic. Despite these problems, during the crucial aeration phase, the modeled concentrations compared well with the measured concentrations. The ISCST2 model overestimated 6 samples, underestimated 4 samples and agreed on 4

samples with no detectable amount. In addition, the model correctly predicted the geographic pattern of high and low sites.

Within limitations, the ISCST2 model can adequately predict methyl bromide concentrations using the site specific data (emission rate, emission source dimensions, weather). However, in order to calculate buffer zones which encompass all types of facilities, 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 on the assumptions used, the resulting buffer zones may be much larger than needed for the great majority of fumigations.

Monitoring within the buildings after aeration indicates that methyl bromide continues to off-gas from the treated commodity for an extended period of time. Either the aeration period must be extended, or additional fresh air must be brought in to maintain concentrations below the target level.

Table 1. Interior methyl bromide concentrations during the treatment of warehouses 1 and 2

Date/Time	Methyl Bromide (ppm)
10/15/93 11:10	3200
10/15/93 14:50	2900
10/15/93 18:55	2800
10/16/93 06:05	3100

Table 2. Ambient methyl bromide concentrations during the treatment of Warehouses 1 and 2

Sample Location	Distance From Source (feet)	Methyl Bromide (ppm) for Each Time Period		
		07:30-19:00	19:00-06:00	Average
1	930	0.021	0.027	0.024
2	780	0.022	0.012	0.017
3	750	0.023	ND*	0.013
4	850	ND	ND	ND
5	350	ND	ND	ND
6	350	ND	ND	ND
7	380	ND	ND	ND
8	860	ND	ND	ND
9	1120	ND	ND	ND
10	1100	ND	ND	ND
11	1100	ND	ND	ND
12	1100	ND	ND	ND
13	600	ND	ND	ND
14	140	ND	ND	ND
15	180	0.008	0.027	0.017
16	200	0.029	0.071	0.050
17	340	0.046	0.142	0.093
18	860	0.030	0.066	0.048
19	220	ND	ND	ND
20	260	ND	ND	ND

* ND - None Detected, detection limit approximately 0.005 ppm for 12-hr sample

Table 3. Ambient methyl bromide concentrations during the aeration of Warehouses 1 and 2

Sample Location	Distance From Source (feet)	Methyl Bromide (ppm) for Each Time Period			
		07:00-09:20	09:20-11:20	Average	24-hr Average
1	930	0.889	0.282	0.620	0.107
2	780	0.036	0.057	0.046	0.008
3	750	ND*	0.016	0.008	0.001
4	850	ND	0.005	0.004	0.001
5	410	ND	0.006	0.004	0.001
6	410	ND	0.007	0.004	0.001
7	410	ND	ND	ND	ND
10	1100	ND	ND	ND	ND
13	600	ND	ND	ND	ND
14	140	0.012	0.036	0.023	0.004
15	180	0.965	0.397	0.705	0.121
16	200	2.842	0.349	1.710	0.296
17	340	5.522	0.473	3.233	0.554
18	860	3.823	0.627	2.387	0.409

* ND - None Detected, detection limit approximately 0.005 ppm for 2-hr sample

Table 4. Interior methyl bromide concentrations during the treatment of warehouse 4

Date/Time	Methyl Bromide (ppm)
10/20/93 13:35	2600
10/20/93 20:35	2300
10/21/93 07:55	2700

Table 5. Ambient methyl bromide concentrations during the treatment of Warehouse 4

Sample Location	Distance From Source (feet)	Methyl Bromide (ppm) for Each Time Period		
		09:00-20:30	20:30-08:10	Average
1	1460	ND*	0.005	0.004
2	1310	ND	0.005	0.004
3	1280	ND	0.007	0.005
4	1560	ND	0.006	0.004
5	980	ND	0.010	0.006
6	860	ND	0.013	0.007
7	740	ND	0.019	0.011
8	790	ND	0.012	0.007
9	900	ND	0.009	0.006
10	750	ND	0.013	0.008
11	610	ND	0.015	0.009
12	620	ND	0.008	0.005
13	220	ND	0.026	0.014
14	110	0.033	0.025	0.029
15	360	0.011	0.011	0.011
16	590	0.009	0.013	0.011
17	810	0.009	0.007	0.008
18	1070	0.005	0.009	0.007
21	100	0.044	0.220	0.131
22	100	0.022	0.048	0.034
23	100	0.014	0.05 1	0.032

* ND - None Detected, detection limit approximately 0.005 ppm for 12-hr sample

Table 6. Ambient methyl bromide concentrations during the aeration of Warehouse 4

Sample Location	Distance From Source (feet)	Methyl Bromide (ppm) 09:00-11:00	24-hr Average
7	830	0.041	0.003
8	900	0.447	0.039
9	1030	0.528	0.044
10	870	0.479	0.041
11	700	0.352	0.030
12	740	0.816	0.070
13	330	3.170	0.277
14	220	0.004	0.000
15	460	ND*	ND
16	700	ND	ND
17	900	ND	ND
21	190	0.028	0.002
22	190	0.380	0.033
23	190	1.119	0.098

* ND - None Detected, detection limit approximately 0.005 ppm for 2-hr samples

Table 7. Measured and modeled methvl bromide concentrations for Warehouse 4

Sample Location	Methyl Bromide (ppm) for Each Time Period 09:00-20:30 Measured	09:00-20:30 Modeled	20:30-08:10 Measured	20:30-08:10 Modeled	Aeration (09:00-11:00) Measured	Aeration (09:00-11:00) Modeled
1	ND*	0.009	0.005	0.000		
2	ND	0.000	0.005	0.000		
3	ND	0.000	0.007	0.000		
4	ND	0.000	0.006	0.000		
5	ND	0.000	0.010	0.000		
6	ND	0.000	0.013	0.000		
7	ND	0.0027	0.019	0.0029	0.041	0.764
8	ND	0.0033	0.012	0.0008	0.447	0.464
9	ND	0.014	0.009	0.0092	0.527	0.548
10	ND	0.021	0.013	0.011	0.479	0.994
11	ND	0.016	0.015	0.015	0.352	0.025
12	ND	0.0024	0.008	0.0043	0.816	0.315
13	ND	0.0056	0.026	0.052	3.170	2.200
14	0.033	0.083	0.025	0.000	ND	0.000
15	0.011	0.041	0.011	0.000	ND	0.000
16	0.009	0.039	0.013	0.000	ND	0.000
17	0.009	0.03 1	0.007	0.000	ND	0.000
18	0.005	0.016	0.009	0.000		
21	0.044	0.019	outlier removed		0.280	0.988
22	0.022	0.019	0.047	0.0088	0.380	0.665
23	0.014	0.093	0.051	0.069	1.120	0.667

* None Detected, detection limit approximately 0.005 ppm

Figure 1. Methyl bromide concentrations (22-hr TWA, ppm) during treatment of Warehouses 1 and 2

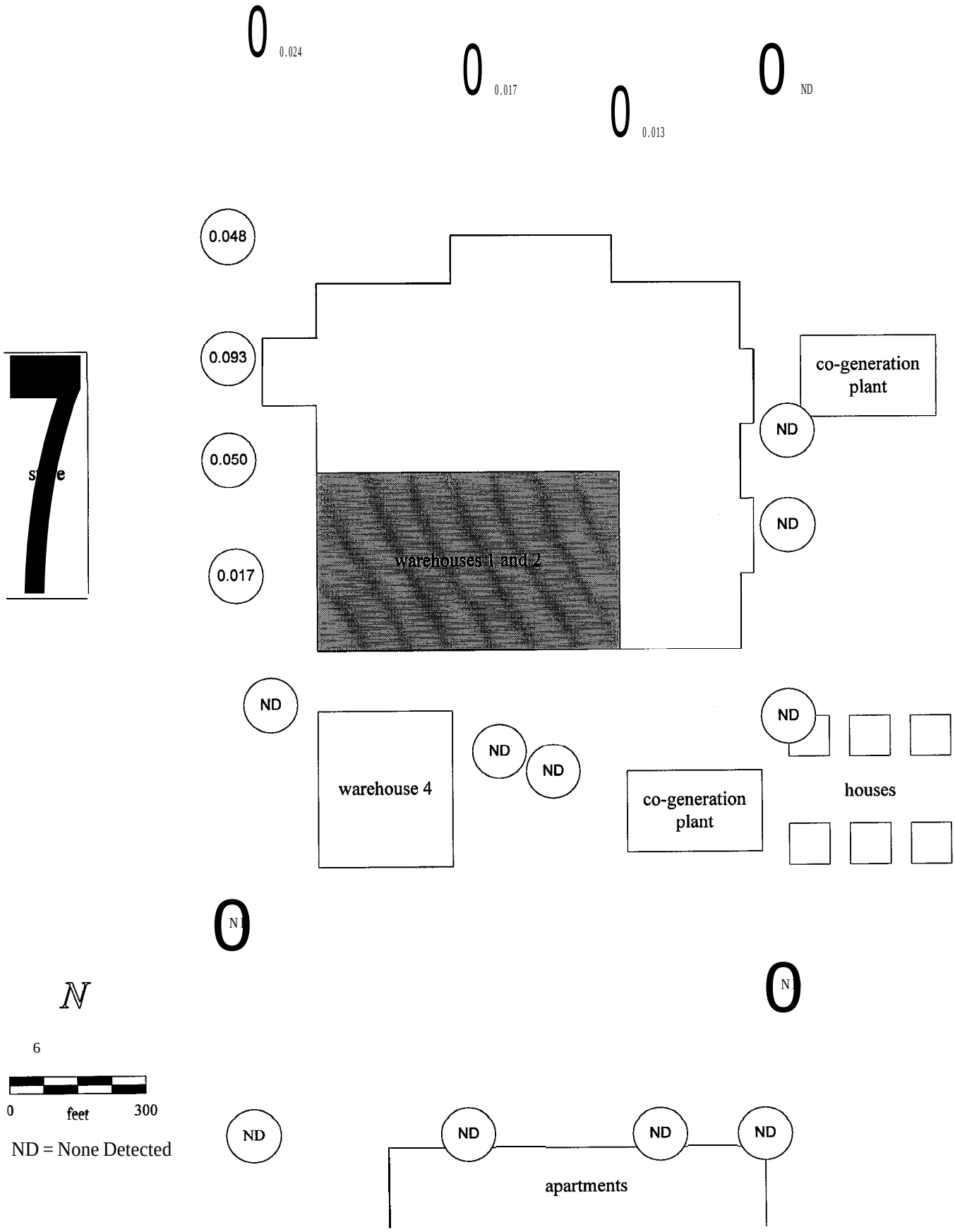

Figure 2. Methyl bromide concentrations (4-hr TWA, ppm) during aeration of Warehouses 1 and 2

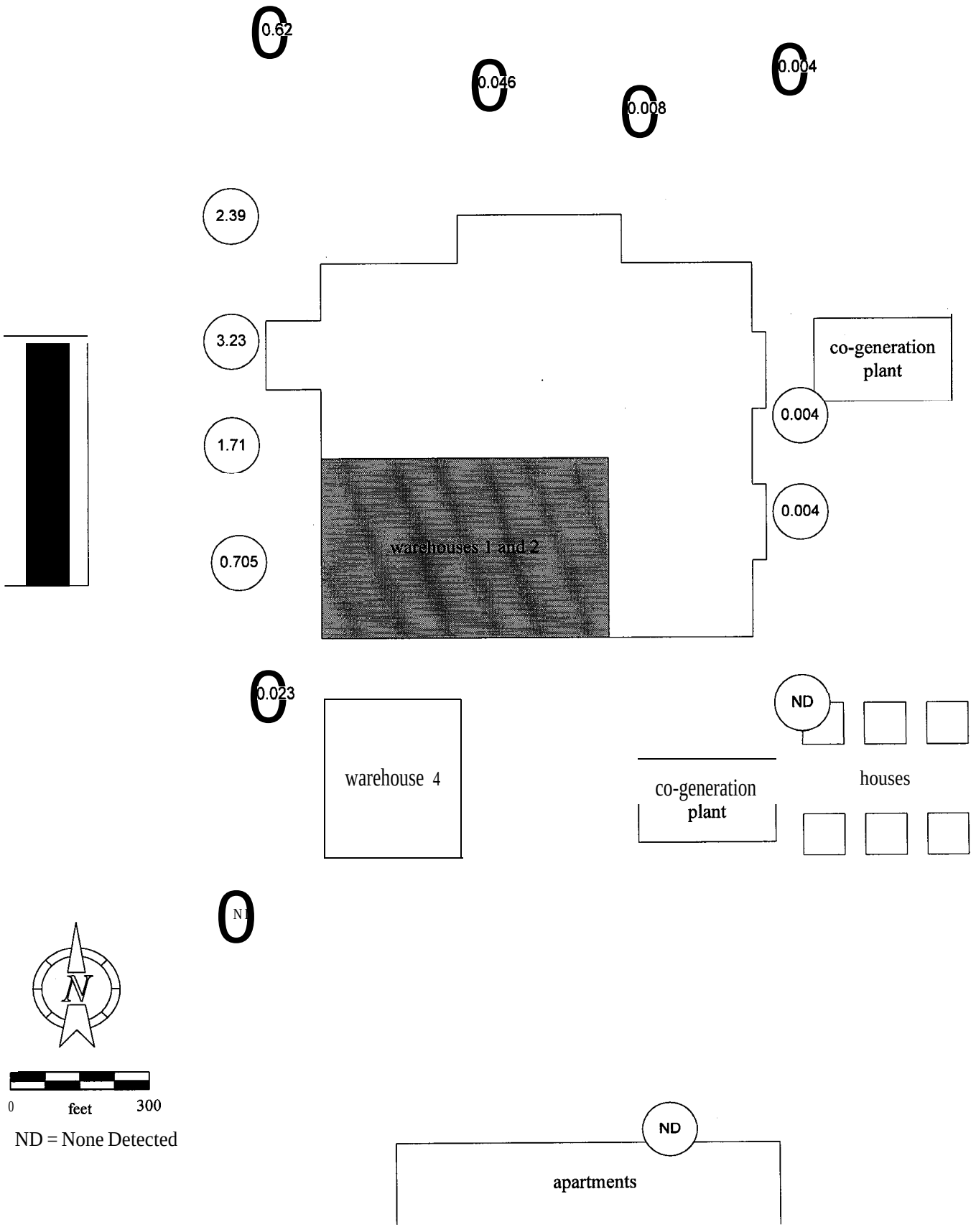

Figure 3. Wind direction during the monitoring of Warehouses 1 and 2

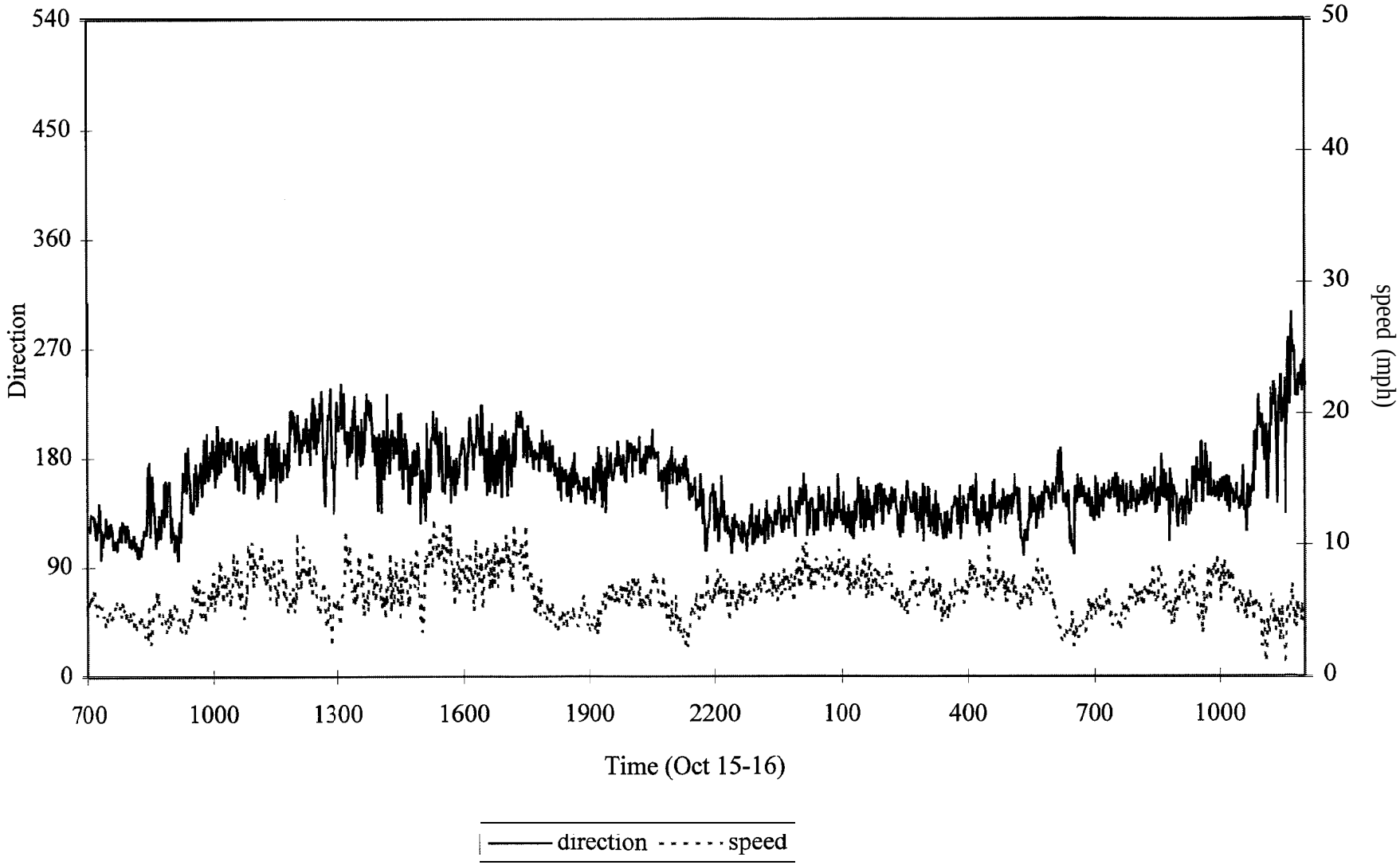

Figure 4. Methyl bromide in warehouse 2

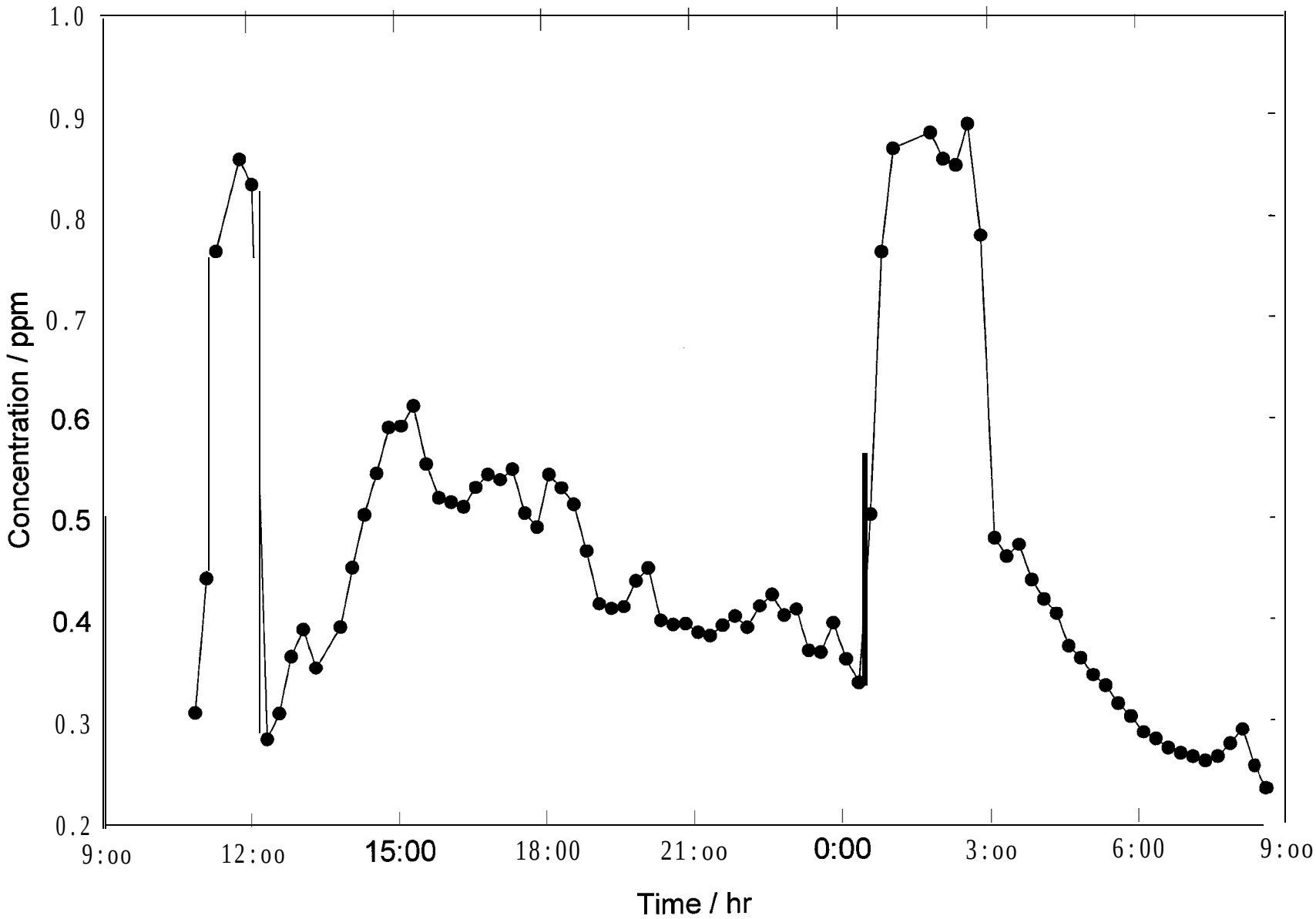

Figure 5. Methyl bromide concentrations (23-hr TWA, ppm) during treatment of Warehouse 4

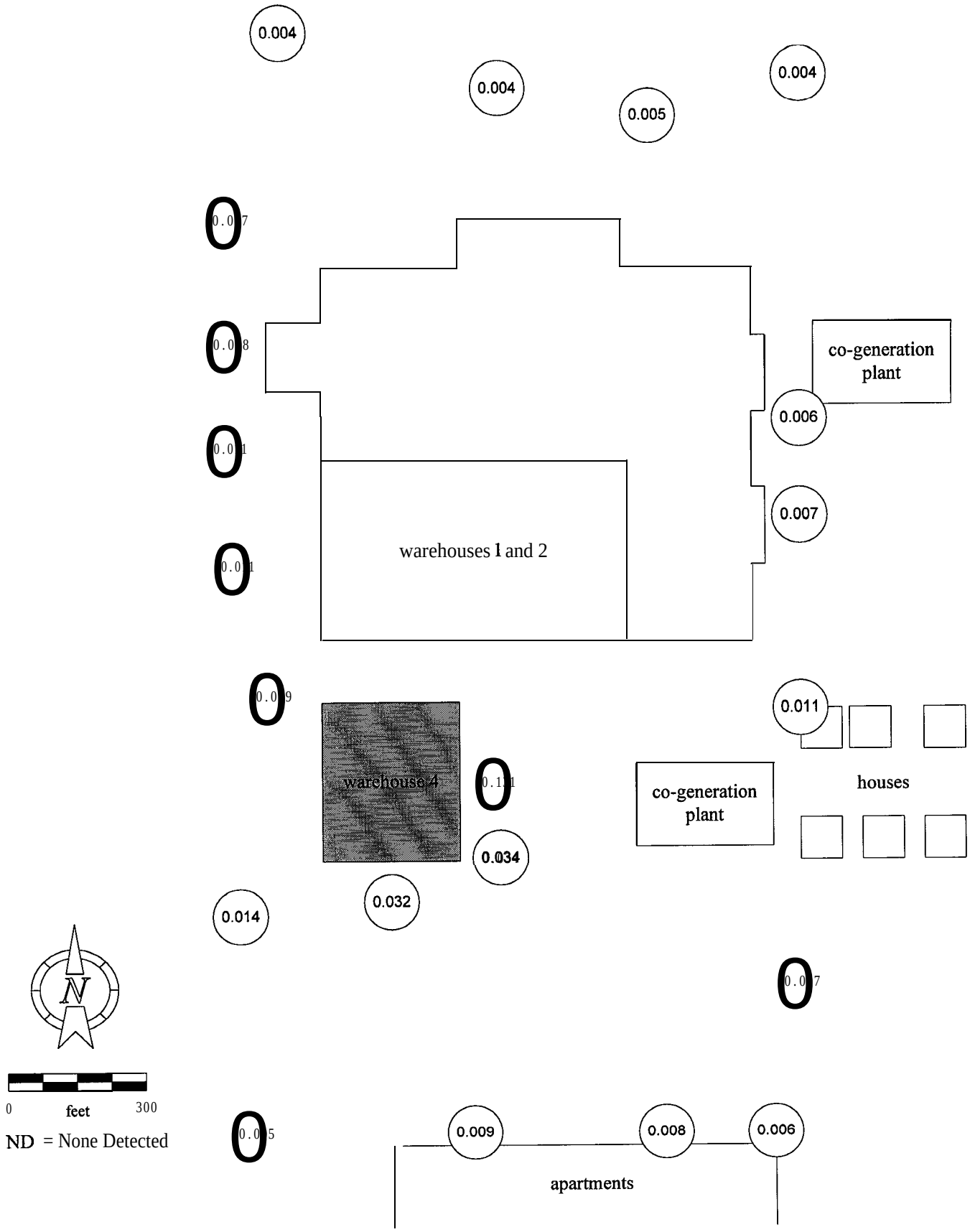

Figure 6. Methyl bromide concentrations (2-hr TWA, ppm) during aeration of Warehouse 4

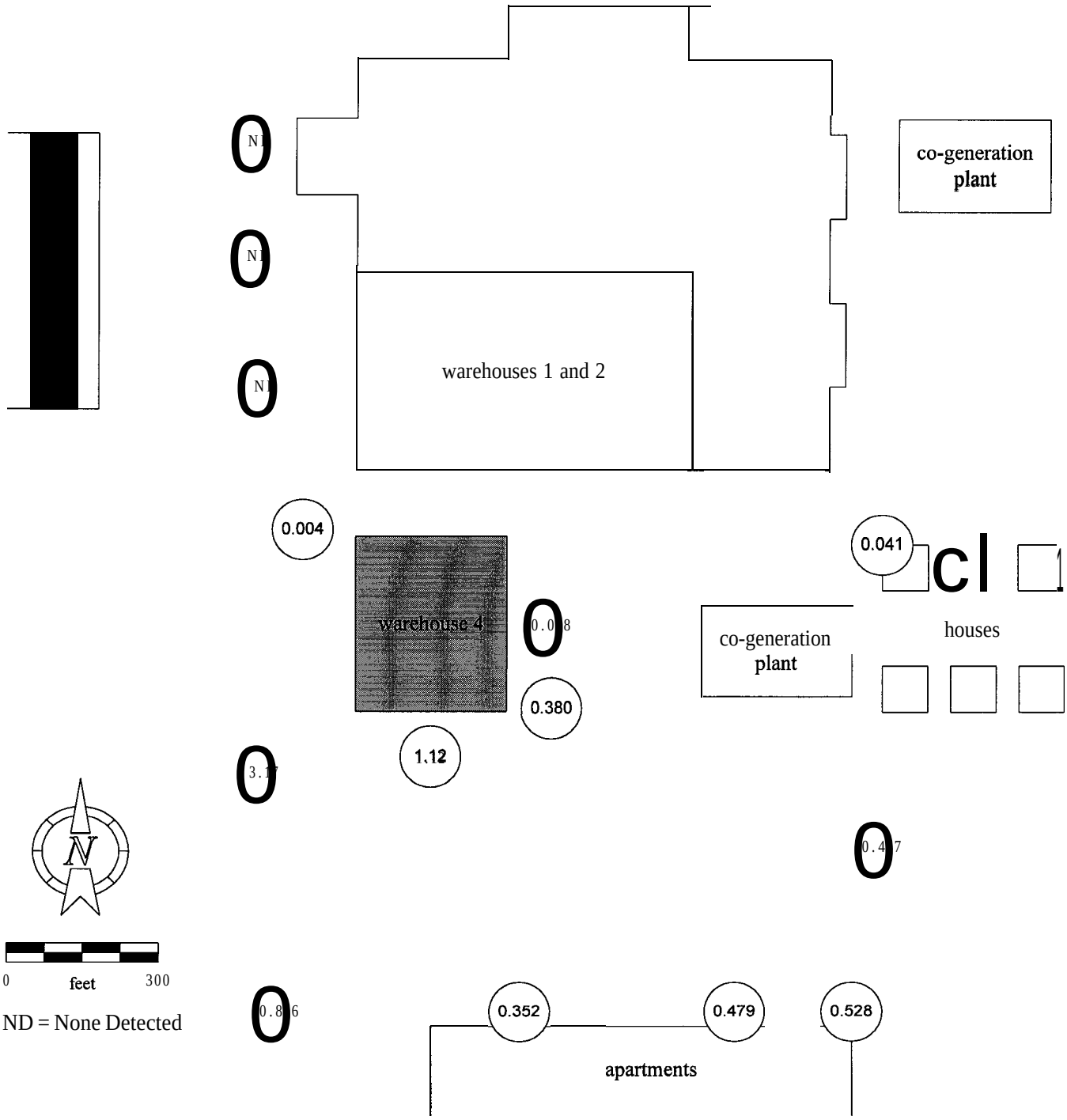

Figure 7. Wind direction and speed during the monitoring of Warehouse 4

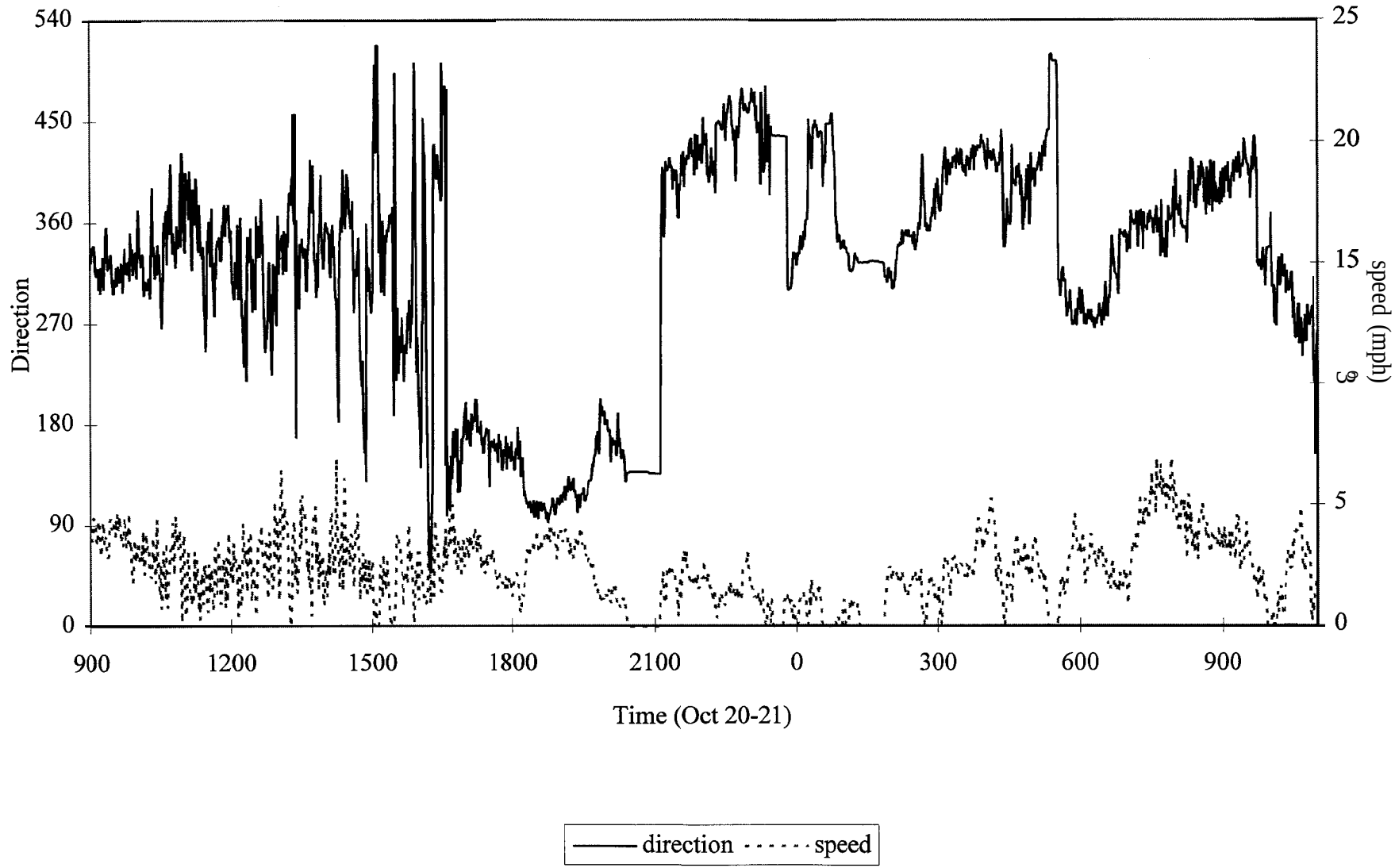
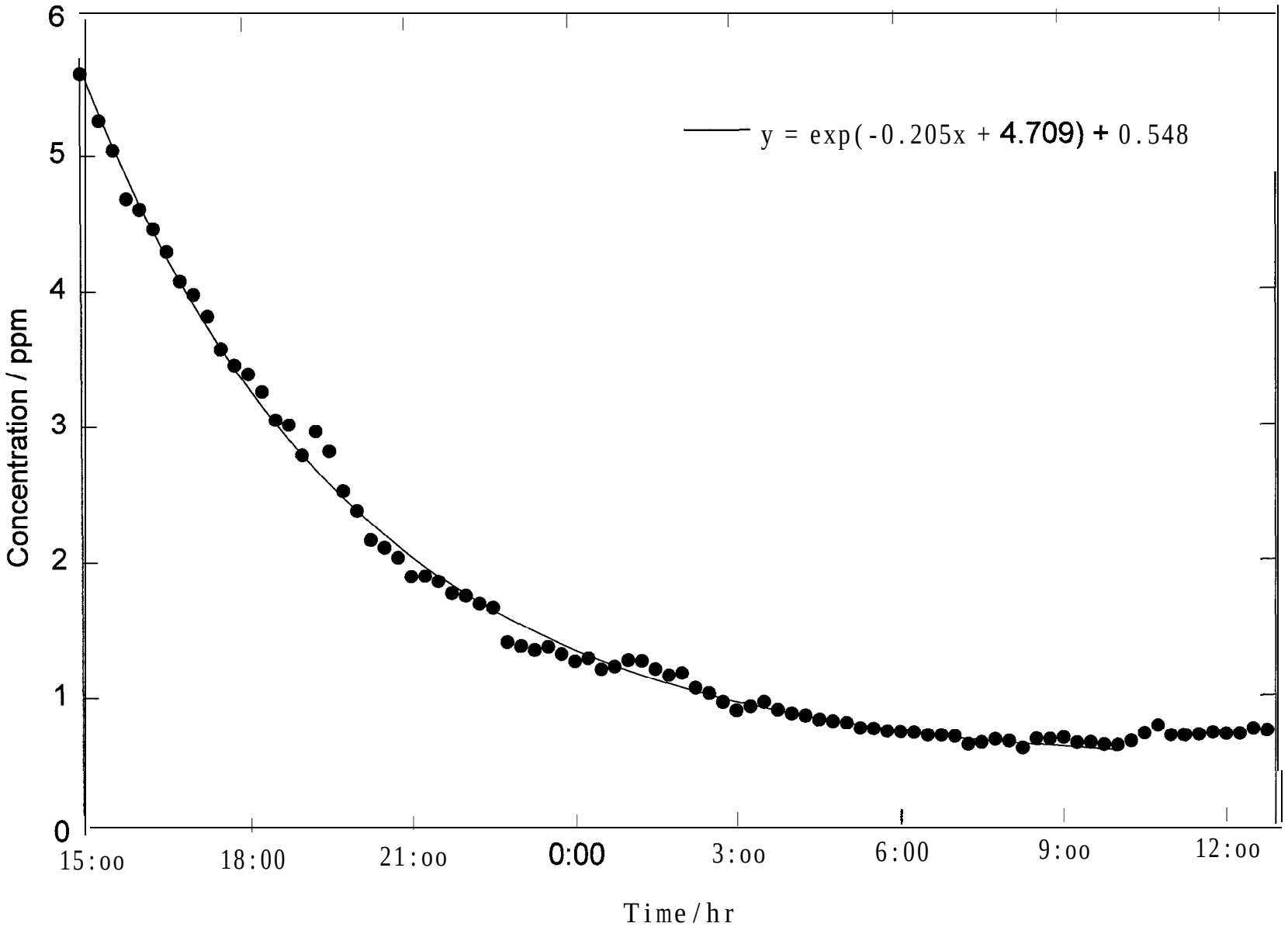
Figure 8. Methyl bromide in warehouse 4