Health Consultation

Exposure Investigation

EXCEL DAIRY

EXCEL TOWNSHIP, MARSHALL COUNTY, MINNESOTA

MARCH 26, 2009

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation
Atlanta, Georgia 30333

Health Consultation: A Note of Explanation

An ATSDR health consultation is a verbal or written response from ATSDR to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

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Prepared by:

Minnesota Department of Health
Under Cooperative Agreement with the
U.S. Department of Health and Human Services
Agency for Toxic Substances and Disease Registry

FOREWORD

This document summarizes public health concerns related to a concentrated animal feeding operation (CAFO) in Minnesota, and is a formal site evaluation prepared by the Minnesota Department of Health (MDH) and the Agency for Toxic Substances and Disease Registry (ATSDR). For a formal site evaluation, a number of steps are necessary:

- *Evaluating exposure:* MDH and ATSDR scientists begin by reviewing available information about environmental conditions at the site. The first task is to find out how much (if any) contamination is present, where it is found, and how people might be exposed to it. For this report ATSDR measured air concentrations of hydrogen sulfide at residences near the site, and relied on measurements of hydrogen sulfide concentrations provided by the Minnesota Pollution Control Agency (MPCA).
- *Evaluating health effects:* If there is evidence that people are being exposed—or could be exposed—to environmental contaminants, MDH and ATSDR scientists will take steps to determine whether that exposure could be harmful to human health. This report focuses on public health— that is, the health impact on the community as a whole. The analysis of health effects in this report is based on existing scientific information.
- *Developing recommendations:* In this report, MDH and ATSDR outline conclusions regarding any potential health threat posed by the site and offer recommendations for reducing or eliminating human exposure to pollutants. The roles of both the MDH and ATSDR are primarily advisory. For that reason, an evaluation report will typically recommend actions to be taken by other agencies that have regulatory capabilities—including the U.S. Environmental Protection Agency (EPA) and MPCA. If, however, an immediate health threat exists, MDH and ATSDR will issue a public health advisory to warn people of the danger and will work to resolve the problem.
- *Soliciting community input*: The evaluation process is interactive. MDH and ATSDR start by soliciting and evaluating information from various government agencies, the individuals or organizations responsible for the site, and community members living near the site. Any conclusions about the site are shared with the individuals, groups, and organizations that provided the information. Once an evaluation report has been prepared, MDH and ATSDR seek feedback from the public. *If you have questions or comments about this report, we encourage you to contact MDH.*

Please write to: Community Relations Coordinator
Site Assessment and Consultation Unit
Minnesota Department of Health
625 North Robert Street / P.O. Box 64975
St. Paul, MN 55164-0975

OR call us at: (651) 201-4897 *or* 1-800-657-3908
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On the Web: http://www.health.state.mn.us/divs/eh/hazardous/index.html

EXECUTIVE SUMMARY

Background: The Excel Dairy is a large concentrated animal feeding operation (CAFO) located in Marshall County, Minnesota about 6 miles north of Thief River Falls. Manure storage basins at the facility are uncovered and are thought to be the source of hydrogen sulfide (H_2S) and other gases which are responsible for odors, health symptoms and stress experienced by nearby residents.

Why was this done? The purpose of this investigation was to find out if exposures to H_2S have been occurring at levels of health concern for nearby residents, especially children. The objective was to obtain measurements of H_2S in residential areas near the Excel Dairy, including peak concentrations and time-weighted average values.

What we did and what we found: ATSDR conducted continuous air monitoring for H_2S at 3 residential properties over a 3-week period in July 2008. MDH and ATSDR analyzed these data and also analyzed continuous air monitoring data for H_2S collected by the Minnesota Pollution Control Agency (MPCA) at two locations at the Excel Dairy property boundary from May through October 2008. ATSDR and MPCA data indicated exceedances of health-based criteria for H_2S in ambient air: a short-term Minimal Risk Level developed by ATSDR, a sub-chronic Health Risk Value developed by MDH, and a chronic Reference Concentration developed by the US Environmental Protection Agency (EPA). Also, MPCA monitoring found hundreds of exceedances of Minnesota ambient air quality standards for H_2S; and ATSDR monitoring found several exceedances of the emergency response planning guideline (ERPG-1) provided by the American Industrial Hygiene Association, meant to be used to guide response to rare or single events.

What do the findings mean?: Unhealthy levels of H_2S are present in the community. Repeated exposures to H_2S at levels detected in this community may cause symptoms such as persistent eye and throat irritation, headache, and nausea. Also, citizens in the vicinity are under stress, and stress may be involved in pathogenesis of disease and exacerbate toxic effects of environmental exposures. Therefore, air emissions from the Excel Dairy are a *public health hazard.*

Recommendations going forward: Rapid, effective and permanent measures, such as applying permanent covers to Excel Dairy manure storage basins and eliminating over land manure transfer, should be accomplished. MPCA should continue to monitor air emissions of H_2S from the Excel Dairy to confirm efficacy of enforcement of Minnesota air quality standards, or to demonstrate the need for more emissions controls. If measures to eliminate exposures to H_2S in excess of Minnesota air quality standards are not effective, ATSDR and MDH will consider further exposure monitoring, and will recommend more stringent measures to reduce emissions.

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OBJECTIVE

The Agency for Toxic Substances and Disease Registry (ATSDR) and the Minnesota Department of Health (MDH) conducted this exposure investigation (EI) to assess potential human exposure to airborne concentrations of hydrogen sulfide (H_2S) in ambient and indoor air at residential properties near the Excel Dairy near Thief River Falls, MN. Air monitoring was conducted at three residential locations over a 3-week period in July 2008 to obtain meteorological and air concentration data for H_2S. The information obtained, in conjunction with air monitoring and meteorological data collected by the Minnesota Pollution Control Agency (MPCA), can be used to better characterize potential human exposure to airborne concentrations of H_2S near the Excel Dairy.

The EI has two objectives:

- To obtain measurements of H_2S in residential areas near the Dairy, including peak concentrations and time-weighted average values.
- To evaluate if exposures are occurring at levels of health concern for residents, especially children, in the community.

1.0 BACKGROUND AND STATEMENT OF ISSUES

The Excel Dairy (Dairy) has been permitted to operate as a dairy farm since 2006 under ownership of The Dairy Dozen of Veblen, South Dakota. It has a capacity of 1544 animal units or 1100 cows weighing over 1,000 pounds (milked or dry) (Permit MN0068594). The Excel Dairy meets the U.S. Environmental Protection Agency (EPA) definition of a large concentrated animal feeding operation (CAFO) (GAO 2008). The Dairy is located in Excel Township, Marshall County, MN, just east of US Highway 59, approximately 6 miles north of Thief River Falls and 300 miles northwest of St. Paul. The Dairy has three free-stall barns, a sand separator building, a feed storage pad, and three earthen manure storage basins or lagoons. The lagoons are uncovered or incompletely covered, and are thought to be the major source of odors and H_2S at the facility. Over 80 chemicals are known to be emitted to air from dairy operations. In addition to H_2S, chemicals that could contribute to odors and irritation include ammonia and other reduced sulfur compounds including dimethyl sulfide and dimethyl disulfide (Filipy et al. 2006).

The MDH received complaints from citizens beginning in early May 2008 about odors and H_2S emissions originating at the Dairy. Citizens complained of eye and respiratory irritation, headaches, and nausea. Approximately 40 people, including about 11 children in 13 families live within 1.5 miles of the Excel Dairy.

In response to complaints received during 2007, the MPCA installed continuous air monitors (CAMs) northeast of the Dairy (May 6, 2008) and west of the Dairy (May 19, 2008). MPCA also installed meteorological equipment alongside the CAM at the northeast site. MPCA H_2S monitors record air concentrations up to, but not in excess of, 90 parts per billion (ppb) of air.

Additionally, citizens acquired a Jerome meter and developed a protocol to document readings of H_2S. In early June 2008, citizens submitted data to MDH showing many periods of H_2S in the hundreds of ppb, and during one day citizen data showed several periods in excess of 1,000 ppb of H_2S. While the methodology for collecting these data was not verifiable, the citizen-reported data were a factor in the decision to conduct an EI.

Minnesota ambient air quality standards (MAAQS) for H_2S require that there be no more than two 30-minute periods of H_2S above 30 ppb in 5 days, or no more than two periods of H_2S above 50 ppb in any year (Minnesota Administrative Rules 7009.0080). Standards are applicable at the property boundary of the facility, and/or at locations to which the general public has access. Large livestock facilities are exempt from these requirements for a maximum of 21 days per calendar year during and for 7 days after manure is removed from barns or manure storage facilities. Operators of livestock facilities claiming this exemption are required to provide notice to either the MPCA or the county feedlot officer. The MPCA may not require air emissions modeling for a type of livestock system that has not had a H_2S emission violation (Minnesota Statutes 116.0713).

On June 20, 2008, the Minnesota Attorney General and the MPCA filed an Interim Order for injunctive relief against the Excel Dairy owner to address operational shortfalls contributing to ambient releases of H_2S exceeding MPCA standards. These exceedances also prompted the EPA to issue a Notice of Violation to Excel Dairy owners on July 18, 2008. In affidavits submitted to Minnesota District Court (2008), MPCA staff stated that methods used by the Dairy to control emissions from manure storage basins are ineffective, unapproved, and experimental (aeration with biological addition), and that the basins must be covered to suppress H_2S emissions. Staff further stated that covering the basins is explicitly required by the Air Emissions Plan included in the facility permit.

On September 19, 2008, after reviewing all existing ambient air data collected since May 2008, ATSDR and MDH wrote a letter to the EPA and MPCA describing interim findings from the EI (Appendix 2). The health agencies found that the Excel Dairy posed a public health hazard for the surrounding community. This document will present MPCA's findings as well as the results of the ATSDR/MDH EI.

1.1 *Demographics*

Marshall County, measuring 1,675 square miles, is entirely rural (Marshall County 2008). According to the 2000 census, the county's population is 10,155, with a minority population of 405 and 9.8% of the population living below the poverty level. According to the US Census (2000), 80 people live in Excel Township. Three families were reported to be living below the poverty level (3.3% compared to 9.2% in the US), while the median family income in 1999 of $50,883 was slightly above the US median of $50,046. Thirteen families, representing approximately 40 people of whom about 11 are children under the age of 18, reportedly live within 1.5 miles of the Excel Dairy.

Members of 11 families have filed affidavits with the Marshall County District Court documenting health and quality of life impacts resulting from the Dairy. In their affidavits and in conversations with MDH staff, these family members have reported emotional responses and alterations in living patterns, indicating prolonged stress (see Section 4.3.3). Some of the families include persons who are vulnerable such as young children, the elderly, and people with health problems.

2.0 ATSDR/MDH EXPOSURE INVESTIGATION

An exposure investigation (EI) is an approach ATSDR and its state partners, including Minnesota, use to characterize past, current, and possible future human exposures to hazardous substances in the environment. The results of exposure investigations are used to inform public health decisions and to recommend appropriate actions to regulatory agencies.

In considering an EI for the Excel Dairy, ATSDR and MDH determined that available MPCA continuous air data indicated violations of ambient air quality standards for H_2S in May and June 2008. However, MPCA monitors are at the facility boundaries to the west and northeast, and do not record air concentrations in excess of 90 ppb. MPCA data indicate a health risk to the community, but the magnitude of the risk (i.e., information about peak levels, especially at residences) is lacking. Data collected by citizens indicated that peak concentrations of H_2S could be considerably higher than 90 ppb. The EI was designed to collect environmental data to better characterize the magnitude, frequency, and duration of residential exposures in the community.

2.1 *Sampling Locations*

The ATSDR EI focused on the outdoor and limited indoor air monitoring of H_2S, measured over a 3-week period at three residences situated in close proximity to the Dairy. ATSDR also located equipment to record meteorological data (i.e., temperature, humidity, wind direction, and wind speed) at Site 1. Outdoor and indoor monitors were placed at Sites 1 and 2. Outdoor monitors only were placed at Site 3. Figure 1 illustrates the locations of the ATSDR sampling locations as well as the MPCA sampling locations.

Figure 1. Excel Dairy with ATSDR and MPCA Monitoring Stations

2.2 *Equipment*

Hydrogen Sulfide- Honeywell single point monitors (SPMs) were used to measure H_2S at all outdoor and indoor monitoring locations during the EI. The manufacturer performed primary calibration certification of the SPMs. Supplemental calibration checks on these instruments were performed at the Eastern Research Group, Inc. (ERG) laboratory prior to field deployment, and again after the EI was completed. Two-point internal optical performance checks were conducted during deployment and at the end of each week of monitoring. Results from the calibration and optical checks are presented in Appendix 1.

The SPMs detected the presence of H_2S and calculated corresponding concentrations using a colorimetric detection method. This method utilizes an optical scanning system that quantifies ambient air concentrations by measuring color change on paper tape impregnated with a chemical reagent specific for H_2S.

Measurement of H_2S was automatic. For each monitor, ambient air was drawn through a humidifier containing distilled/de-ionized water which was checked and supplemented daily as needed across the duration of the monitoring program. From the humidifier, ambient air was then drawn into the instrument through a thin wall Teflon tubing sample line. An inverted glass funnel was connected at the inlet end of the sample line to prevent rain from entering the measurement device. As the sampled air passed through the instrument's measurement tape, H_2S in the sampled air reacted with the reagent on the tape to form a colored stain. The intensity of the stain was proportionate to the concentration of H_2S present in the sampled air. An electro-optical sensor measured the stain intensity, which was then converted to a measured concentration of H_2S based on instrument-specific calibration data.

For this EI, the measurement frequency for collecting H_2S measurements was once per minute. However, it should be noted that the length of sampling time required for an SPM measurement to be completed (i.e., for the reagent to be expended) can vary from 3-7 minutes depending on the concentration of H_2S present in the sample air stream (i.e., the higher the concentration, the faster the reagent is expended). As a result, it is typical to observe three to seven measurements that present the same concentration before each new measurement occurs. When the reagent is expended (i.e., after the measurement is completed), the SPM automatically provides the H_2S measurement in the form of a 4-20 milliampere (mA) output signal that correlates to a specific H_2S concentration, and then advances the tape to a fresh reagent spot. The SPM continues to present the output signal until the next time it updates the measurement and advances the tape. Thus, the SPM holds the data point at the same level until the next update occurs (i.e., 3-7 minutes later). A HOBO Micro Station data acquisition system (DAS) coupled with a dedicated 4-20 mA adapter was used to poll the SPM once per minute. At each polling, the SPM output signal (i.e., 4-20 mA) was logged by the DAS. Because the DAS polls the SPM at a rate that is faster than the SPM accomplishes each measurement update, several data points at the same concentration are collected.

Two SPM instrument configurations were used during the EI. ChemKeys (i.e., programmable read-only memory chips) were used to set the measurements range on each instrument to allow an overall measurement range of 0–1,500 ppb. “Low level” instruments were those with a detection range of 0–90 ppb, while “mid level” instruments had a detection range of 76–1,500 ppb. All outdoor measurements for Sites 1, 2, and 3 were made using two SPMs at each site, with one SPM having a measurement range of 0–90 ppb and the other having a measurement range of 76–1,500 ppb. All indoor measurements for Sites 1 and 2 were made using an SPM at each site that was equipped with a measurement range of 0–90 ppb.

Meteorology- Measurements of continuous meteorological parameters were collected using a stand alone meteorological monitoring system at Site 1. This system incorporates a cup anemometer to measure wind speed, a directional mast and vane to measure wind direction, a resistance/capacitance wire-wound salt coated bobbin assembly to measure relative humidity, and a resistance temperature detector to measure outdoor temperature. Measurements were made at a height of approximately 10 feet above grade (see Appendix 1).

2.3 *Monitoring Schedule*

ATSDR and its contract staff members were in the investigation area throughout the monitoring period. Staff visited each of the sites daily to assess the functional status of the chemical and meteorological measurement equipment and to correct any problems identified. On a weekly basis, staff downloaded data from the H_2S instruments and performed quality assurance activities such as reloading measurement tapes and performing internal optical calibration checks. Staff downloaded meteorological data weekly and performed a visual check of the meteorological sensors daily (see Appendix 1).

2.4 *Quality Assurance/Quality Control*

Data quality objectives (DQOs) are established to ensure that data collected during sampling are of sufficient quality to achieve the project goals. DQOs are used to design data collection procedures. The DQOs for this EI are presented in detail in Appendix 1.

Measures of data validity include: data completeness, measurement precision, measurement accuracy, and quality control activities. These are summarized below.

2.4.1 Data Completeness

Completeness refers to the number of valid measurements collected compared to the number of possible measurements expected from the measurement methods conducted.

During the 3-week EI period, the overall completeness of the monitoring network was 87.6%. The program DQO of 80% data capture was exceeded at all monitoring stations except for H_2S measured outside at Site 1, where the measurement completeness was 67.1% because of problems with the data logger during the first week of monitoring.

2.4.2 Measurement Precision and Accuracy

Measurement precision for this EI was defined as the ability to acquire the same concentration from the same or different instruments, within an acceptable level of uncertainty. *Measurement accuracy* for this project was defined as the ability to acquire the correct concentration from an instrument or an analysis with an acceptable level of uncertainty while measuring a known concentration reference gas stream.

To determine the precision and accuracy associated with the H_2S measurements acquired during this EI, a known concentration reference gas stream was measured for each of the eight instruments (low-range detectors at Sites 1, 2, and 3 outside; low-range detectors at Sites 1 and 2 inside; and mid-range detectors at Sites 1, 2, and 3). Each instrument completed 10 concentration determinations. Overall measurement precision was 1.7% relative standard deviation, and accuracy was 1.3% relative standard deviation.

2.4.3 Quality Control Activities

ATSDR and ERG staff performed optical performance checks to ensure that the SPM instrument lamp and detector assembly functioned within manufacturer specifications. Every instrument was found to respond within specifications.

2.5 ***Hydrogen Sulfide Monitoring Results***

ATSDR collected H_2S measurements at three locations, ranging from 15 to 21 days. The three sampling locations were between 600 and 1,000 meters from the Dairy. ATSDR and MDH used MAAQS and health-based criteria, and a review of scientific studies to evaluate the public health risks posed by hydrogen sulfide, as described in Section 4.3. Health Implications.

Table 1 is a summary of episodes of elevated H_2S concentrations, defined as an exceedance of the 30-minute MAAQS of 30 ppb, monitored at the three residential sites. The time denoting the beginning of an episode is the first minute when the mean concentration for 30 minutes was above 30 ppb for that minute and the next 29 minutes. “Rolling” periods were calculated every minute. The time denoting the end of the episode is the last minute of the last rolling period. The “Mean ppb” is the mean of all of the air concentrations recorded each minute from the beginning to the end of the episode. Note that not all of the individual minutes need to be above 30 ppb for the average or mean to be above 30 ppb. This method, rather than calculating the mean of the mean 30 minute periods, is a more accurate representation of air concentrations throughout an episode. The “Max ppb” is the maximum average air concentration for a consecutive 30-minute period in the episode.

Table 1. Consecutive 30-Minute Rolling Periods > 30 ppb Hydrogen Sulfide

Location	*Date*	*Begin Episode*[1]	*End Episode*	*Mean ppb*[2,3]	*Max ppb*[4]
S1, Outside	19-Jul	0:39	2:07	72	158
16-31 July		4:24	6:06	80	165
	21-Jul	1:00	2:28	94	229
		21:42	23:30	97	227
		23:17	2:23	87	183
	22-Jul	3:34	6:23	101	143
	27-Jul	6:55	8:07	37	69
		22:31	00:14	55	105
	30-Jul	10:07	11:14	51	111
S1, Inside	15-Jul	3:42	4:19	29	32
9-31 July	16-Jul	3:10	4:29	32	38
		4:52	5:40	29	32
	19-Jul	1:12	2:14	31	37
		5:06	6:15	31	37
	21-Jul	1:11	3:20	41	67
		22:17	23:21	32	46
	22-Jul	0:10	2:31	33	41
		4:06	6:59	38	57
S2, Outside	19-Jul	0:33	1:41	34	59
9-31 July					
S3, Outside	19-Jul	1:08	2:52	52	89
16-31 July	20-Jul	2:49	4:26	42	71
	21-Jul	0:57	1:33	30	42
		1:06	1:52	30	56
		1:31	2:45	39	61
	22-Jul	20:43	21:52	32	38
		21:27	22:10	28	30
		22:49	2:35	87	202
	23-Jul	3:38	7:50	84	178
	28-Jul	2:48	3:52	32	45
		3:29	8:38	77	154
		22:52	0:14	49	99
	30-Jul	10:34	11:54	62	147
	31-Jul	5:26	6:22	30	37

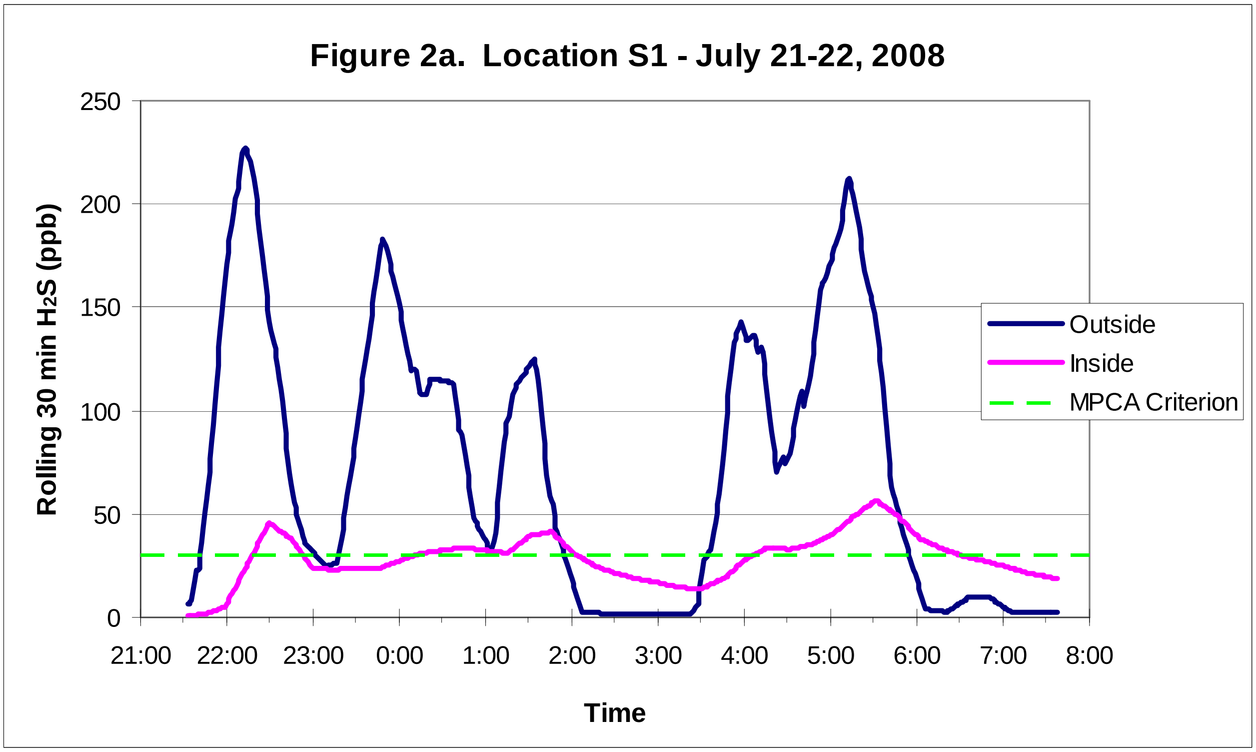
Notes:

1. 30-minute rolling averages calculated every minute beginning at the noted time.
2. If the length of the episode is short, the mean, which includes shoulders at both ends, may be slightly less than 30 ppb.
3. The mean ppb is the mean for each minute in the episode.
4. The max ppb is the 30-minute period with the greatest mean in the episode.

H_2S concentrations were plotted against meteorological data (wind speed and wind direction). For this purpose, the MPCA meteorological data were used because ATSDR meteorological equipment does not record wind speed below 4 miles per hour (mph) (Dave Dayton, ERG, personal communication). Many of the high H_2S episodes occurred at low wind speeds, or still conditions. H_2S levels were only plotted against wind direction when wind speeds were at or above 2 mph. MPCA meteorological data (and corresponding H_2S air concentrations) are averaged over consecutive half-hour periods, so there could be considerable variation in wind direction within the periods. This may sometimes result in a loss of precision in relating winds to air concentrations.

2.5.1 ATSDR Site 1

Monitoring occurred from July 9 to July 31 at S1. However, because the data logger at S1 outdoors, failed during the first week of monitoring, data was only recorded at S1 outdoors from July 16 to July 31st. The data logger failure did not affect the monitoring at S1 indoors. Recorded data showed extended time periods (episodes) when air concentrations of H_2S exceeded the MAAQS of no more than two 30-minute periods of H_2S above 30 ppb in five days (Table 1). Thirty-minute maximum detections exceeded 200 ppb during two of nine episodes and 100 ppb during eight episodes. All 30-minute maximum detections were above 50 ppb. Average concentrations recorded for eight of nine episodes exceeded 50 ppb. According to Minnesota regulations, the 50 ppb MAAQS is not to be exceeded more than twice in a calendar year *at the fenceline*. The most intense period recorded contained three closely spaced episodes occurring on July 21 and July 22, lasting almost 9 hours. During a period lasting over 3 hrs (23:17 to 2:24), the average air concentration of H_2S was 87 ppb, and the concentration for the maximum 30-minute period was 227 ppb (Figure 2a). There is no information suggesting that the Dairy was exempt from Minnesota regulations during this time.



High levels of H_2S penetrated the indoor environment at location S1 (Table 1), with 30-minute maximum detections above 50 ppb during one episode on July 21 and one episode on July 22. As can be seen in Figure 2a, indoor levels rose following the rise outdoors; H_2S stayed elevated after outside levels fell to near zero during the period from approximately 2 a.m. to 3:30 a.m. and after 6 a.m. on July 22.

Figure 2b shows that most of the high air concentrations occurred at low wind speeds (below 2 mph). At low wind speeds, wind direction is unimportant for determination of plume location or origin. When wind speeds were higher, winds during episodes of elevated H_2S were from the northeast (i.e., from the direction of the Excel Dairy) (Figure 2c), except for the episode on July 30. All of the episodes, except the July 30 episode at outdoor Site 1, occurred in late evening or early morning (see Table 1).

Figure 2b. S1 Out - Wind Speed(MPCA) vs H_2S - 30 Min Avgs

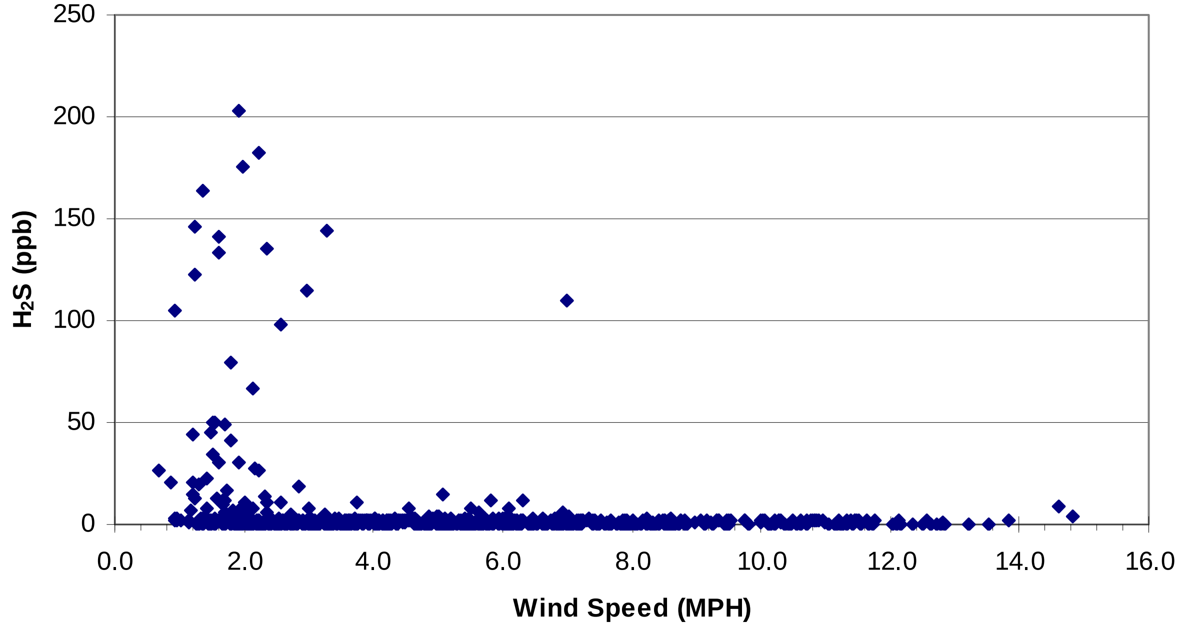
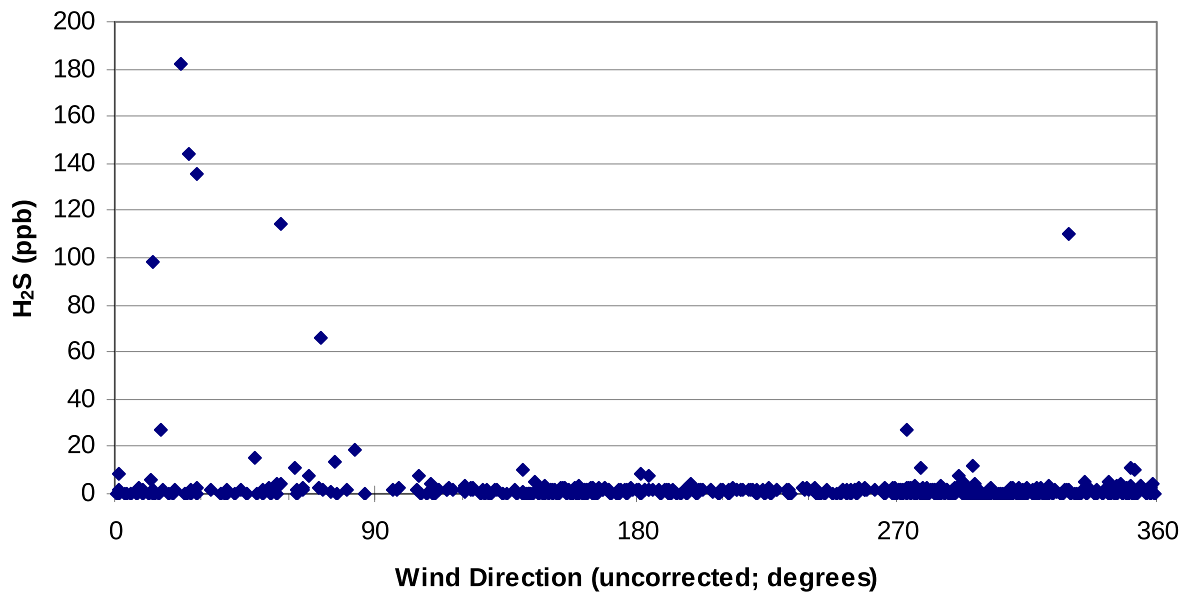


Figure 2c. S1 Out - Wind Direction(MPCA) vs H_2S
30 Min Avgs (≥ 2 MPH)



2.5.2 ATSDR Site 2

Monitoring occurred from July 9 to July 31 at S2 outdoors and indoors. One episode lasting for over 1 hour was recorded during which the outside air concentration of H_2S exceeded the MAAQS of 30 ppb (Table 1). The average air concentration during the episode was 34 ppb, and the 30-minute maximum exceeded the 50 ppb MAAQS (not to be exceeded more than twice in a calendar year *at the fenceline*). The episode is shown in Figure 3a, which also shows the corresponding indoor air levels of H_2S. Figure 3b shows that most instances of H_2S above 20 ppb, the ATSDR intermediate Minimal Risk Level, and an indicator of air concentrations approaching or over the Minnesota 30 ppb ambient air standard, occurred when wind speeds were low. Figures 3b and 3c show one instance when H_2S was above 20 ppb and the wind speed was above 2 mph when the wind was from the north (i.e., from the direction of the Dairy). Another instance when H_2S approached 20 ppb occurred when the wind speed was relatively high (about 16 miles/hr) and the winds were predominantly from the east–southeast.

Figure 3a. Location S2 - July 19, 2008

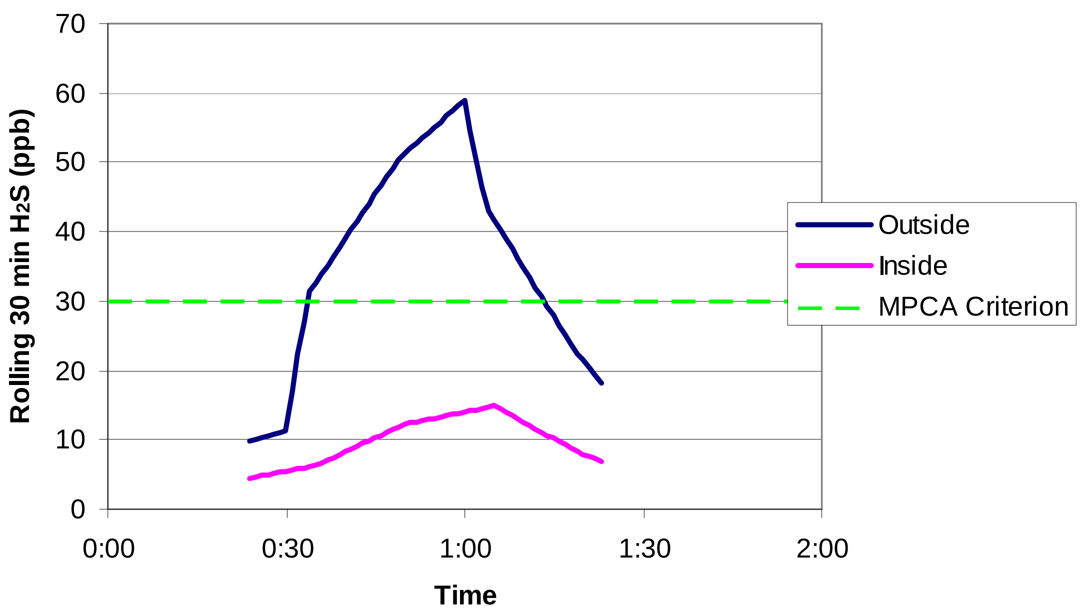


Figure 3b. S2 Out - Wind Speed(MPCA) vs H_2S - 30 Min Avgs

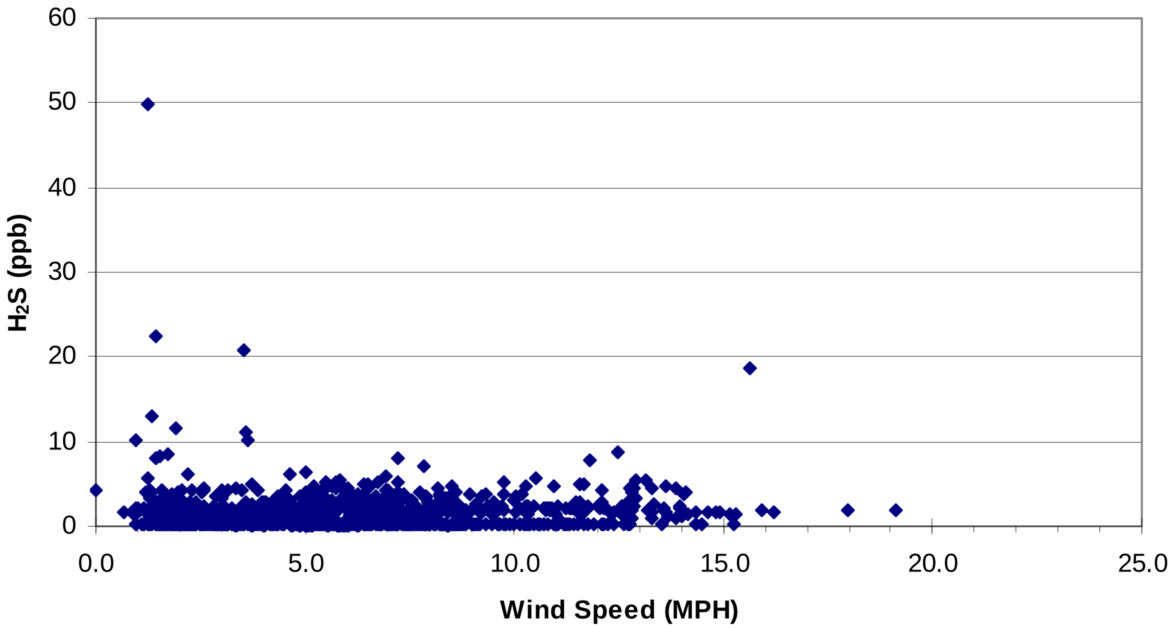
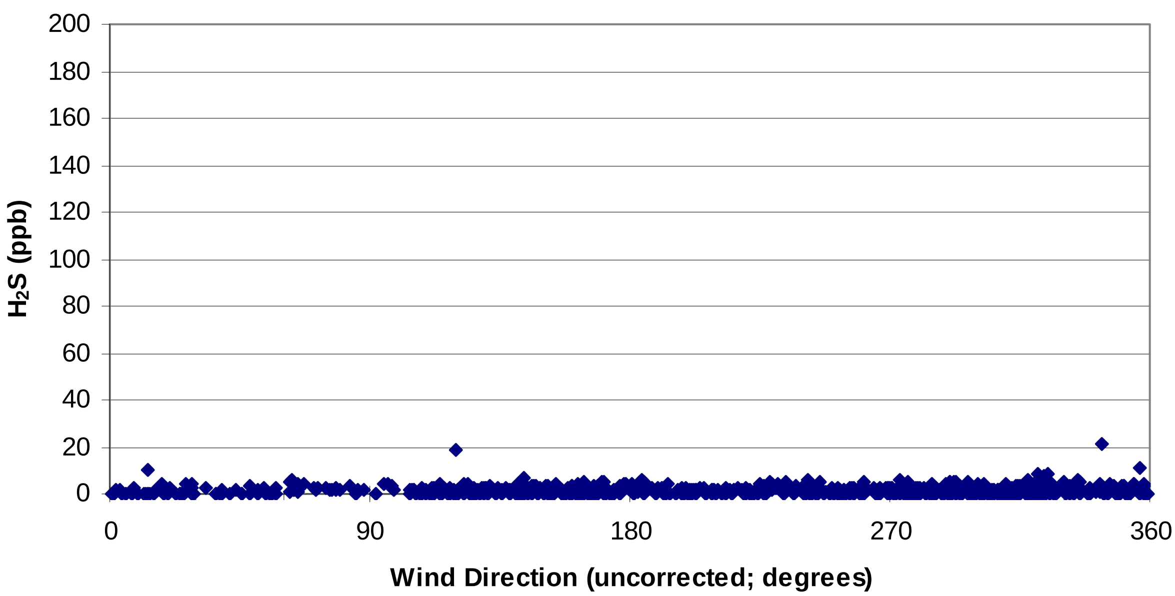


Figure 3c. S2 Out - Wind Direction(MPCA) vs H_2S
30 Min Avgs (≥ 2 MPH)

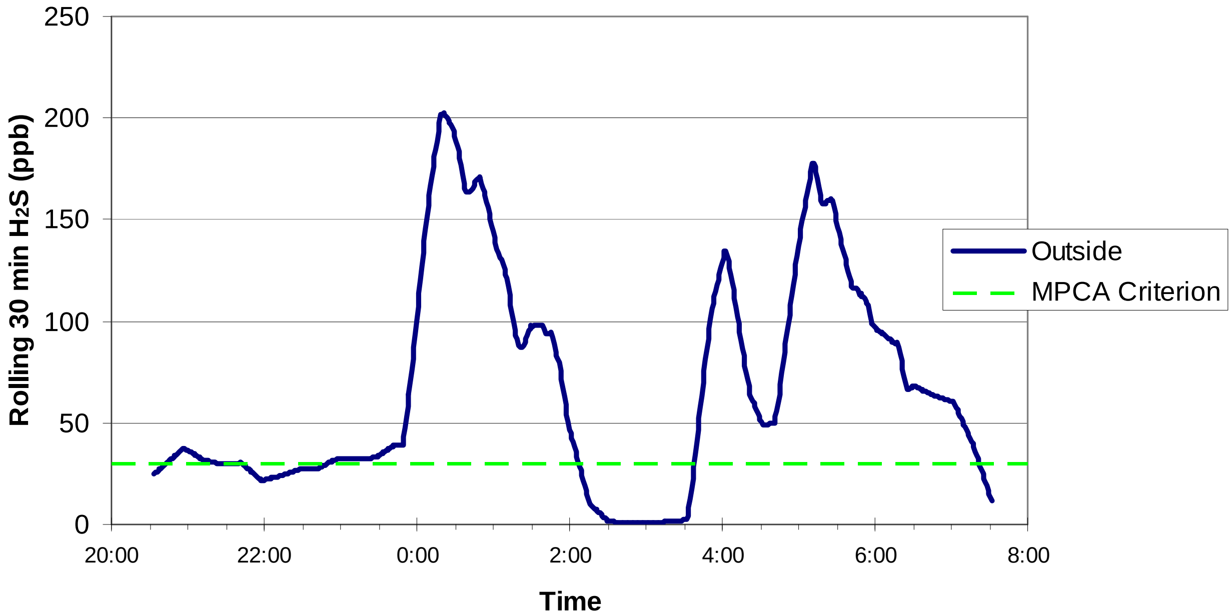


2.5.3 ATSDR Site 3

Monitoring occurred from July 16 to July 31 at S3 outdoors. There was no indoor monitor at this site. Extended episodes were recorded during which air concentrations of H_2S exceeded the MAAQS of 30 ppb (Table 1). During an episode lasting over 5 hours on July 28, the mean air concentration was 77 ppb and the maximum 30-minute concentration was 154 ppb. Maximum concentrations of H_2S during 30-minute periods exceeded 50 ppb in 9 of 14 episodes, exceeded 100 ppb in 4 episodes, and exceeded 200 ppb in 1 episode. The average H_2S concentrations recorded for 5 of 14 episodes exceeded the 50 ppb MAAQS. Closely spaced episodes beginning on July 22 at 8:43 p.m. and lasting until 7:50 a.m. on July 23 are shown in Figure 4a.

Figure 4b shows that many of the high air concentrations occurred at low wind speeds (below 2 mph). When wind speeds were higher, with one exception, winds were from the southeast (i.e., from the direction of the Excel Dairy) (Figure 4c). The episode on July 30 (see Table 1) occurred when winds were from the north at an atypical time of day (i.e., not in late evening or early morning). All of the other episodes occurred in late evening or early morning.

Figure 4a. Location S3 - July 22-23, 2008



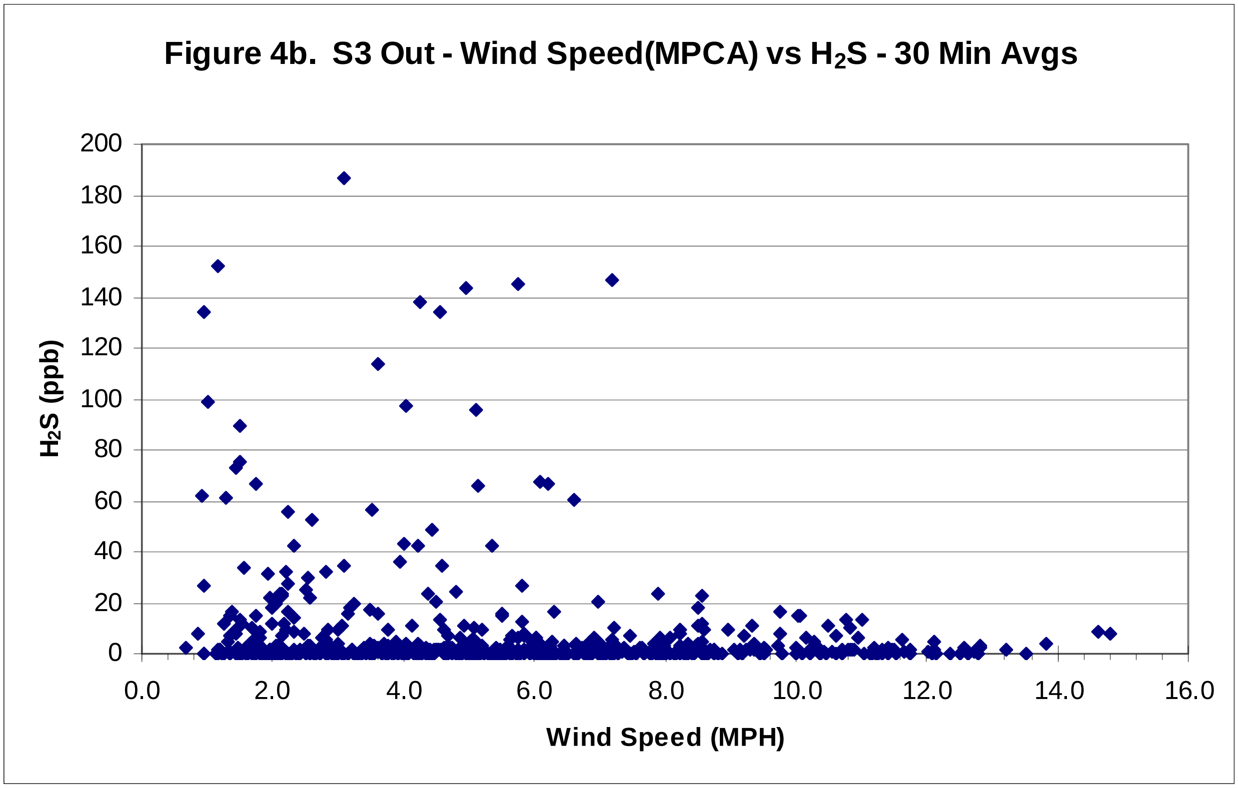


Figure 4b. S3 Out - Wind Speed(MPCA) vs H2S - 30 Min Avgs
H2S (ppb)
200
180
160
140
120
100
80
60
40
20
0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Wind Speed (MPH)

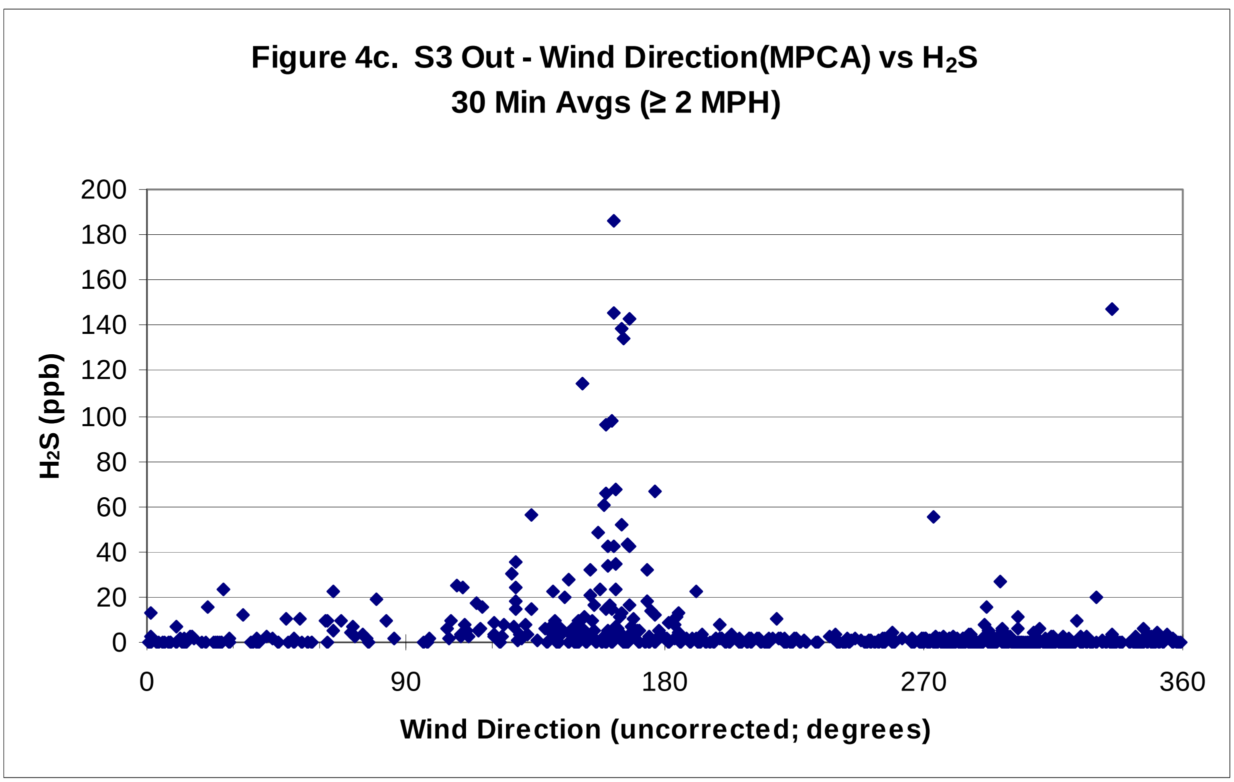


Figure 4c. S3 Out - Wind Direction(MPCA) vs H2S
30 Min Avgs (≥ 2 MPH)
H2S (ppb)
200
180
160
140
120
100
80
60
40
20
0
0
90
180
270
360
Wind Direction (uncorrected; degrees)

3.0 MPCA AIR MONITORING

MPCA began collecting data at Site 1 (Northeast Continuous Air Monitor; CAM) on May 6, 2008, and at Site 2 (West CAM) on May 19, 2008 (Figure 1). Sampling ended for the year on October 30, 2008.

3.1 *Description of Sampling Equipment*

According to affidavits from MPCA staff (Minnesota District Court 2008), MPCA uses Honeywell/Zellweger MDA Single Point Monitors to determine H_2S air concentrations. These monitors are similar to those used by ATSDR and many other governmental and academic institutions. The monitors are routinely calibrated in the field according to an EPA-certified protocol. Field tests have shown that the monitors accurately record H_2S levels. The CAMs record H_2S average air concentrations up to 90 ppb. When a concentration of 90 ppb is recorded, the actual concentration is at least 90 ppb but may be greater. Therefore, the actual magnitude of half-hour air concentrations recorded as at or above 90 ppb is not known. MPCA uses hydride tapes to detect H_2S, and calculates mean ambient levels of H_2S for consecutive half-hour periods. Because ATSDR's monitors humidified the gas stream, the EI monitors were checked daily. When hydride tapes are used, such as with the MPCA CAMs, these monitors did not have be checked as often .

MPCA also collected meteorological data (temperature, wind speed, and wind direction) at Site 1 (northeast CAM).

3.2 *Results*

3.2.1 Site 1 (Northeast Monitor)

From May 6 through October 29, this monitor detected 41 half-hour periods when H_2S air concentrations were above 30 ppb; during 5 of these half-hour periods average air concentrations were at or above 90 ppb, the maximum recorded by MPCA equipment.

3.2.2 Site 2 (West Monitor)

From May 19 through October 29, this monitor detected 435 half-hour periods during which air concentrations were above 30 ppb; 97 of these periods had average air concentrations at or above 90 ppb. Table 2 compares MPCA data with the 30 ppb MAAQS and other health-based criteria for protection of public health. These criteria are discussed in more detail in Section 4.3.2.

As shown in Table 2, data from this monitor recorded exceedances of health-based exposure limits recommended by ATSDR, MDH, and EPA, in addition to hundreds of exceedances of the MAAQS. Table 2 also shows the number of consecutive 30 minute periods at or above 90 ppb. For calculating exceedances of ATSDR and MDH health-based criteria, the minimum assumption was made for these 97 periods: i.e., that the air concentration of H_2S was 90 ppb.

The exceedance of the ATSDR acute minimum risk level (MRL) indicates a single particularly intense period (26 hours) of H_2S ambient levels of more than 70 ppb on June 3 and 4. Exceedances of the ATSDR and MDH values are minimum findings because of the inability of MPCA equipment to measure levels above 90 ppb. No exceedance of the ATSDR intermediate MRL (20 ppb for a period of at least 15 days) was measured (not shown). If actual air concentrations of H_2S above 90 ppb were measured, the number of exceedances of the ATSDR acute or intermediate MRLs and the MDH HRV could have been greater, and actual air concentrations could have been calculated during these episodes. The exceedance of the EPA data is also a minimum finding for this reason, and also because, lacking a full year of data, an annual average concentration of H_2S was calculated assuming that no H_2S will be detected at the West Monitor between October 29, 2008 and May 18, 2009. If conditions remain the same throughout the year ending in May 2009, then the annual average would be substantially higher.

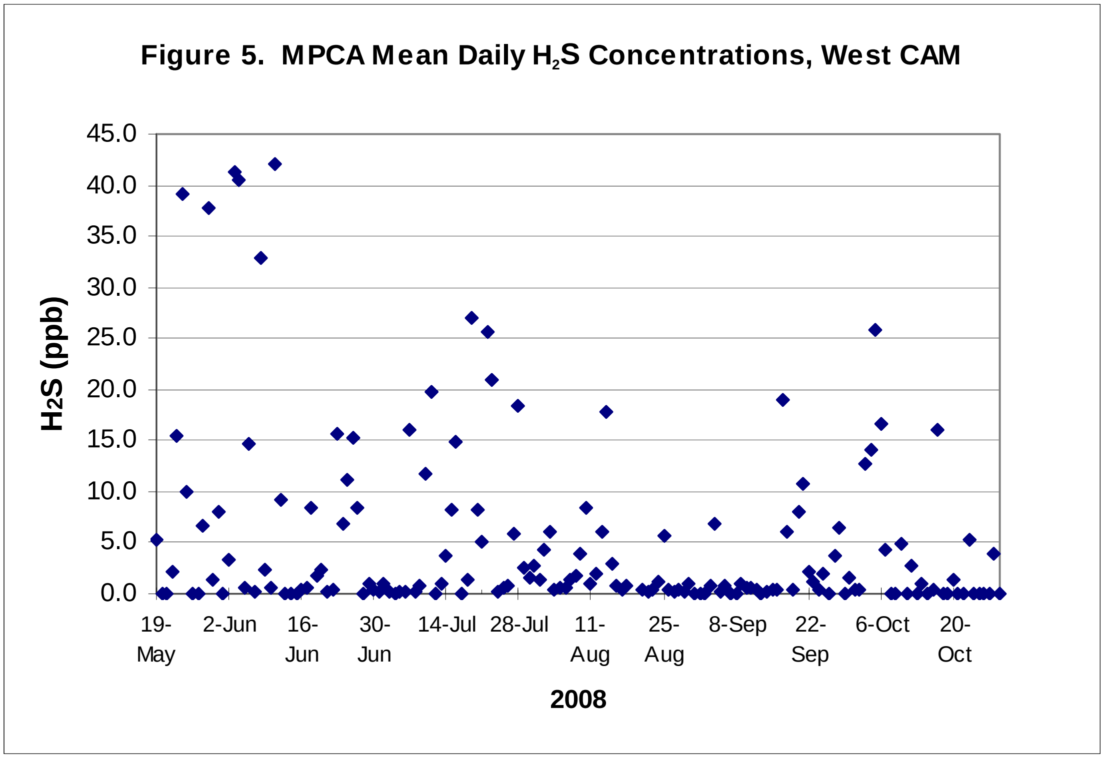
Affidavits from MPCA staff (Minnesota District Court, 2008) indicate that meteorological data support the conclusion that H_2S emissions originate from the Dairy manure storage lagoons.

Table 2. MPCA West CAM Monitoring Data (19 May through 29 October 2008): Comparisons with H_2S Criteria

Agency	*Criterion (ppb)*	*Number of exceedances*	*Dates (time)*
MN Ambient Air Quality Standard#	30	435	Various
MPCA maximum measurement	90	97	Various
ATSDR MRL (1-14 days)*	70	1	3 June (9:00)-4 June (11:00)
		Measured ppb	
MDH Subchronic HRV (13 weeks)	7	>7.1*	19 May-17 Aug
EPA IRIS RfC (annual average)	1.4	>2.4*^	19 May08-18 May09

Notes
#number of half-hour periods, not number of rule violations
*value is a minimum, because all detections >=90 ppb are assumed to =90 ppb
^value is a minimum, because it is assumed no hydrogen sulfide is detected after 29 October

Figure 5 shows mean daily H_2S ambient air concentrations detected at the west CAM. It illustrates that the H_2S levels peaked in late May and early June, but also shows that high levels of H_2S occurred throughout the entire 5-month MPCA monitoring period. Again, these are underestimates, because all of the periods during which a concentration of 90 ppb or greater H_2S was measured, were assumed to be at 90 ppb.



3.2.3 Comparison of ATSDR and MPCA Data

Table 3 compares the number of half hour periods during which H_2S concentrations were nominally above ATSDR's acute and intermediate MRL numerical criteria at three monitors to the west of the Dairy—the ATSDR monitors at S1 and S3 and the MPCA West CAM—from July 16 to July 31, days when all three monitors were functional. ATSDR data at monitor S2 was not included for comparison because it is in a different direction (south of the Dairy). (Note that ATSDR monitors were not operating for full days on July 16 and July 31; hence the total hours for the time period are fewer for these monitors than for the MPCA CAM). The MPCA West CAM, which was the closest to the Dairy, registered the most time when H_2S concentrations were above both acute and intermediate MRLs. ATSDR S3, the next closest monitor to the Dairy, had less time when H_2S concentrations were above the MRLs than the MPCA West CAM but more time than ATSDR S1. It is again noted that all three instruments recorded extended periods of high levels of H_2S using ATSDR benchmarks, as well as standards and guidelines from other agencies as already discussed.

Conclusion: Taken together, these data demonstrate that proximity to the Dairy is strongly related to occurrence of high ambient levels of H_2S. These data also illustrate general agreement between the H_2S concentrations recorded by both the ATSDR and MPCA monitoring.

Table 3. Comparison of ATSDR and MPCA Data, July 16-July 31, 2008

Location	*Total time*	*Detection Limits*	*Detection Range*	*Half hours above H_2S acute MRL (70 ppb)*	*Half hours above H_2S intermediate MRL (20 ppb)*
ATSDR S1: Outdoors	352 hr	0-1500 ppb	0-481 ppb	15	30
ATSDR S3: Outdoors	353 hr 9 min	0-1500 ppb	0-254 ppb	16	55
MPCA West CAM	381 hr 30 min	0-90 ppb	0-90 ppb	21	110

4.0 DISCUSSION

4.1 *Evaluation of Environmental Data*

ATSDR and MDH used Minnesota Ambient Air Quality Standards (MAAQSs) and health-based standards and guidelines to evaluate the likelihood of a public health risk posed by H_2S. These standards and guidelines are based on studies of humans and animals and are briefly discussed in Section 4.3.1. When standards and guidelines are not exceeded, health risks can generally be assumed to be small, if not altogether absent. Exceedances of standards and guidelines are interpreted in light of information available from reports of case histories or communities exposed to elevated levels of H_2S. These studies are discussed in Section 4.3.2. Finally, citizen reports and community exposures and impacts near the Dairy are discussed in Section 4.3.3.

4.2 *Limitations of Exposure Investigation*

Exposure investigations (EIs) are not designed to be long-term environmental contaminant sampling programs. If a need for longer term sampling is identified as a result of an EI, ATSDR may recommend to the appropriate agency or authority that sampling data be collected and indicate the sampling duration needed. An EI is also not designed to characterize emissions from a facility or monitor facility emissions. The objectives of an EI, by design, are to fill data gaps relating to community exposures to environmental contaminants by characterizing exposures for community members with the highest likelihood of exposure. There are always limitations in conducting these investigations due to the duration of sampling and the number of locations to be sampled. This investigation was designed to evaluate areas that may represent the highest levels of exposure to H_2S. However, the selection of the 3-week period in July was likely not the period of most intense exposures. MPCA data indicate that the highest exposures likely occurred in late May and early June (Figure 5). As previously noted, the true magnitude of exposures measured by MPCA is unknown because the equipment does not measure H_2S above 90 ppb.

Another limitation is that H_2S was the only compound sampled. Other chemicals, including other reduced sulfur compounds and ammonia, have been found to be released from dairies (Filipy et al. 2006), and the toxic effects of these chemicals are additive with many of the effects of H_2S (ATSDR, 2006) .

4.3 *Health Implications*

During the health consultation-exposure investigation process, MDH/ATSDR compared measured H_2S concentrations to health-based screening values (see Table 4). To be protective of public health, screening values are typically based on contaminant concentrations many times lower than levels at which effects were observed in experimental animals or human epidemiologic studies. In the present investigation, H_2S concentrations above health-based values were therefore further evaluated to see how observed concentrations of H_2S compared with concentrations at which adverse health effects have been reported in various scientific studies.

As shown in Table 3, illustrating data collected during the EI and data collected by the MPCA during the same time period (i.e., July 16-July 31, 2008), community exposures were measured at or above 70 ppb for 15-21 30-minute periods (depending on monitor location), during a 2-week period. The highest 30-minute measurements at residential properties during the EI were over 200 ppb. As described in Section 4.3.2, people exposed to hydrogen sulfide at levels lower than those detected by ATSDR/MDH and MPCA exhibit symptoms such as eye and throat irritation, headaches, nausea, and dizziness. These are consistent with symptoms reported by area residents. These effects are expected to be reversible with no lasting adverse health effects, assuming exposures at these levels are not continuous over days to weeks.

4.3.1 Regulatory and Health Risk Based Criteria

1. *Minnesota Ambient Air Quality Standards (MAAQSs)*. These are enforceable "bright line" standards. These standards are based on toxicity information, along with information on odor, quality of life, and cost, feasibility, and economic impact of compliance. MAAQSs provide a measure of health protection, but because they are not strictly health risk-based standards there may be some health impacts as ambient air concentrations approach the standards, especially for sensitive sub-populations such as children, the elderly, and people with chronic health problems (e.g., asthma, cardiovascular disease, ulcerative colitis or compromised immune systems). MAAQSs for H_2S are in *Minnesota Administrative Rules* (7009.0080). Standards are applicable at the property boundary of the facility, and/or at locations to which the general public has access. MAAQSs are listed in Table 4.

2. *Health Risk Based Standards and Guidelines*. These are derived by agencies with responsibilities for protecting public health, and are used to give advice to risk managers in regulatory programs who often use them for permitting and enforcement. The purpose of these criteria is to provide limits to *prevent* health effects, even in sensitive sub-populations. Consequently, criteria are generally well below levels that are known to engender health impacts, and are therefore considered to be *conservative*. If these guidelines are exceeded, exposures may be in a "gray" area, in which health agencies are unsure whether or not at

least some people may experience adverse effects.

When deriving these criteria, agencies with responsibilities for protecting public health choose a critical study which examined exposures in animals or humans. They then use uncertainty factors to extrapolate from exposure concentrations investigated in studies of animals or humans to lower appropriate limits for the general public. The risk assessment process is transparent, but agencies may arrive at different criteria because they choose different critical studies with differences in exposures to the toxic substance or they apply different uncertainty factors to arrive at a limit for public exposure. Agency health-based standards and guidelines used to evaluate health implications of H_2S monitoring data near the Excel Dairy are listed in Table 4. More details can be found in the references below.

a. *MDH Health Risk Value (HRV)* (Minnesota Administrative Rules 4717.8000-4717.8600) (http://www.health.state.mn.us/divs/eh/air/hrvtable.htm).

b. *EPA chronic exposure values or Reference Concentrations (RfCs)* published in the Integrated Risk Information System (IRIS) (EPA 2003) (http://www.epa.gov/ncea/iris/intro.htm).

c. *ATSDR MRLs*. The basis of the MRLs for hydrogen sulfide can be found in ATSDR (2006) (http://www.atsdr.cdc.gov/toxprofiles/tp114.html).

EPA (2003) and ATSDR (2006) discuss the possibility that developing organisms have greater susceptibility to neurological effects from H_2S exposure based on animal studies indicating neurochemical and neuroanatomical effects in the developing central nervous system of rats (Hannah and Roth 1991; Skrajny et al. 1992). Both agencies conclude that their intermediate and chronic guidelines are protective for developmental neurological effects (ATDSR 2006; EPA 2003). In EPA (2003), the agency mentions the possibility that children may be more susceptible than adults to acute effects from high level H_2S exposures. ATSDR (2006) states that studies are needed to determine whether children are more sensitive than adults to H_2S exposure, but that toxicological effects in children exposed to H_2S are likely to be similar to those seen in adults.

3. *Emergency Response Criteria*. These criteria are used for guiding emergency response planning, and are meant to be used only for one-time or rare exposures originating from accidental or single events. They are not meant for evaluation of on-going community exposures because exposures at these levels will cause health effects in most people. The American Industrial Hygiene Association (AIHA) has Emergency Response Planning Guidelines “intended to provide estimates of concentration ranges where one reasonably might anticipate observing adverse effects” (http://orise.orau.gov/emi/scapa/erpg-defn.htm). The ERPG-1 for hydrogen sulfide is listed in Table 4 (http://www.aiha.org/1documents/Committees/ERP-erpglevels.pdf).

Table 4: Criteria for Hydrogen Sulfide Exposures

	Exposure Value	***Exposure Period/Intent***
State of Minnesota	30 ppb, no more than twice in 5 days	Ambient Air Quality Standard—not to be exceeded except for exceptions noted in Minnesota Laws.
State of Minnesota	50 ppb no more than twice per calendar year	Ambient Air Quality Standard—not to be exceeded except for exceptions noted in Minnesota Laws.
ATSDR	70 ppb	Acute Minimal Risk Level—up to 14 days of continuous exposure. Exposures below this value are not expected to result in non-cancerous adverse health effects.
ATSDR	20 ppb	Intermediate Minimal Risk Level—between 15-365 days of continuous exposure. Exposures below this value are not expected to result in non-cancerous adverse health effects.
State of Minnesota	7 ppb	Health Risk Value—subchronic exposure (up to 13 weeks). Exposures below this value are not expected to result in adverse health effects.
U.S. EPA	1.4 ppb	Reference concentration—concentration for a substance in air unlikely to cause non-cancer health effects over a lifetime of chronic exposure.
American Industrial Hygiene Association	100 ppb	Emergency Response Planning Guideline-1—maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.

4.3.2 Health Effects of Hydrogen Sulfide Exposure

Hydrogen sulfide causes a number of health effects. The severity of the health impacts is related to the magnitude, frequency, and duration of the exposure. Exposures are generally categorized as acute, intermediate or subchronic, or chronic. People living in communities impacted by industrial (including agricultural) emissions of H_2S are more likely to have chronic exposures to low ppb ambient concentrations, with possible intermittent acute events ranging up to low part per million (ppm) ambient concentrations (ATSDR, 2006).

Short-term single exposures to H_2S at low ppm concentrations may cause adverse health effects. For example, one study demonstrated bronchial constriction in 2 out of 10 asthmatics exposed to 2,000 ppb (2 ppm) H_2S for 30 minutes (Jappinen et al. 1990). Other studies also document changes in oxygen uptake (Bhambini and Singh 1991), and an inhibition of the aerobic capacity of muscle tissue in healthy men exposed to between 5,000 and 10,000 ppb (5 and 10 ppm) for short periods of time (Bhambini et al. 1996a, 1996b). At still lower concentrations, people report various symptoms. For example, workers in a mobile laboratory monitoring H_2S downwind from an oil refinery for 5 hours were exposed to 90 ppb (30-minute downwind averages), and reported eye and throat irritation, headache, and nausea. Symptoms generally disappeared within a few hours after leaving the sampling site, although throat irritation persisted in two workers for a day (EPA 2000). Other chemicals were also detected at levels not expected to cause health effects, although they could have contributed to the findings. These results are consistent with the ERPG-1 guideline of 100 ppb (Table 4), suggesting that single exposures to H_2S above 90 to 100 ppb will cause reversible health effects.

A recent study examining health effects in a community exposed to low levels of H_2S has noted that after days when H_2S levels were above 30 ppb, there was an increase in asthma-related hospital visits among adults and children (Campagna et al. 2004). Kilburn and Warshaw (1995) studied chronic exposures to sulfide gases in oil processing plants and found that people working at the plant or living downwind from of the plant experienced nausea, headache, vomiting, breathing abnormalities, nosebleeds, depression, and personality changes at levels between 10 ppb and 100 ppb.

4.3.3 Community Exposures Near the Excel Dairy

MPCA data indicate that residents living near the Dairy have been exposed to hundreds of half hour periods of elevated H_2S levels above the MAAQSs (Table 2) beginning in May 2008 through October 2008. Data collected during the EI indicate that the longest continuous exposures to hydrogen sulfide at levels above the acute MRL of 70 ppb lasted for 2-4 hours. Three 30-minute average periods during the EI (2 at S1 and 1 at S3) exceeded 200 ppb. ATSDR data are a “snapshot” of a 3-week period in July (Table 1). MPCA data indicate numerous periods of H_2S at or above 90 ppb beginning in May 2008 (Table 2). ATSDR and MPCA data document periods of H_2S concentrations in air near and above the health guideline values presented in Table 4. Exposures to H_2S at these concentrations and for these durations have been shown to result in symptoms such as eye and throat irritation, headaches, nausea, and dizziness, but are generally considered reversible (ATSDR 2006). Sensitive sub-populations could experience health impacts at even lower levels of H_2S. For example, as noted above, an increase in asthma-related hospitalizations were reported in one community study when H_2S levels were above 30 ppb.

If these were single or relatively few exposures to elevated H_2S, then it is highly likely that effects would be temporary and reversible. However, the monitoring conducted by MPCA indicates that the potential exists for longer term exposures to levels of concern for H_2S. As shown in Table 2, calculated averages estimated over several weeks or over a year’s time exceed the MDH subchronic HRV and the EPA chronic RfC, respectively. These criteria represent limits to protect people from possible adverse health effects associated with more prolonged exposures to elevated levels of H_2S. Generally, health guidelines for longer periods of time are lower than those set for shorter-term exposures, reflecting that people may experience health effects at lower levels when exposed to a chemical for longer periods of time. MPCA monitoring over a 5 month period and projection for a year long exposure, suggest that people could be exposed to levels above these guidelines over the longer term. Additional concern is warranted as the magnitude of exceedances of intermediate, subchronic and chronic H_2S criteria are not fully known since the MPCA monitors did not quantify ambient concentrations above 90 ppb. Additionally, only H_2S was measured, but other chemicals that have similar effects have been identified and documented at other CAFOs and are likely also present (Filipy et al, 2006). As noted in Section 4.3.2, longer term exposures to H_2S could engender more lasting effects, including depression and personality changes, that may be indicative of long term stress. These effects are consistent with reports of citizens living near the Dairy.

Residents from 11 families living within 1.5 miles of the Dairy reported that they had been experiencing health effects (including nausea, headaches, fatigue, difficulty concentrating, difficulty breathing, and throat and eye irritation) related to odors and repeated H_2S exposures during the spring, summer, and autumn of 2008 (citizen affidavits, Minnesota District Court, 2008). Two of the residents have been pregnant during this time and are particularly concerned about effects on their developing fetuses, as well as effects on their young children. Symptoms reported by citizens are consistent with effects reported in other communities at similar (and often lower) levels of exposure to H_2S in outdoor air (ATSDR 2006).

Citizen affidavits also report that the bad odors have had other consequences including fear for their children, anxiety, frustration, worry, depression, inability to plan events at their houses, inability to work around their property, inability to have visitors, and necessity to leave their houses when odors are bad or they experience health symptoms. All of these emotional responses and alterations in living patterns are responses to a perceived threat, and are signs of stress. There is reason to believe that stress itself, because of induced chronic activity of the sympathetic nervous system, hypothalamo-pituitary-adrenal axis, and cardiovascular and immune systems, can be involved in pathogenesis of disease (McEwen 1998). While the stress response is highly variable and difficult to quantify, prolonged stress is damaging to health and renders people more vulnerable to other adverse effects from environmental exposures (McEwen 1998). Some studies have shown neurobehavioral changes or irritability in workers following H_2S exposures, but generally at levels hundreds of times higher than those measured near the Dairy (ATSDR 2006).

4.4 *Child Health Considerations*

ATSDR and MDH recognize that in communities faced with contamination of their air, water, soil, or food, the unique vulnerabilities of fetuses, infants, and children demand special emphasis. ATSDR and MDH are committed to evaluating the health impact of environmental contamination on children, and uses health guidelines in investigations that are protective of children. One child was seen on the Dairy property.

<u>Conclusion:</u> *Concentrations of H_2S in the community present an unacceptable risk to residents in the area, particularly children and others with compromised respiratory systems.*

4.5 *Physical Hazards*

There is a safety hazard for adults and children living at the Dairy from unfenced manure lagoons. MDH and ATSDR staff observed a toddler on the Dairy site in July.

5.0 CONCLUSIONS

- Air emissions from the Dairy are a *public health hazard*. ATSDR applies this category to sites where there is evidence of chronic, site-related exposure to hazardous substances that could result in adverse health effects.

- Emissions from the uncovered lagoons at the Dairy are uncontrolled and largely unpredictable, and methods used to control emissions, such as aeration with biological addition, are ineffective, unapproved, and experimental.

- Over 400 exceedances of the MAAQSs for H_2S have been recorded by MPCA from mid-May to early October 2008, with the most intense periods occurring in late May and early June.

- MPCA and ATSDR data document community exposures to H_2S at concentrations above health guidelines, and at concentrations shown in the literature to be associated with adverse health effects; unhealthy levels of H_2S are present in the community. Repeated exposures to H_2S at levels detected in this community may cause acute symptoms such as persistent eye and throat irritation, headache, and nausea. Also, citizens in the vicinity are under stress, and stress may exacerbate on-going medical conditions, as well as toxic effects of exposures to H_2S and other gases emitted from the Dairy.

- The potential for longer-term exposures to H_2S also exist. Longer-term averages are shown to exceed chronic health-based criteria; however, the full extent of long-term exposures is unknown because the concentrations cannot be quantified in terms of levels greater than 90 ppb given that MPCA air monitoring equipment does not record levels of H_2S above 90 ppb.

- A physical safety hazard exists for children living on the Dairy property due to the unfenced manure lagoons.

6.0 RECOMMENDATIONS

- The Excel Dairy should take immediate steps to ensure the health and safety of non-workers, especially children, on the Dairy property. MDH and local public health officials can advise on appropriate measures, such as fencing the lagoons.

- The Dairy should take rapid, efficacious, and permanent measures, such as applying permanent covers for manure lagoons and eliminating over land manure transfer to assure compliance with Minnesota Ambient Air Quality Standards.

- MPCA should continue to monitor air emissions of H_2S from the Dairy, particularly at the west monitoring site, to confirm efficacy of enforcement or to demonstrate the need for more emissions controls.

- The Public Health Action Plan is as follows:

  - MDH will work with local public health officials to provide people living at the Dairy with appropriate information to protect their health and safety.

  - MDH and ATSDR will hold a public meeting to convey the results of the EI and Health Consultation and discuss conditions at the Dairy at the time of the public meeting.

  - If measures to eliminate exceedances of the MAAQSs for H_2S are not effective, ATSDR and MDH will consider conducting further exposure monitoring, and will recommend more stringent measures to reduce emissions.

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9.0 CERTIFICATION

The Minnesota Department of Health prepared this Excel Dairy Exposure Investigation under a cooperative agreement with the Agency for Toxic Substances and Disease Registry (ATSDR). At the time this Health Consultation was written, it was in accordance with the approved methodologies and procedures. Editorial review was completed by the Cooperative Agreement partner.

Technical Project Officer, Cooperative Agreement Team, CAPEB, DHAC, ATSDR

The Division of Health Assessment and Consultation, ATSDR, has reviewed this public health consultation and concurs with the findings.

Team Leader, Cooperative Agreement Team, CAPEB, DHAC, ATSDR

Exposure Investigation

Field Investigation Report

Excel Dairy

Thief River Falls, MN

Cost Recovery Number A0LG00

November 2008

Prepared by
Division of Health Assessment and Consultation
Exposure Investigation and Site Assessment Branch
Agency for Toxic Substances and Disease Registry

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List of Acronyms

ARD	Air and Radiation Division
ATSDR	Agency for Toxic Substances and Disease Registry
CV	comparison value
DAS	data acquisition system
DQO	data quality objective
EI	exposure investigation
EPA	US Environmental Protection Agency
ERG	Eastern Research Group, Inc.
°F	Fahrenheit
H_2S	hydrogen sulfide
m/s	meters per second
mA	milliampre
MDH	Minnesota Department of Health
MPCA	Minnesota Pollution Control Agency
MRL	minimal risk level
ppb	parts per billion
ppm	parts per million
QA/QC	quality assurance and quality control
RSD	relative standard deviation
RTD	resistance temperature detector
SPM	single point monitor

1.0 Introduction

In order to better assess potential human exposure to airborne concentrations of hydrogen sulfide (H_2S) in ambient and indoor air at residential properties near the Excel Dairy Farm near Thief Rivers Falls, Minnesota, the Agency for Toxic Substances and Disease Registry (ATSDR) conducted an Exposure Investigation (EI). During this EI, an ambient and limited indoor air monitoring program was conducted over a three week period to obtain representative concentration data of hydrogen sulfide, as well as meteorological parameters at three residential properties. The information collected through this exposure investigation was used in conjunction with air monitoring data collected by the Minnesota Pollution Control Agency (MPCA) to better determine potential human exposure to airborne concentrations of hydrogen sulfide near the Excel Dairy Farm (see Excel Dairy Public Health Consultation – Exposure Investigation).

2.0 Background

Excel Dairy Farm (Excel Dairy) is a concentrated animal feeding operation located in Thief River Falls, Minnesota (EPA 2008) (see Figure 1 in Appendix A). The farm is located in Marshall County in northwestern Minnesota, about 60 miles northeast of Grand Forks, North Dakota, and 76 miles south of the Canadian border (Mapquest 2008). According to Marshall County public health officials, approximately 12 families live within ½ mile of the Excel Dairy and are potentially affected by gases such as hydrogen sulfide (H_2S) that are emitted from the facility (Messing 2008).

After a prior owner/operator of the dairy had gone out of business in 2002, Excel Dairy constructed a new, larger barn and began operating the new dairy in the fall of 2007 (Appendix A). Currently, Excel Dairy is permitted to house 1,544 dairy cows, but is expected to increase that number to about 2,000 (Appendix A; MPCA 2007). According to resident complaints, strong odors have emanated from the facility since it reopened in 2007. Specifically, complaints reported to the Minnesota Department of Health (MDH) included reports of significant odors emanating from the dairy farms, particularly from the lagoons and manure pit. In addition, residents have expressed concerns about health impacts, including headaches, nausea, eye irritation, and respiratory tract irritation (Messing 2008).

On June 8, 2008, Minnesota health officials advised several families to evacuate their homes after measured levels of H_2S suspected of being emitted from Excel Dairy exceeded state air quality standards. On June 10, 2008, a citizens group notified the US Environmental Protection Agency's (EPA's) Region 5 Air and Radiation Division (ARD) about the evacuations. On June 11, 2008, a local citizen contacted ARD, notifying the agency that 12 families live near the dairy, including his family which has young children (i.e., ages 3 and 5) (Appendix A).

In June 2008, the Minnesota Pollution Control Agency (MPCA) installed two continuous air monitors (CAMs) along the facility fenceline to measure ambient H_2S concentrations. The MPCA CAMs had a detection range of less than or equal to 90 parts per billion (ppb). To increase this detection range, ATSDR loaned MPCA two H_2S monitors with a detection range of 53-1,500 ppb for placement on or near the facility boundary. In addition, the MDH requested that

ATSDR conduct an exposure investigation (EI) to measure H_2S levels at two residences located near the Excel Dairy. In response, ATSDR conducted this EI to address identified data gaps.

ATSDR was assisted with this EI by Eastern Research Group, Inc. (ERG) During the monitoring program, air quality measurements were collected for 3 weeks at three monitoring locations within the investigation area.

This report describes ATSDR's EI monitoring program and the results generated from the program. ATSDR and MDH presented the findings of its health effects evaluation in a separate document (see Excel Dairy Public Health Consultation – Exposure Investigation).

For more detailed background and exposure investigation planning information, see ATSDR's Exposure Investigation Protocol presented in Appendix A.

1.1 Exposure Investigation Overview

This section summarizes the EI's targeted pollutants and siting criteria. Additional details are provided in ATSDR's Exposure Investigation Protocol and Monitoring and Health and Safety Plan for this EI, both of which are presented in Appendix A.

1.1.1 Targeted Pollutants

In this EI, ATSDR measured ambient and limited indoor concentrations of H_2S because it presents a high potential to be emitted from dairy farms and because elevated concentrations of H_2S have been measured by both the MPCA and community members. This targeted pollutant corresponds with the objectives of the EI. The primary objective of the EI was to characterize concentrations, including peak concentrations and time-weighted average values, of H_2S in residential areas near the Excel Dairy Farm. The second objective of the EI was to provide information to evaluate whether people living near the facility are exposed to H_2S at concentrations that pose a health hazard.

1.1.2 Siting Criteria

The EI monitoring locations were selected because these sites are residential properties within the close proximity to the Excel facility and because some of the residents at these locations were individuals who reported concerns about odors emanating from the lagoons and manure pit to MDH and had requested air monitoring at their residences. To address community concerns, three monitoring stations were established in areas surrounding the facility. These locations were documented by longitude and latitude using a hand held global positioning system.

2.0 Monitoring Locations, Sample Collection, and Monitoring Methods

This section describes the monitoring sites, sample collection, and monitoring methodologies used during the EI.

2.1 Monitoring Sites

As shown in Figure 2-1, the EI used a network of three monitoring locations:

- Site 1 was located approximately 0.50 miles to the southwest of the facility.
- Site 2 was located approximately 0.75 miles to the southeast of the facility.
- Site 3 was located 0.33 miles to the west of the facility.

As indicated on Figure 2-1, MPCA also operated two continuous monitoring sites close to the facility. As shown in the figure, MPCA Site 1 was located approximately 0.25 miles to the northeast of the facility, while MPCA Site 2 was located approximately 0.25 miles to the southwest of the facility.

Table 2-1 presents information on the three monitoring locations, including the site identification (site ID) number used in the project database, a description of the site ID, a brief site description, and the parameters measured. All parameters were measured using continuous monitoring. Figures 2-2 through 2-7 present photographs of the sampling equipment installed at each site.

Table 2-1. Site-Specific Information

Site ID	*Description of Site ID*	*Site Description*	*Parameter Measured*
S1 Out – Low	Outside monitoring using instrument with detection range of 0–90 ppb	Private building (breathing height in zone of 6–10 feet for monitoring, 8 feet above grade)	H_2S
S1 Out – Mid	Outside monitoring using instrument with detection range of 76–1,500 ppb		H_2S
S1 In – Low	Inside monitoring using instrument with detection range of 0–90 ppb		H_2S
S1 – Met	Meteorological measurement data collection	Private building (10 feet above grade)	Wind speed, wind direction, temperature, and relative humidity
S2 Out – Low	Outside monitoring using instrument with detection range of 0–90 ppb	Private building (breathing height in zone of 6–10 feet for monitoring, 6 feet above grade)	H_2S
S2 Out – Mid	Outside monitoring using instrument with detection range of 76–1,500 ppb		H_2S
S2 In – Low	Inside monitoring using instrument with detection range of 0–90 ppb		H_2S
S3 Out – Low	Outside monitoring using instrument with detection range of 0–90 ppb	Private building (breathing height in zone of 6–10 feet for monitoring, 6 feet above grade)	H_2S
S3 Out – Mid	Outside monitoring using instrument with detection range of 76–1,500 ppb		H_2S

Figure 2-1. Excel Dairy EI Monitoring Network Map

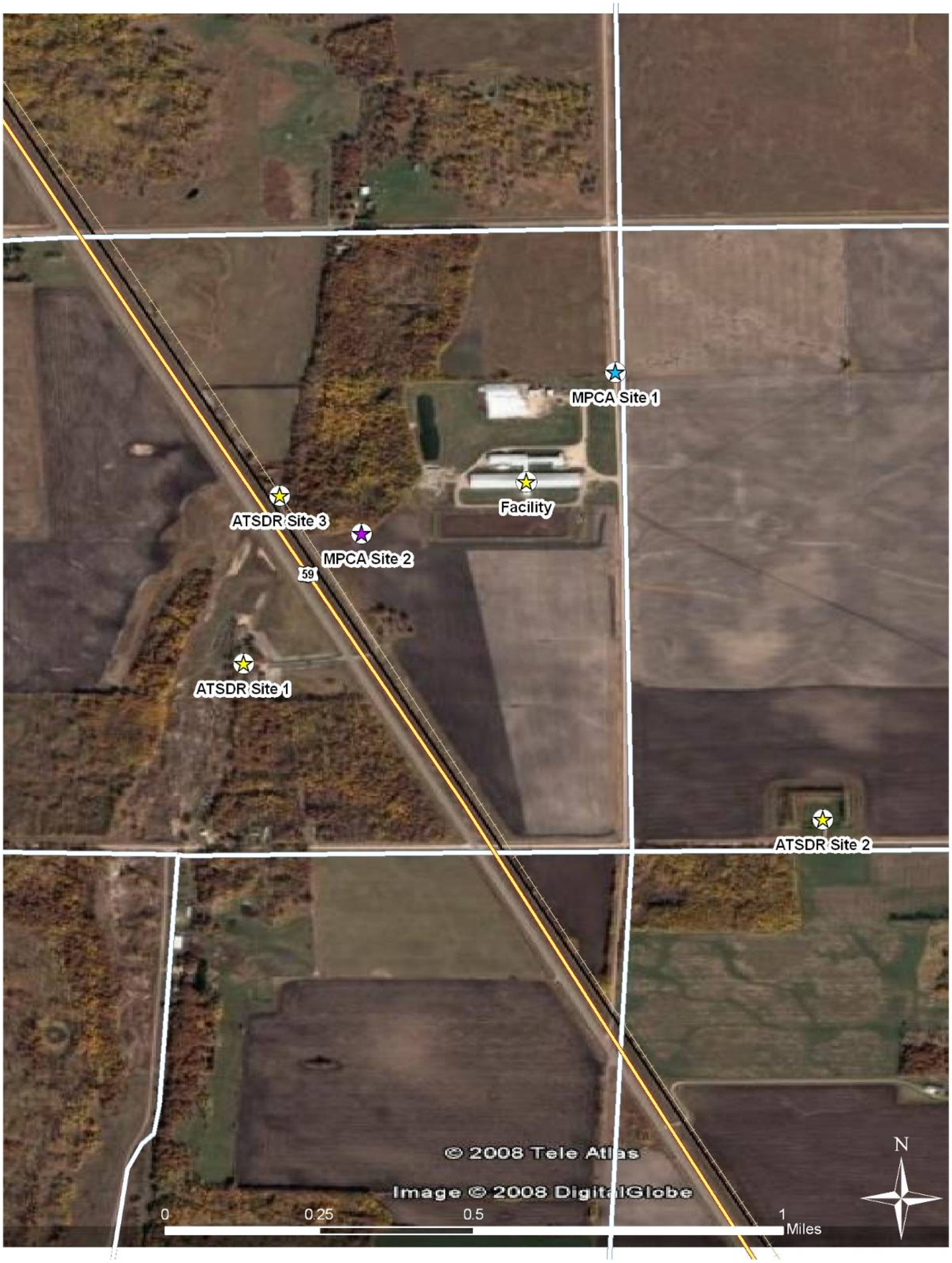


Figure 2-2. Site 1 Outdoor Monitoring Equipment and Setup

Figure 2-3. Site 1 Indoor Monitoring Equipment and Setup

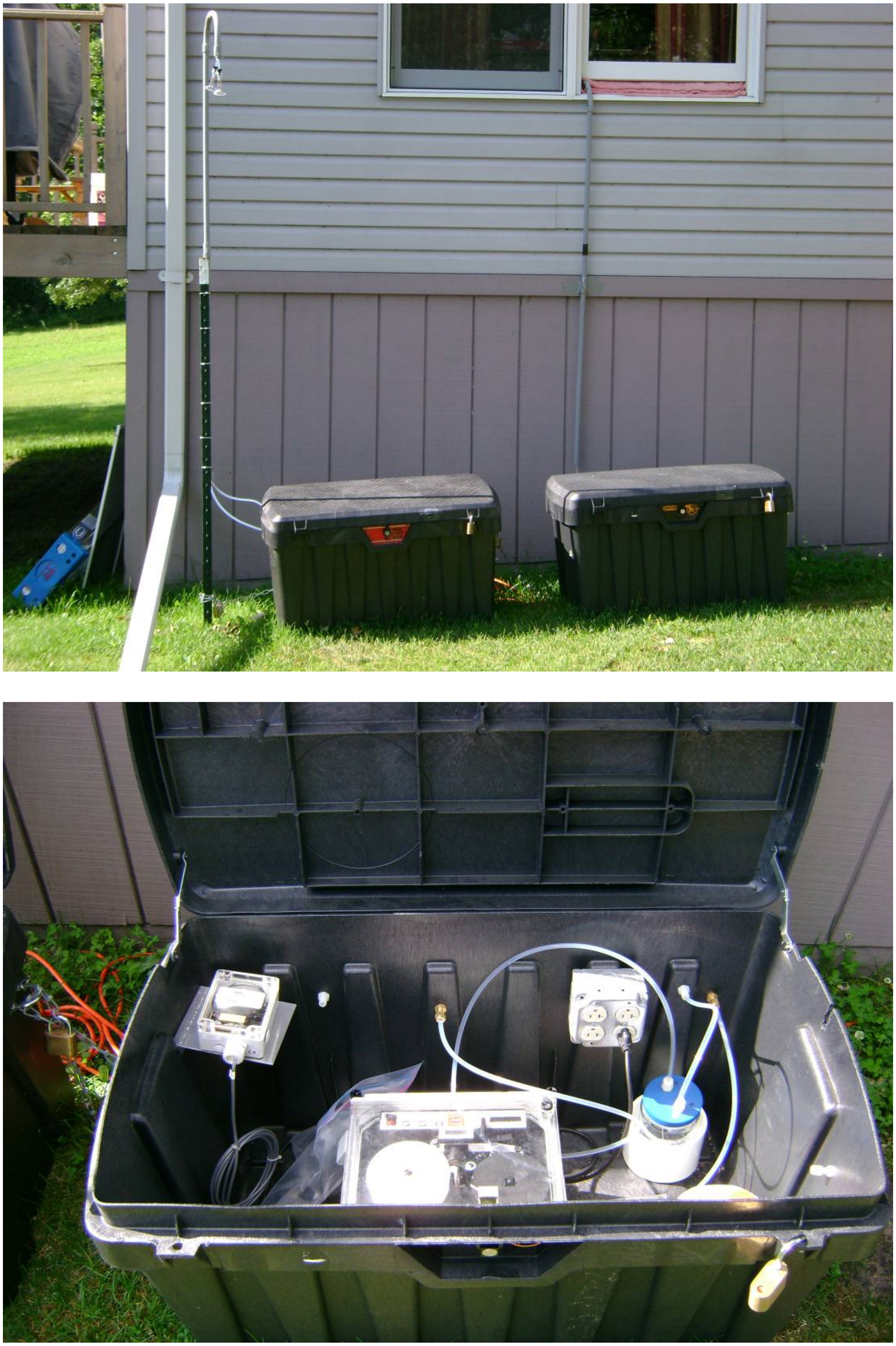


Figure 2-4. Site 1 Meteorological Measurements System and Setup

Figure 2-5. Site 2 Outdoor Monitoring Equipment and Setup

Figure 2-6. Site 2 Indoor Monitoring Equipment and Setup

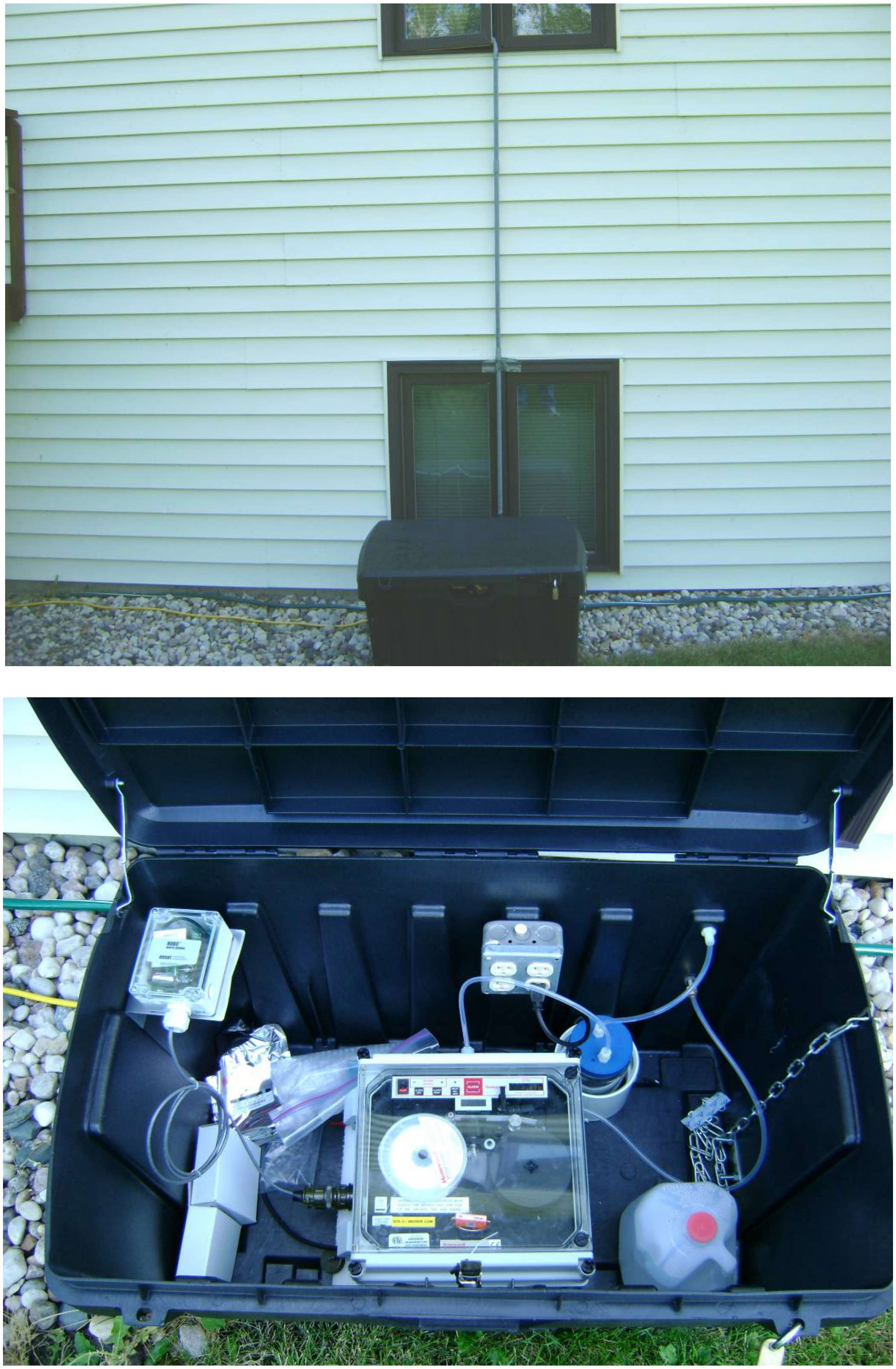
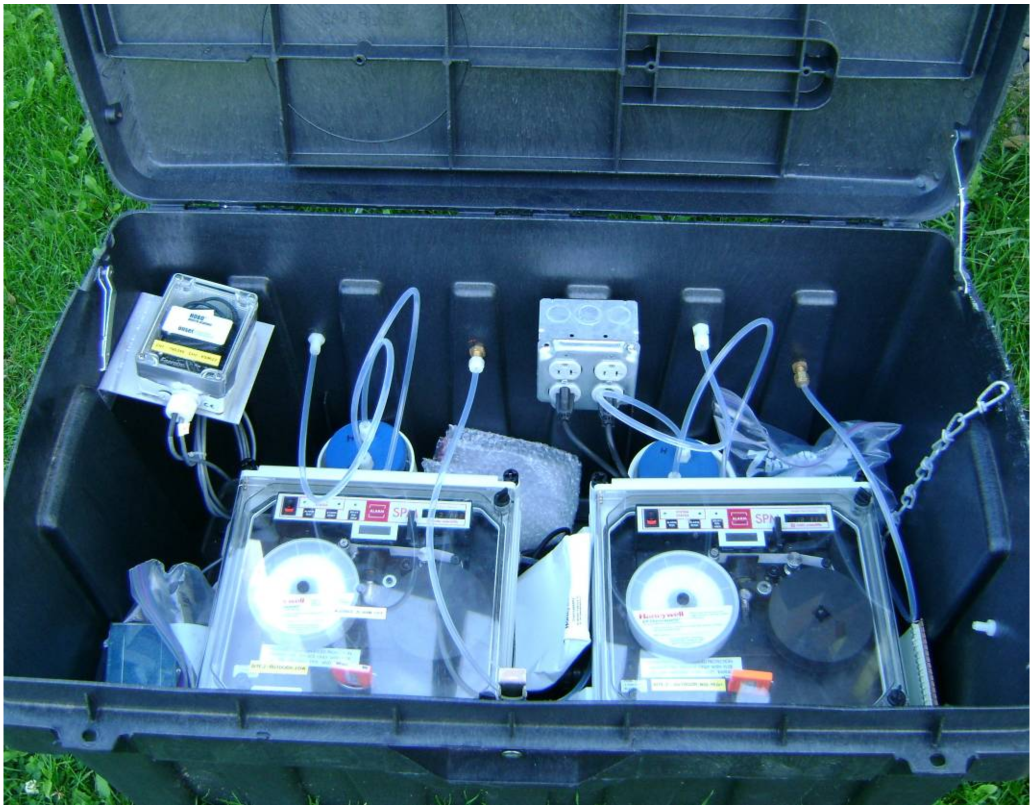


Figure 2-7. Site 3 Outdoor Monitoring Equipment and Setup



2.1.1 Deployment

EI Field Staff transported and set up all monitoring equipment and the meteorological measurements system at the established sites (see Table 2-1). Once installations were completed all measurement systems were tested to ensure that damage had not occurred during transport. Internal optical two-point calibration checks were performed on the systems. Monitoring at each EI site commenced after that location's measurement systems were determined to be operating correctly.

2.1.2 Duration/Schedule

The EI monitoring period was selected to correspond with typical facility operations and representative emissions from the Excel Dairy facility and to complement the MPCA monitoring program. After the measurement systems were brought on line, monitoring was conducted continuously for 3 weeks.

Field sampling personnel visited the monitoring sites daily to assess the functional status of the measurement equipment and to correct any identified problems. On a weekly basis, the field sampling personnel downloaded data from the H_2S instruments and performed quality assurance activities (e.g., reloaded measurement tapes as needed, performed internal optical calibration checks). Maintenance was performed on these monitoring systems as required. In addition, meteorological measurements system data was downloaded weekly, and visual checks of the meteorological sensors were performed daily. Any issues and/or concerns were discussed with the ATSDR lead investigator as they occurred.

For the purposes of the EI report, the following terms are defined as indicated below.

- Total possible measurements: The total number of measurements possible is proportionate to the total number of minutes during which H_2S measurements were scheduled during the EI monitoring period while applying a 1-minute measurement frequency. This value can change over the course of an EI if the technical approach changes (e.g., sites are moved, indoor or outdoor sampling is terminated).

- Valid measurements: The total number of possible measurements actually accomplished and determined to be accurate and representative during the EI monitoring period.

- Invalid measurements: The total number of possible measurements actually determined to be inaccurate and not representative during the EI monitoring period (e.g., those recorded during observed instrument malfunction).

Table 2-2 presents the monitoring schedule for valid data collection during the EI. As shown in the table, H_2S valid measurements were collected at some sites during the entire EI, while valid measurements at other sites were obtained during shorter periods of time. The following valid monitoring occurred at each site during the EI:

- Valid measurements were collected on all dates during the entire 3-week EI—July 9 to July 31—at S1 In – Low, S2 Out – Low, S2 In – Low, and S1 – Met.
- As a result of a malfunctioning data logger during the first week of monitoring (see Section 3.1.1 for more information), valid measurements at S1 Out – Low and S1 Out – Mid were only collected from July 16 to July 31.
- Because two monitor locations (Sites 1 and 2) were originally planned for this EI, the monitors at outdoor Site 3 were not put in operation until the second week of the EI. Site 3 was added the second week of the EI program based on conditions on-site and the professional judgment of the EI Field Staff. It was also the professional judgment of the EI Field Staff that placing an indoor monitor at Site 3 would not provide valid or representative data.
- S3 Out – Low was installed and brought on-line on July 16, and operated through July 31.
- S3 Out – Mid was installed and brought on-line after the EI program had been running for several days, with valid measurements collected from July 20 to July 31. The original S2 Out – Low monitoring equipment was used for this purpose.

Table 2-2. Schedule of Valid Monitoring Data Collection During the EI

Site ID	*Begin Date*	*End Date*
S1 Out – Low	7/16/08	7/31/08
S1 Out – Mid	7/16/08	7/31/08
S1 In – Low	7/09/08	7/31/08
S1 – Met	7/09/08	7/31/08
S2 Out – Low	7/09/08	7/31/08
S2 Out – Mid	7/09/08	7/20/08
S2 In – Low	7/09/08	7/31/08
S3 Out – Low	7/16/08	7/31/08
S3 Out – Mid	7/20/08	7/31/08

2.2 Sampling and Monitoring Methodologies

The following subsections describe in detail the processes used to collect continuous H_2S measurements, as well as measure meteorological parameters.

2.2.1 H_2S Measurements

Honeywell single point monitors (SPMs) were used to measure H_2S at all outdoor and indoor monitoring locations during the EI. The manufacturer performed primary calibration certification of the SPMs. Supplemental calibration checks on these instruments were performed at the ERG laboratory prior to field deployment, and again after the EI was completed. Two-point internal optical performance checks were conducted during deployment and at the end of each week of monitoring. Results from the calibration and optical checks are presented in Section 3.

The SPMs detected the presence of target analytes and calculated corresponding concentrations using a colorimetric detection method. This method utilizes an optical scanning system that quantifies ambient air concentrations by measuring color change on a chemically impregnated paper tape specific to the target analyte. In this program, ATSDR used a measurement tape impregnated with a specially formulated chemical reagent specific for H_2S.

Measurement of H_2S was automatic. For each monitor, ambient air was drawn through a humidifier containing distilled/de-ionized water which was checked and supplemented daily as needed across the duration of the monitoring program. From the humidifier, ambient air was then drawn through into the instrument through a thin wall Teflon tubing sample line. An inverted glass funnel was connected at the inlet end of the sample line to prevent rain from entering the measurement device. As the sampled air passed through the instrument's measurement tape, H_2S in the sampled air reacted with the reagent on the tape to form a colored stain. The intensity of the stain is proportionate to the concentration of H_2S present in the sampled air (i.e., the darker the stain, the higher the concentration of H_2S). An electro-optical sensor measured the stain intensity, which is then converted to a measured concentration of H_2S based on instrument-specific calibration data.

For this EI, the measurement frequency for collecting H_2S measurements was once per minute. However, it should be noted that the length of sampling time required for an SPM measurement to be completed (i.e., for the reagent to be expended) can vary from 3-7 minutes depending on the concentration of H_2S present in the sample air stream (i.e., the higher the concentration, the faster the reagent is expended). As a result, it is typical to observe three to seven measurements that present the same concentration before each new measurement occurs. When the reagent is expended (i.e., after the measurement is completed), the SPM automatically provides the H_2S measurement in the form of a 4-20 milliampre (mA) output signal that correlates to a specific H_2S concentration, and then advances the tape to a fresh reagent spot. The SPM continues to present the output signal until the next time it updates the measurement and advances the tape. Thus, the SPM holds the data point at the same level until the next update occurs (i.e., 3-7 minutes later). A HOBO Micro Station data acquisition system (DAS) coupled with a dedicated 4-20 mA adapter was used to poll the SPM once per minute. At each polling, the SPM output signal (i.e., 4-20 mA) was logged by the DAS. Because the DAS polls the SPM at a rate that is faster than the SPM accomplishes each measurement update, several data points at the same concentration are collected.

Two SPM instrument configurations were used during the EI. ChemKeys (i.e., programmable read-only memory chips) were used to set the measurements range on each instrument to allow an overall measurement range of 0–1,500 ppb. "Low level" instruments were those with a detection range of 0–90 ppb, while "mid level" instruments had a detection range of 76–1,500 ppb. All outdoor measurements data for Sites 1, 2, and 3 were made using two SPMs at each site, with one SPM having a measurement range of 0–90 ppb and the other having a measurement range of 76–1,500 ppb. All indoor measurements data for Sites 1 and 2 were made using an SPM at each site that was equipped with a measurement range of 0–90 ppb.

2.2.2 Meteorological Parameters Measurements

Meteorological parameters during the EI were monitored using a stand-alone meteorological measurements system attached to a secured tripod assembly. The meteorological measurements system was installed at Site 1. The system incorporated the following sensor technologies:

- A cup anemometer to measure wind speed: The cup anemometer used three wind-catching cups that relate the rate of rotation (i.e., revolutions per second) to the speed of the wind at the time of measurement. Calibration data for the sensor measuring the revolutions per second were used to calculate the corresponding wind speed in meters per second.

- A directional mast and vane to measure wind direction: The mast and vane used a balanced fin, mounted on a vertical shaft. As wind force was applied, the shaft rotated seeking the minimum force position. The shaft turned within a vane transducer/potentiometer and supplied an analog output signal. The transducer was fixed in a position orientating it towards the direction of North. Transducer calibration data allowed the analog signal to be converted into 0–360 degree compass directions.

- A resistance temperature detector (RTD) to measure ambient temperature: The RTD used a thermistor resistance bridge to provide the relationship between temperature (as °F) and output signal change. Calibration data for the thermistor were used to calculate corresponding temperature measurements.

- A resistance/capacitance wire-wound salt-coated bobbin assembly to measure relative humidity: The bobbin assembly used a thin hygroscopic film affected by the presence of moisture to provide the relationship between percent relative humidity and output signal change. Calibration data for the bobbin sensor were used to calculate the corresponding relative humidity measurements.

Measurements were made at a height of approximately 10 feet above grade. This height was selected because it is the highest point above grade that is still within breathing height. Electronic signals from the meteorological monitoring systems' sensors were collected and stored using HOBO Micro Station DASs and BoxCar Pro 4.3 software.

3.0 Quality Assurance/Quality Control

This section presents various quality assurance and quality control (QA/QC) measures implemented throughout the EI.

Data quality objectives (DQOs) help determine the critical question of how good data must be to achieve a project's specific technical goals and objectives. This EI used DQOs to develop the criteria that the data collection design should satisfy, including where to conduct monitoring, when to conduct monitoring, measurement frequency, and acceptable measurement precision and accuracy. The operational DQOs (see Table 3-1) and technical DQOs (see Table 3-2) are consistent with the goals and objectives of this EI, considering the monitoring logistics, target pollutants, and specifications of the monitoring and sampling collection systems used.

Table 3-1. Operational DQOs

Operational Element	*Objective*
Where to conduct monitoring (siting)	All monitoring locations must be in close proximity to the potentially impacted population.
When to conduct monitoring (duration)	Daily from 0000 to 2359 hours across 3 continuous weeks.
Frequency of monitoring (measurement intervals)	Continuous for H_2S to allow assessment of short duration excursions and calculations of hourly and daily average concentrations.

Table 3-2. Technical DQOs

Technical Element	*Objective*
Measurement completeness	80% data capture or greater
H_2S measurement precision	+/- 20% relative standard deviation (RSD)
H_2S measurement accuracy	+/- 15% difference

Operational DQOs

The Excel Dairy EI met all of its specified operational DQOs. Detailed operational DQO performance information is presented below.

- Siting: As presented in Section 2.1, all monitoring locations were within 0.75 miles of the Excel Dairy facility. The monitoring locations included in the EI were selected at the request of MDH because those locations directly represented the potentially impacted population.
- Duration: The monitoring program began on July 9 and ended on July 31, for a program total duration of 3 weeks. Measurements occurred throughout the day, using continuous monitoring. See Table 2-2 for the schedule of valid monitoring data collection during the EI organized by monitoring location.
- Measurement intervals: H_2S and meteorological measurements occurred continuously, with outputs recorded every minute.

Technical DQOs

The Excel Dairy EI met all of its technical DQOs:

- Measurement completeness: For this EI, completeness was defined as the number of valid measurements collected, compared to the number of possible measurements expected. Monitoring programs that consistently generate valid results tend to have higher measurement completeness than programs that consistently invalidate samples. Therefore, the completeness of an air monitoring program is a qualitative measure of the reliability of air sampling and laboratory analytical equipment and the efficiency with which the field program and laboratory analysis was managed.

- Measurement precision: For this EI, measurement precision was defined as the ability to acquire the same concentration from the same or from different instruments with an acceptable level of uncertainty, while concurrently sampling the same gas stream. In other words, precision characterizes the repeatability of measurements made by a particular monitoring or measurement approach.

- Measurement accuracy: For this EI, measurement accuracy was defined as the ability to acquire the correct concentration measurement from an instrument or an analysis within an acceptable level of uncertainty. Accuracy was assessed to determine whether systematic deviations occurred from the true concentrations being reported.

Technical DQO performance and quality control information is presented below.

3.1 Measurement Completeness

This section describes the ranges of measurement completeness, first for H_2S and then for meteorological parameters.

3.1.1 H_2S

Measurement completeness for H_2S ranged from 67.08% at Site 1 Out – Low to 99.94% at Site 2 Out – Mid, with an overall program completeness of 87.58% (see Table 3-3). See Section 2.1.2 for definitions of terms used in this table. The program DQO of 80% data capture was exceeded for all monitoring locations throughout the EI, with the exception of H_2S measured at outdoor Site 1. At outdoor Site 1, over 30% of all H_2S measurements were invalidated due to a malfunctioning data logger during the first week of monitoring. The unit appeared to be working properly at all of the daily checks performed, so the problem was not identified until the first data download attempt. Once this problem was identified, the data logger was replaced and no other problems were encountered at outdoor Site 1 during the duration of the EI.

Table 3-3. H_2S Measurement Completeness

Site ID	*Total Possible Measurements*	*Valid Measurements*	*Invalid Measurements*	*Completeness (%)*
S1 Out – Low	31,447	21,096	10,351	67.08
S1 Out – Mid	31,447	21,110	10,337	67.13
S1 In – Low	31,446	31,176	270	99.14
S2 Out – Low	31,245	30,654	591	98.11
S2 Out – Mid	15,358	15,349	9	99.94
S2 In – Low	31,229	26,277	4,952	84.14
S3 Out – Low	21,189	21,103	86	99.59
S3 Out – Mid	15,865	15,847	18	99.89
Overall	209,216	183,234	25,982	87.58

3.1.2 Meteorological Parameters

The following meteorological parameters were measured at Site 1 during the EI:

- Temperature as degrees F
- Relative humidity as % RH
- Wind speed as meters per second
- Wind direction as degrees compass

Throughout the duration of the EI, no malfunctions occurred with any of the sensors used to monitor these parameters, and data were only lost during brief periods required to download the data (i.e., approximately 10 minutes each week). Specifically, there were 31,462 total possible measurements, with 31,447 valid and 15 invalid measurements. The overall completeness for meteorological parameters monitoring was 99.95%.

3.2 Measurement Precision

As part of the post-deployment QC checks, the H_2S SPM instruments were challenged with known concentrations of H_2S standard gas. During these challenges, eight instruments each completed 10 concentration determinations (labeled in Table 3-4 as “M-1” through “M-10”). An overall estimate of measurement precision, expressed as % relative standard deviation (RSD), was calculated using the average concentration from the 10 determinations made by the eight instruments considered; instrument-specific measurement precision was also quantified. As Table 3-4 shows, the post-deployment challenge revealed instrument-specific measurement precision ranging from 0.45% RSD to 2.63% RSD, with an overall method measurement precision of 1.70% RSD.

Table 3-4. H_2S Measurement Precision and Accuracy

Site ID	*Ref. Conc. (ppb)*	*M-1*	*M-2*	*M-3*	*M-4*	*M-5*	*M-6*	*M-7*	*M-8*	*M-9*	*M-10*	*M-Avg.*	*M-Std. Dev.*	*RSD (%)*	*Diff. (%)*
S1 Out – Low	83	85	86	83	82	85	87	84	83	85	83	84.3	1.57	1.86	1.57
S1 In – Low		84	86	88	87	88	85	84	83	83	82	85.0	2.16	2.54	2.41
S2 Out – Low		83	87	85	87	84	83	83	83	82	83	84.0	1.76	2.10	1.20
S2 In – Low		83	83	83	86	85	83	83	87	84	85	84.2	1.48	1.75	1.45
S3 Out – Low		87	82	87	82	86	83	83	87	85	82	84.4	2.22	2.63	1.69
S1 Out – Mid	1,304	1,321	1,316	1,301	1,307	1,308	1,303	1,310	1,319	1,303	1,305	1,309	7.07	0.54	0.41
S2 and S3 Out – Mid		1,317	1,317	1,307	1,308	1,303	1,304	1,309	1,302	1,301	1,303	1,307	5.84	0.45	0.24
Overall method average														1.70[A]	1.28[B]

[A] = calculated measured precision
[B] = calculated measured accuracy

3.3 Measurement Accuracy

As was done for measurement precision, post-deployment QC checks were conducted by challenging each of the H_2S SPM instruments with a known concentration of H_2S standard gas. During these challenges, each instrument completed ten concentration determinations (labeled in Table 3-4 as “M-1” through “M-10”). The average concentrations from the ten determinations were used to calculate instrument-specific and overall method-specific estimates of accuracy, expressed as the percent difference. As Table 3-4 shows, instrument specific measurement accuracy ranged from 0.24% to 2.41% for post-deployment QC checks, with an overall method accuracy difference of 1.28%.

3.4 Quality Control Activities

To assess performance of the H_2S SPM instruments in the field, sampling personnel performed optical performance checks. The optical performance checks were performed to ensure that the SPM instrument lamp and detector assembly was functioning within manufacturer specifications. In this optical check, a manufacturer-supplied test card was inserted into the optical path and the instrument response was recorded. When the lamp and detector assembly is performing properly, the instrument produces a response between 10 and 13 mA. Across the duration of the EI, four optical performance checks were performed on each H_2S SPM instrument. For these checks, responses ranged from 11.15 mA to 11.72 mA, indicating that every instrument performed within manufacturer specifications (see Table 3-5).

Table 3-5. Field Optical Performance Check Data

Site ID	***Instrument Response***							
	Date	***mA***	***Date***	***mA***	***Date***	***mA***	***Date***	***mA***
S1 Out – Low	07/09/08	11.27	07/16/08	11.41	07/22/08	11.46	08/04/08	11.33
S1 Out – Mid	07/09/08	11.33	07/16/08	11.53	07/22/08	11.72	08/04/08	11.66
S1 In – Low	07/09/08	11.35	07/16/08	11.42	07/22/08	11.22	08/04/08	11.31
S2 Out – Low	07/09/08	11.45	07/16/08	11.15	07/22/08	11.46	08/04/08	11.62
S2 and S3 Out – Mid†	07/09/08	11.47	07/16/08	11.54	07/22/08	11.52	08/04/08	11.58
S2 In – Low	07/09/08	11.53	07/16/08	11.53	07/22/08	11.23	08/04/08	11.33
S3 Out – Low*	07/09/08	NA	07/16/08	11.24	07/22/08	11.41	08/04/08	11.47

NA = not available
† S2 Out – Mid was moved to function as S3 Out – Mid on July 20, 2008.
*The SPM instrument at S3 Out – Low was not brought on line until after July 9, 2008.

4.0 Results

This section summarizes the final validated H_2S and meteorological measurements collected during the EI from July 9 to July 31, 2008. See Section 2.1.2 for definitions related to valid and invalid measurements. ATSDR compared the measurement results to health-based comparison values (CVs) (see text box)—screening values that enable ATSDR to identify contaminants requiring further evaluation. To be protective of public health, screening values are generally based on contaminant concentrations *many times lower than levels at which no effects were observed* in experimental animals or human epidemiologic studies. Therefore, exposure to concentrations detected above CVs will not necessarily cause adverse health effects. ATSDR further evaluates concentrations detected above CVs on a case-by-case basis to identify any potential public health implications. Specifically for the Excel Dairy EI, screening values for H_2S consisted of ATSDR's acute (i.e., contact with a substance that occurs once or for only a short time up to 14 days) and intermediate (i.e., contact with a substance that occurs for more than 14 days and less than a year) minimal risk levels (MRLs) and MPCA air quality standards. More details on these screening values are presented below. In a separate report (see Excel Dairy Public Health Consultation – Exposure Investigation), ATSDR and MDH evaluated the public health significance of the concentrations measured during this EI and data collected by MPCA.

ATSDR defines a comparison value (CV) as a calculated concentration of a substance in air, water, food, or soil that is unlikely to cause harmful (adverse) health effects in exposed people. The CV is used as a screening level during the public health assessment process. Substances found in amounts greater than their CVs might be selected for further evaluation in the public health assessment process.

4.1 Hydrogen Sulfide

This section includes three subsections describing the results of the EI. Section 4.1.1 presents the overall findings of the H_2S measurements, including low, high, and average measurements, and compares these measurements to ATSDR's MRLs and MPCA's air quality standards for H_2S. Discussed in Section 4.1.2 are instances where elevated readings occurred over an extended period of time (e.g., greater than 30–60 minutes). The final subsection, 4.1.3, discusses patterns observed between H_2S concentrations and different times of the day.

4.1.1 Overall Findings

H_2S measurements for each monitoring location are summarized in Table 4-1. Specifically, each station's program-average concentration, the lowest 1-minute instantaneous concentration, and the highest concentrations for 1-minute instantaneous measurements and 30-minute averaging periods are presented. The 1-minute instantaneous measurements are used to readily identify excursions of elevated concentration measurements and to allow representative 30-minute averages to be calculated. However, individual 1-minute instantaneous measurements should not be used to make public health k determinations. The 30-minute averages are more representative of exposure and are accordingly used to generate estimates that could be applied to assess short-term exposures and to enable comparisons to ATSDR's acute MRL and MPCA's air quality standards—all of which are based on H_2S exposures for 30-minute periods (for more information, refer to Section 2.2.1). All averages presented in Table 4-1 are based on continuous 1-minute instantaneous measurements data downloaded from location-specific instrumentation. As noted previously, all of the indoor measurements data for Sites 1 and 2 were made with an SPM using a measurement range of 0–90 ppb. All of the outdoor measurements data for Sites 1, 2, and 3 were made using two SPMs at each site, one with a measurement range of 0–90 ppb and the other with a measurement range of 76–1,500 ppb. For the purposes of data analysis, these measurements were combined to provide an overall measurement range of 0–1,500 ppb at each outdoor monitoring site.

Table 4-1. Summary of Ambient Air Monitoring of H_2S

Site ID	*Number of Valid 1-Minute Measurements*	*Lowest 1-Minute Concentration (ppb)*	*Highest 1-Minute Concentration (ppb)*	*Highest 30-Minute Average (ppb)*	*Program-Average (ppb)*	*Standard Deviation for Program-Average (ppb)*
S1 Out	21,096	0.12	481.24	214.72	5.32	24.47
S1 In	31,176	0.00	75.79	60.98	3.31	6.54
S2 Out	30,654	0.01	169.85	54.42	1.67	2.86
S2 In	26,277	0.18	18.23	14.18	1.62	1.47
S3 Out	21,103	0.04	253.79	188.88	6.68	22.20

See Table 2-2 for the dates monitoring occurred at each site.
Program-average and highest 30-minute average concentrations were calculated from continuous 1-minute instantaneous measurements.

As shown in Table 4-1, H_2S concentrations varied across the air monitoring locations and also varied with averaging time. The highest program-average outdoor H_2S concentrations were observed at Sites 1 (5.32 ppb) and 3 (6.68 ppb), with the lowest outdoor level at Site 2 (1.67 ppb). The two indoor monitoring locations—Site 1 and Site 2—detected H_2S often, with program-average concentrations of 3.31 ppb and 1.62 ppb, respectively.

As also presented in Table 4-1, the highest 30-minute average H_2S concentrations ranged from 14.18 ppb at indoor Site 2 to 214.72 ppb at outdoor Site 1. In addition, the highest 30-minute average concentrations at all sites except indoor Site 2 exceeded ATSDR's intermediate MRL of 20 ppb and outdoor Sites 1 and 3 exceeded the acute MRL of 70 ppb. Presented in Table 4-2 are the number of times that 30-minute average concentrations at each monitoring site exceeded ATSDR's acute and intermediate MRLs for H_2S during the EI.

Table 4-2. Number of Times that 30-Minute Average H_2S Concentrations Exceeded ATSDR's MRLs at Each Monitoring Station During the Excel Dairy EI

Site ID	*ATSDR Intermediate MRL of 20 ppb*	*ATSDR Acute MRL of 70 ppb*
S1 Out	30	15
S1 In	37	0
S2 Out	2	0
S2 In	0	0
S3 Out	55	16

ATSDR defines acute as contact with a substance that occurs once or for only a short time (up to 14 days), and intermediate as contact with a substance that occurs for more than 14 days and less than a year.

In addition to comparing the H_2S concentrations measured during the EI to ATSDR's MRLs, comparisons with the MPCA air quality standards for the state of Minnesota are also presented. These state standards are written such that H_2S concentrations should not exceed 30 ppb during more than two 30-minute periods in 5 days or 50 ppb in two 30-minute periods during any given year. The date and number of times that 30-minute average concentrations exceeded 30 ppb and 50 ppb at each monitoring site during the EI are presented in Table 4-3. As shown in the table, both of the state air quality standards for H_2S were exceeded during the EI at all monitoring sites except indoor Site 2 (i.e., where no concentrations exceeded 30 ppb) and outdoor Site 2 (i.e., where 30 ppb and 50 ppb were only exceeded once during the time period, not twice as the air quality standard specifies). Note that this table only presents dates when 30-minute average concentrations exceeded 30 ppb; it does not include dates when all 30-minute average concentrations were ≤ 30 ppb.

Table 4-3. Number of 30-Minute Average Concentrations above 30 ppb and 50 ppb by EI Monitoring Location and Date

Site ID	*Date*	*Number of 30-Minute Average Concentrations above 30 ppb*	*Number of 30-Minute Average Concentrations above 50 ppb*
S1 Out	07/19/08	5	4
	07/21/08	6	4
	07/22/08	8	7
	07/27/08	4	1
	07/30/08	1	1
S1 In	07/16/08	3	0
	07/19/08	2	0
	07/21/08	4	1
	07/22/08	9	1
S2 Out	07/19/08	1	1
S3 Out	07/19/08	2	2
	07/20/08	2	1
	07/21/08	2	1
	07/22/08	4	0
	07/23/08	12	11
	07/28/08	13	10
	07/30/08	1	1
	07/31/08	1	0

MPCA's state standards specify that H_2S concentrations should not exceed 30 ppb during more than two 30-minute periods in 5 days or 50 ppb in two 30-minute periods during any given year.

For added perspective, Table 4-4 is a summary of how often 1-minute instantaneous measurements of H_2S were observed between three different concentration ranges: 1) below ATSDR's intermediate MRL of 20 ppb, 2) above the intermediate MRL of 20 ppb and below or equal to the acute MRL of 70 ppb, and 3) above the acute MRL of 70 ppb. As shown in Table 4-4, the percent of time that 1-minute H_2S concentrations exceeded ATSDR's MRLs varied by monitoring location. Overall, more than 90% of the 1-minute measurements at all of the sites were below ATSDR's MRL of 20 ppb. Outdoor Site 3 had the most 1-minute measurements detected in the range of >20 ppb and ≤70 ppb (5.33%), followed by indoor Site 1 (3.49%) and outdoor Site 1 (1.76%). Less than 0.5% of all 1-minute measurements exceeded ATSDR's acute MRL of 70 ppb at indoor Site 1, indoor Site 2, and outdoor Site 2. Outdoor Site 3 had the highest percentage of 1-minute measurements above 70 ppb (2.28%), followed by outdoor Site 1 (1.89%).

Table 4-4. Concentration Ranges of 1-Minute Average Measurements by EI Monitoring Location

Site ID	***Number of Minutes (and Percent of Time) that 1-Minute Average H_2S Measurements Fell in Different Concentration Ranges***		
	≤20 ppb	***>20 ppb and ≤70 ppb***	***>70 ppb***
S1 Out	20,327 (96.35%)	371 (1.76%)	398 (1.89%)
S1 In	30,074 (96.47%)	1,087 (3.49%)	15 (0.05%)
S2 Out	30,575 (99.74%)	75 (0.24%)	4 (0.01%)
S2 In	26,277 (100%)	0 (0%)	0 (0%)
S3 Out	19,498 (92.39%)	1,124 (5.33%)	481 (2.28%)

Notes:

- This table presents the number of 1-minute measurements that exceeded comparison values during any 1-minute period throughout the entire EI investigation. The table indicates the total number of individual measurements that were measured above comparison values during single minute intervals—it does not indicate any consecutive time periods that exceedences occurred. Thus, the individual 1-minute measurements data presented here cannot be combined to derive an estimated continuous period of exposure.
- As described in this field report, use of 30-minute averaging periods is most appropriate for comparison with available comparison values. Although 30-minute averaging is more appropriate given the instrument functional output, 1-minute readings are presented here for additional perspective only.
- ATSDR defines acute as contact with a substance that occurs once or for only a short time (up to 14 days), and intermediate as contact with a substance that occurs for more than 14 days and less than a year.
- MPCA's state standards specify that H_2S concentrations should not exceed 30 ppb during more than two 30-minute periods in 5 days or 50 ppb in two 30-minute periods during any given year.
- Numbers in parentheses indicate the percentage of 1-minute measurements that exceeded the specific comparison value (i.e., 20, 30, 50, or 70 ppb).

4.1.2 Excursions

To identify "excursions," H_2S concentrations observed during the EI were analyzed to identify instances where two consecutive 30-minute averages exceeded 20 ppb (i.e., ATSDR's intermediate MRL) at each indoor and outdoor monitoring site. All excursions identified at indoor or outdoor sites were plotted graphically, and are presented in Figures 4-1 to 4-14. Note that Site 2 is not included in any of these graphs: no concentrations detected at indoor Site 2 exceeded 20 ppb and the two 30-minute average concentrations that exceeded 20 ppb at outdoor Site 2 (21.27 ppb and 54.42 ppb) did not occur in consecutive 30-minute time periods. When excursions occurred at a site with an indoor and outdoor monitoring location (i.e., Site 1), concentrations for both sites were plotted. For example, if an excursion was identified at outdoor Site 1 but not at indoor Site 1 during a specified time period, both the indoor and outdoor concentrations were plotted for that period. The concentration data in all 14 figures are shown on consistent scales to facilitate visual comparisons across the EI monitoring sites. The plotted concentrations in the figures are compared to ATSDR's intermediate (20 ppb) and acute MRL (70 ppb) as well as MPCA's 30-minute air quality standard values of 30 ppb and 50 ppb. The results are summarized below by EI monitoring site.

Site 1

- Excursions occurred at indoor and outdoor Site 1 on July 19, 21, 22, and 27, and at indoor Site 1 on July 16 and 28.
- Figures 4-2 to 4-6 show excursions at outdoor Site 1 corresponded with increased concentrations at indoor Site 1.
- With the exception of Figure 4-5 that shows an excursion at outdoor Site 1 from 7:00 to 8:00 a.m., the excursion graphs (see Figures 4-1 to 4-4 and 4-6) demonstrate that measured H_2S concentrations were considerably lower during the daylight hours when compared to those measured after sundown and before sunrise.

Site 3

- Excursions occurred more often at outdoor Site 3 than Site 1, with H_2S concentrations exceeding 20 ppb during two or more 30-minute consecutive periods on nine days: July 19, 20, 21, 22, 23, 28, 29, 30, and 31.
- With the exception of Figure 4-11, which displays an excursion from 6:00 to 8:00 a.m., and Figure 4-13, which displays elevated readings from 10:30 to 11:30 a.m., the graphs (see Figures 4-7 to 4-12 and 4-14) demonstrate that measured H_2S concentrations were considerably higher after sundown and before sunrise than during the daylight hours.

4.1.3 Diurnal Variations

For insights into diurnal variations in H_2S concentrations, the minute-level observations were pooled into 48 separate data sets, each set corresponding to measurements made during a different 30-minute period of the day. Average concentrations were then calculated for each 30-minute period and plotted for each site and measurement device (see Figures 4-15 through 4-19). The concentration data in the three figures are shown on consistent scales to facilitate visual comparisons across the EI monitoring sites. See Table 2-2 for the schedule of monitoring at each site. With the exception of outdoor and indoor Site 2, in general, measured ambient air concentrations of H_2S were considerably lower during the daylight hours when compared to those measured after sundown and before sunrise. Various mechanisms may contribute to the observed diurnal variations. Winds during the day disburse gases throughout the air, which results in lower ambient H_2S concentrations. During nighttime and early morning hours, however, winds are typically calmer, which usually results in less efficient dilution and dispersion of the H_2S gas and in ambient concentrations that are higher than during daytime hours. In addition, increased dispersion occurs as mixing heights rise during the day. Further, photochemical reactions occur during the day that break down H_2S.

Figure 4-1. 30-Minute Average H_2S Concentration at Site 1 on July 16, 2008

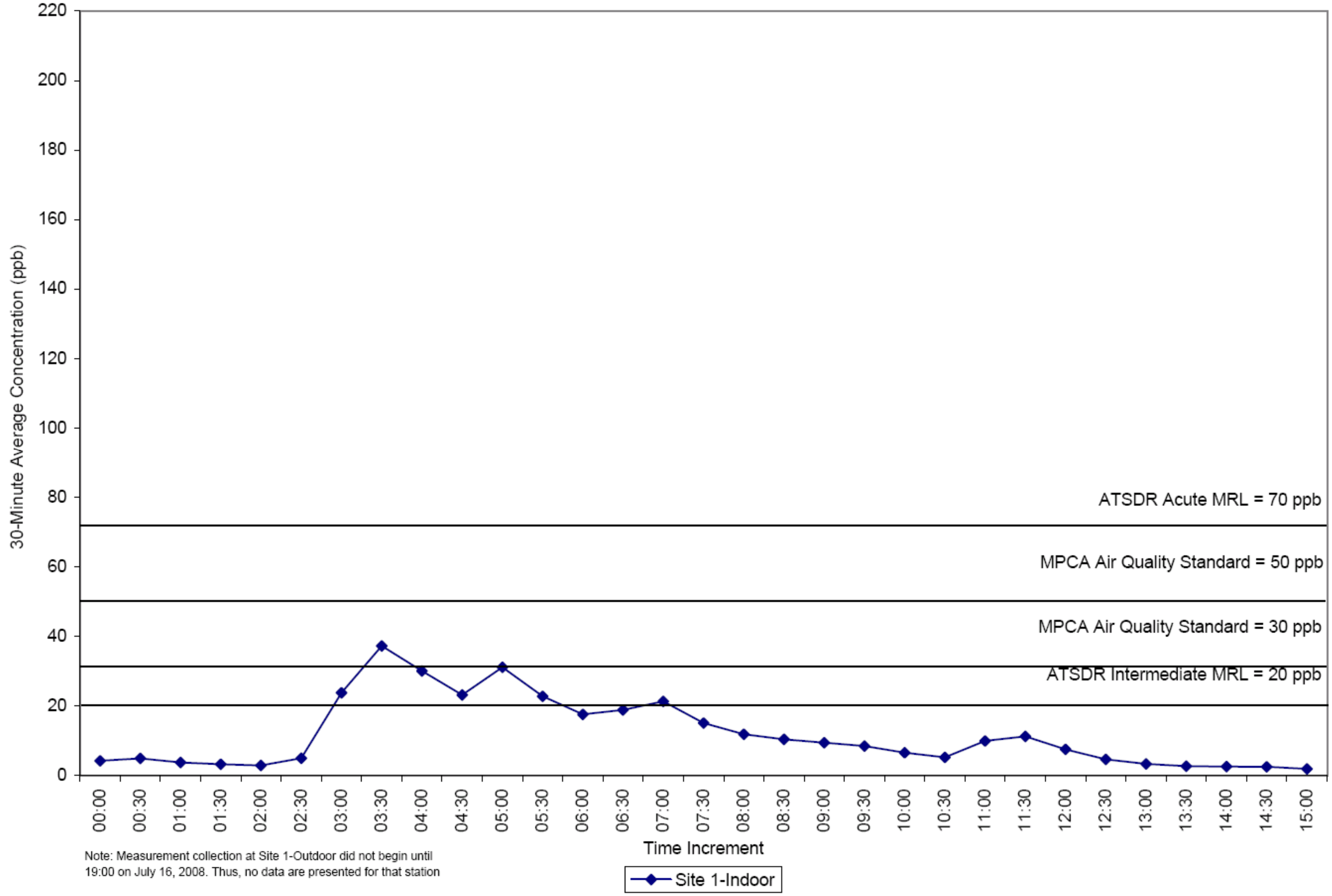


Figure 4-2. 30-Minute Average H_2S Concentration at Site 1 on July 18–19, 2008

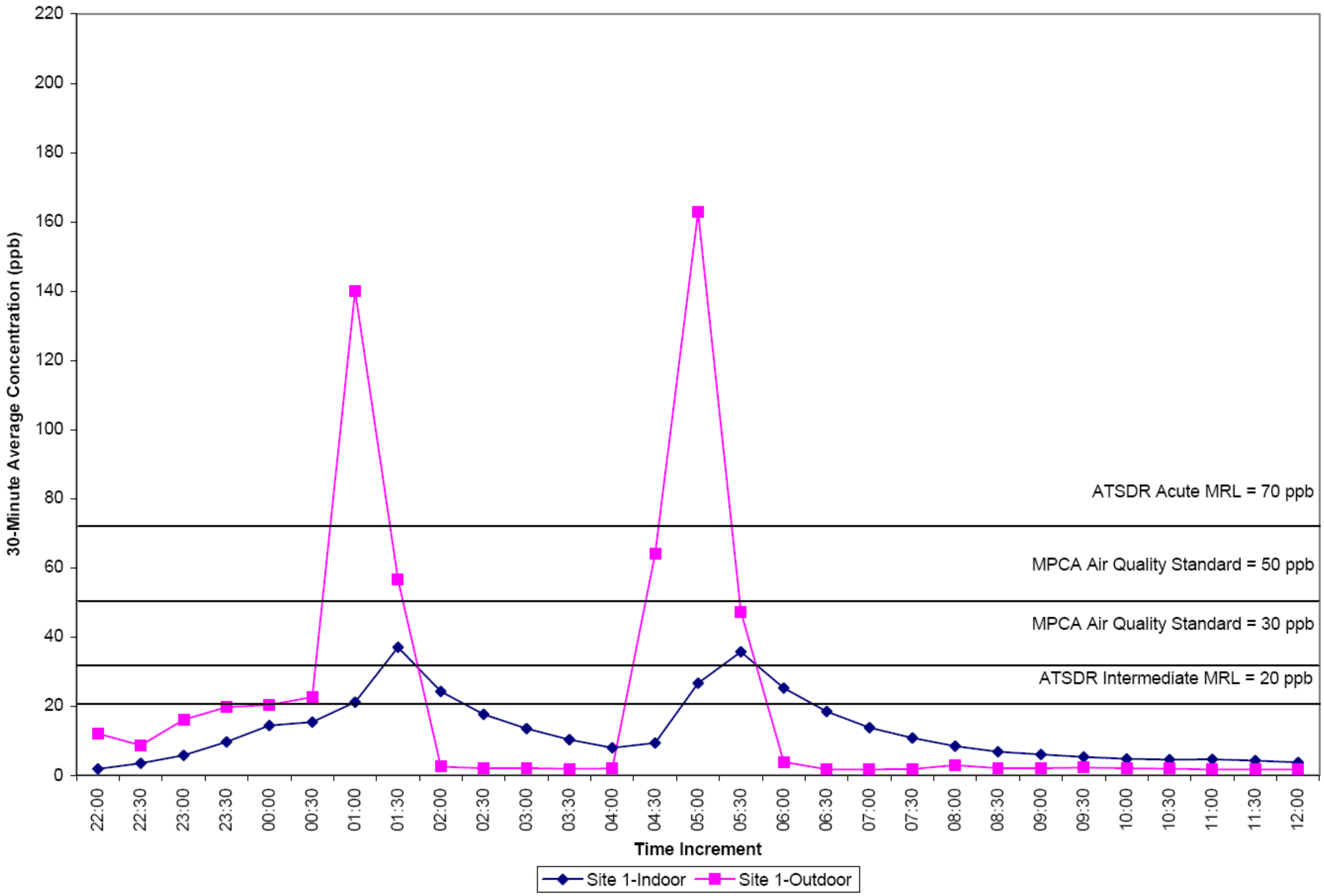


Figure 4-3. 30-Minute Average H_2S Concentration at Site 1 on July 20–21, 2008

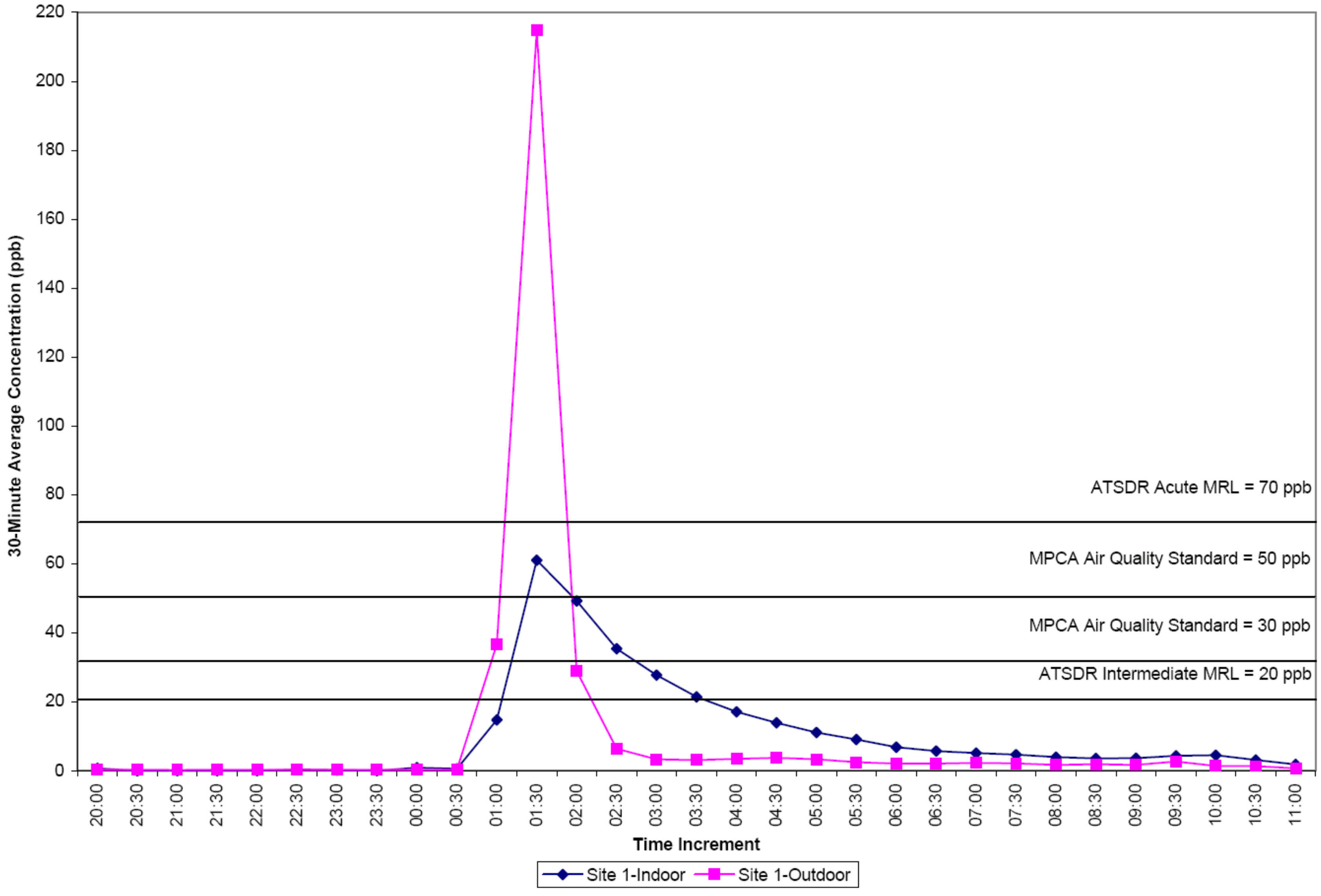


Figure 4-4. 30-Minute Average H_2S Concentration at Site 1 on July 21–22, 2008

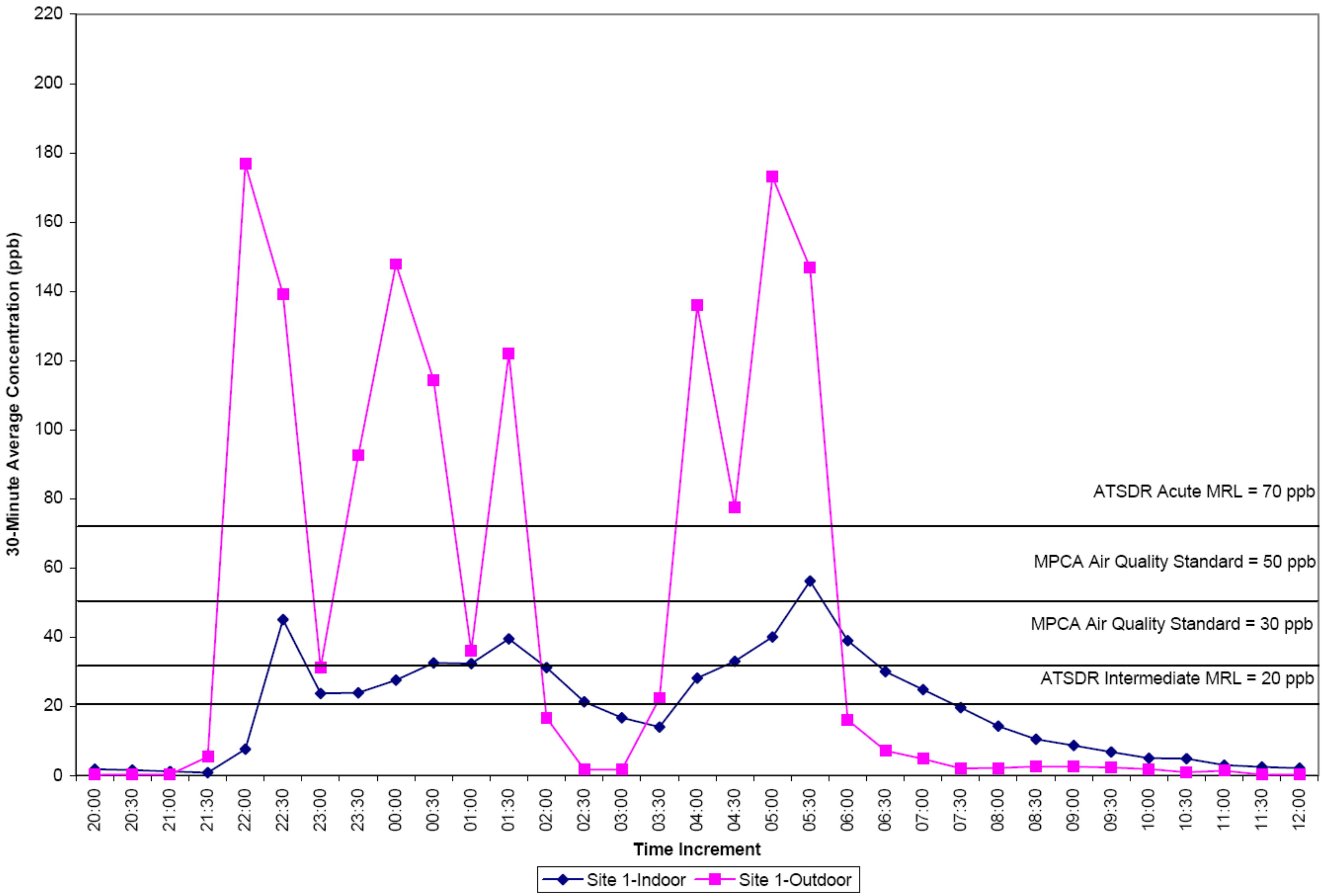


Figure 4-5. 30-Minute Average H_2S Concentration at Site 1 on July 27, 2008

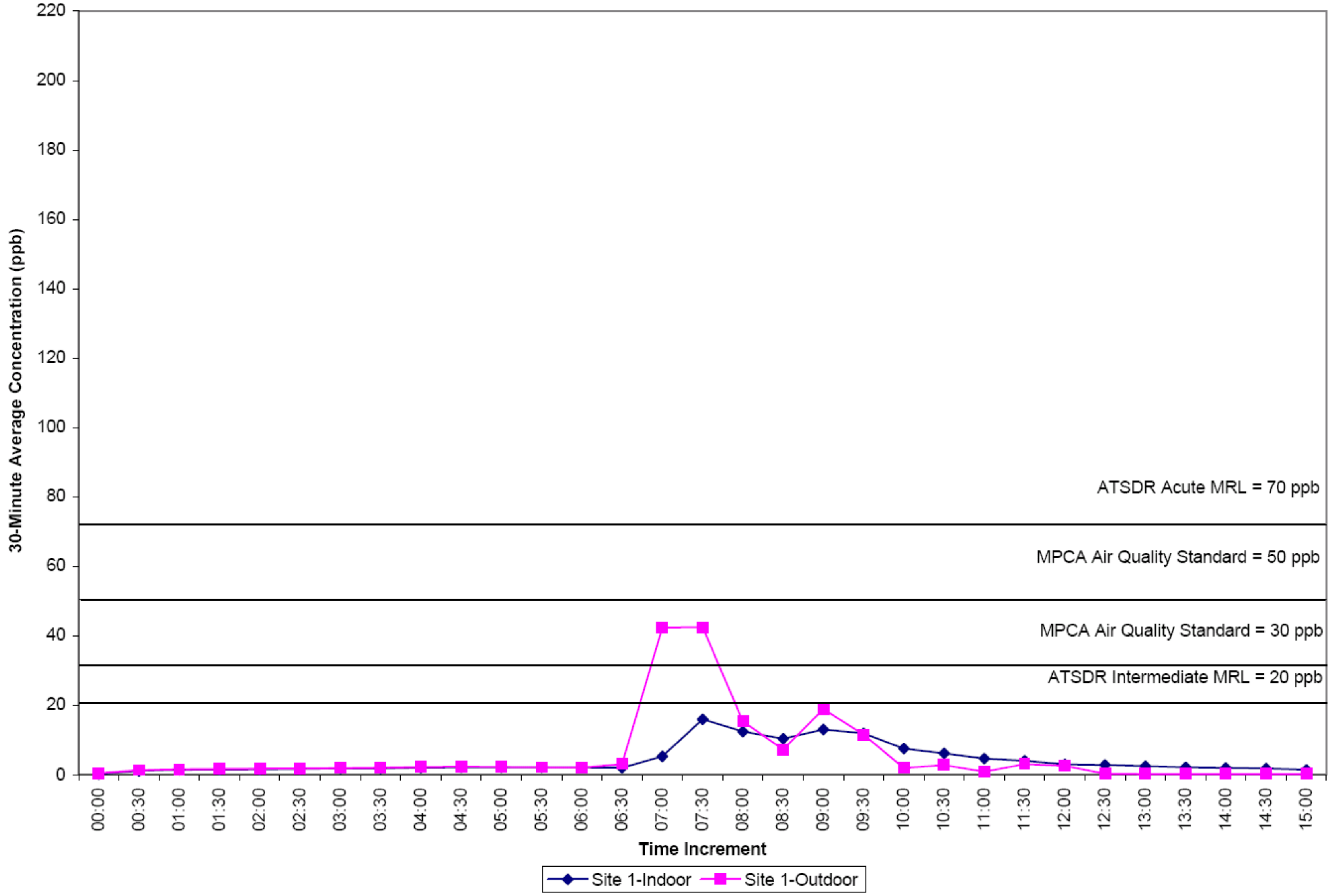


Figure 4-6. 30-Minute Average H_2S Concentration at Site 1 on July 27–28, 2008

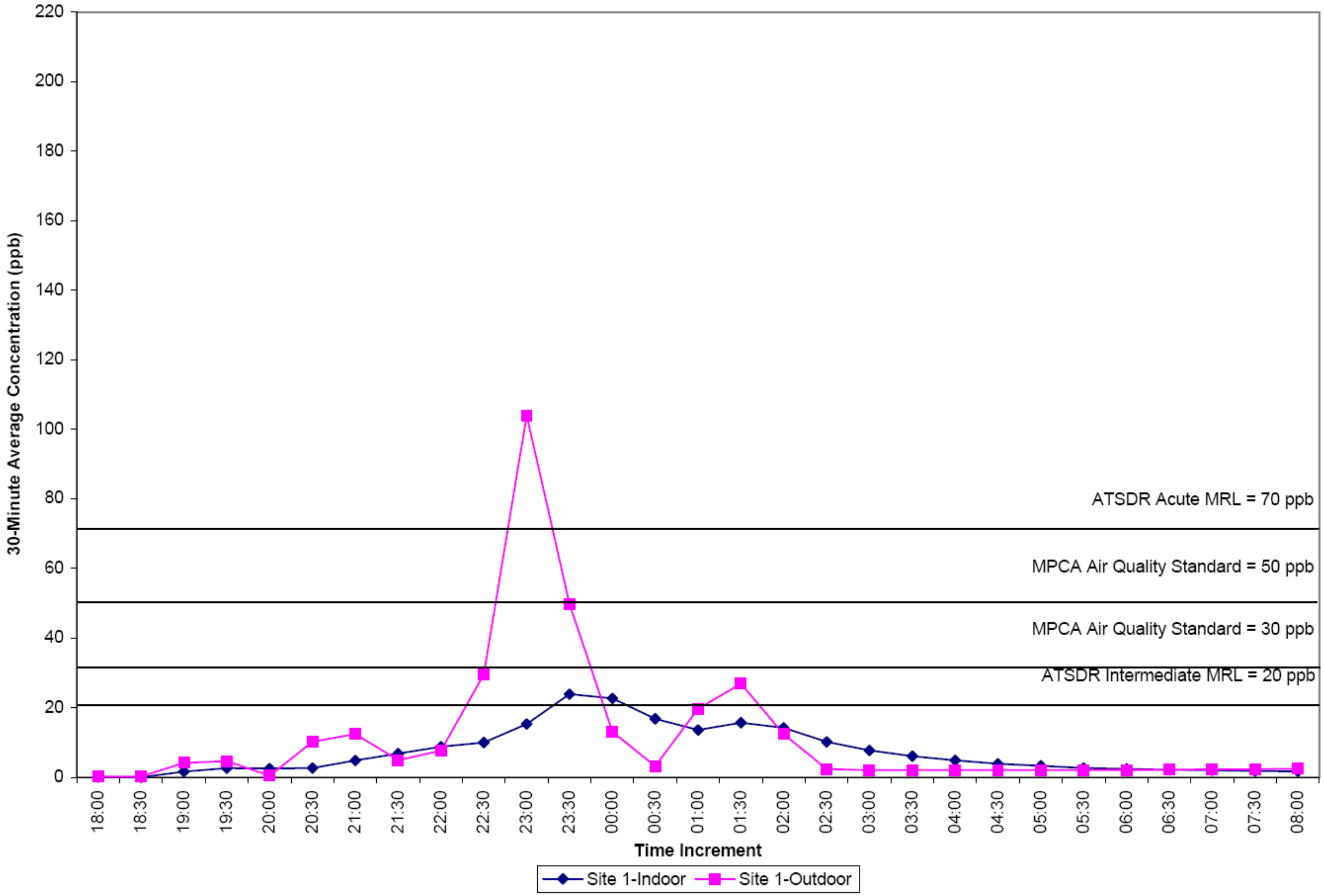


Figure 4-7. 30-Minute Average H_2S Concentration at Site 3 on July 18–19, 2008

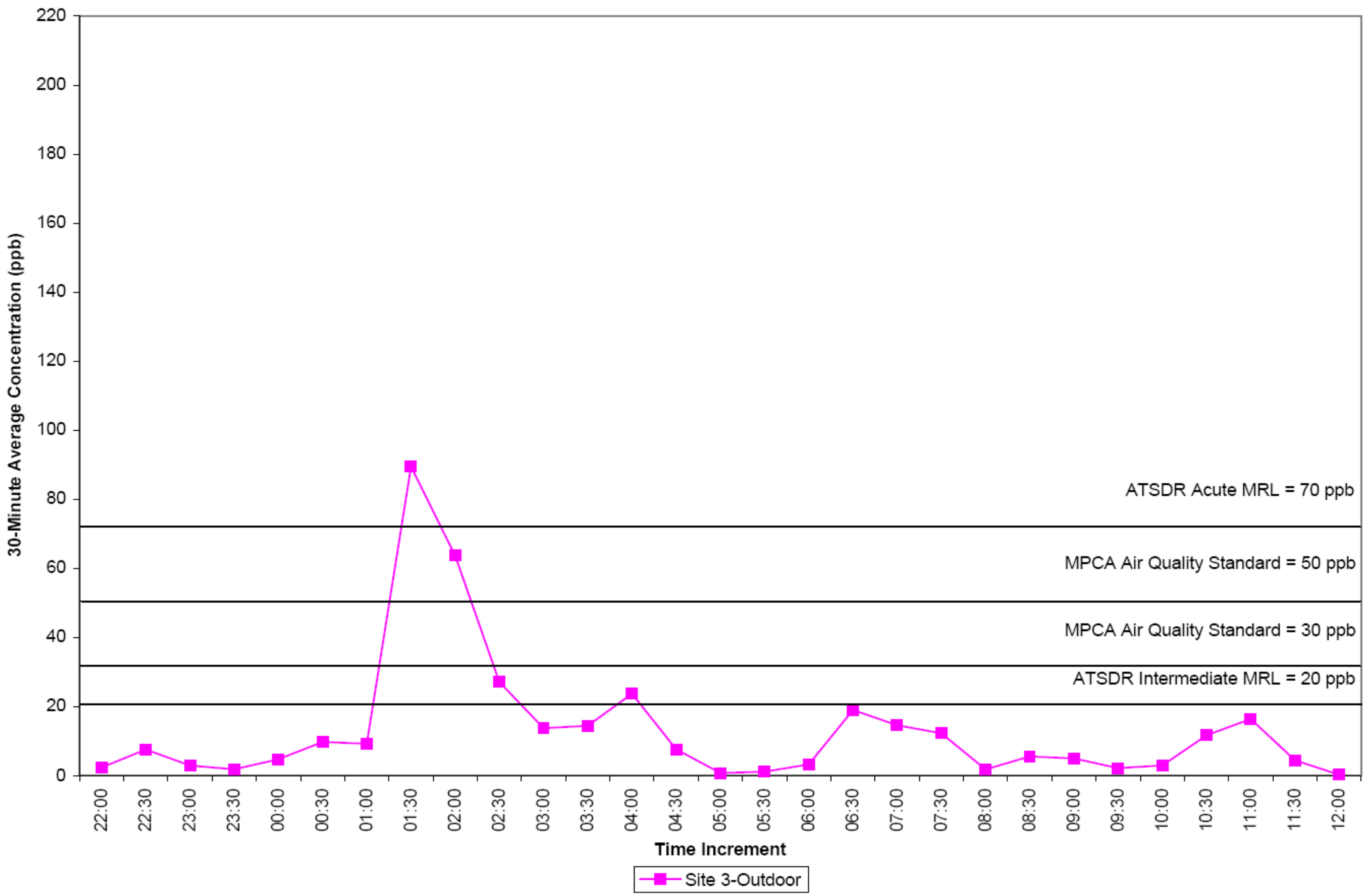


Figure 4-8. 30-Minute Average H_2S Concentration at Site 3 on July 19–20, 2008

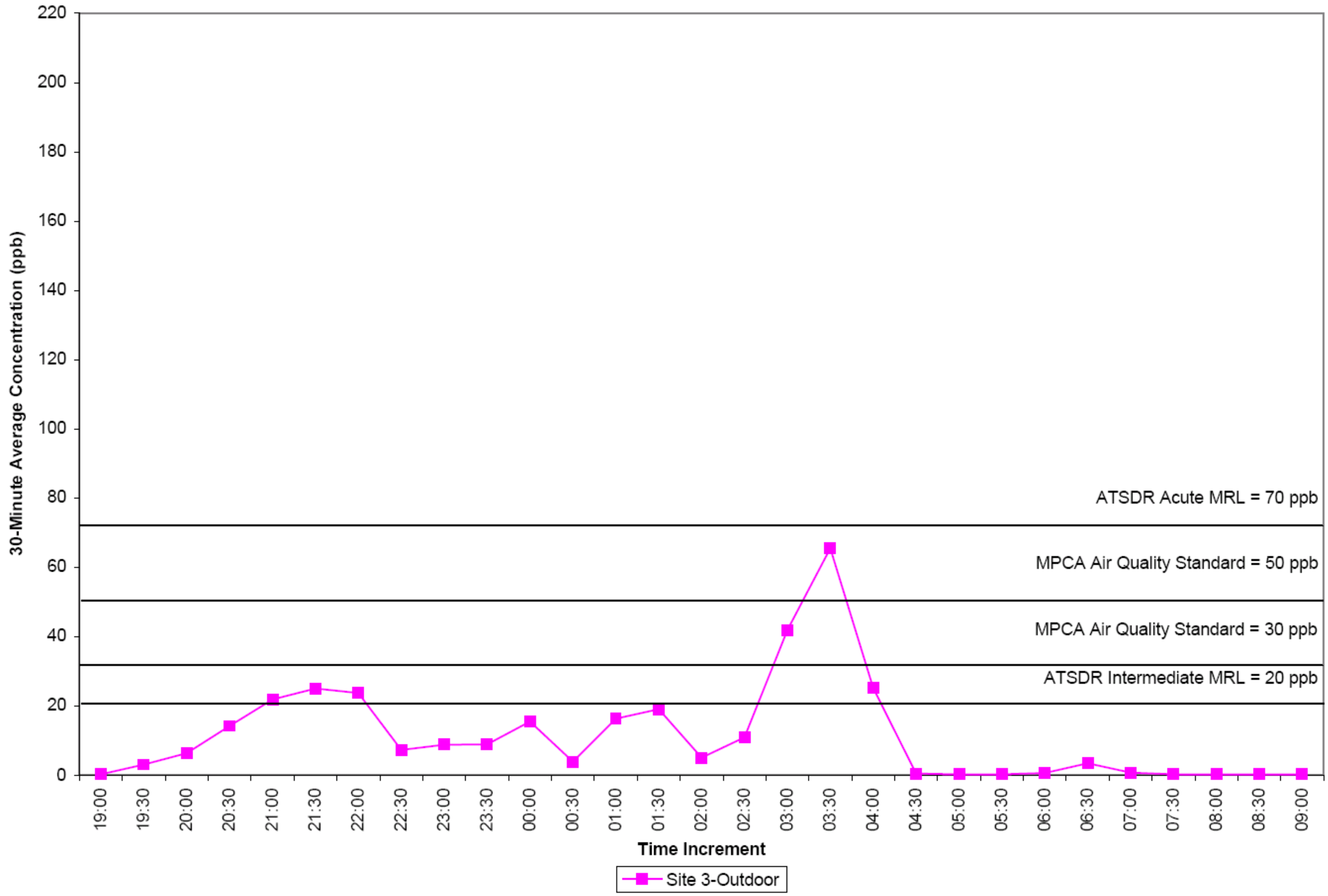


Figure 4-9. 30-Minute Average H_2S Concentration at Site 3 on July 20–21, 2008

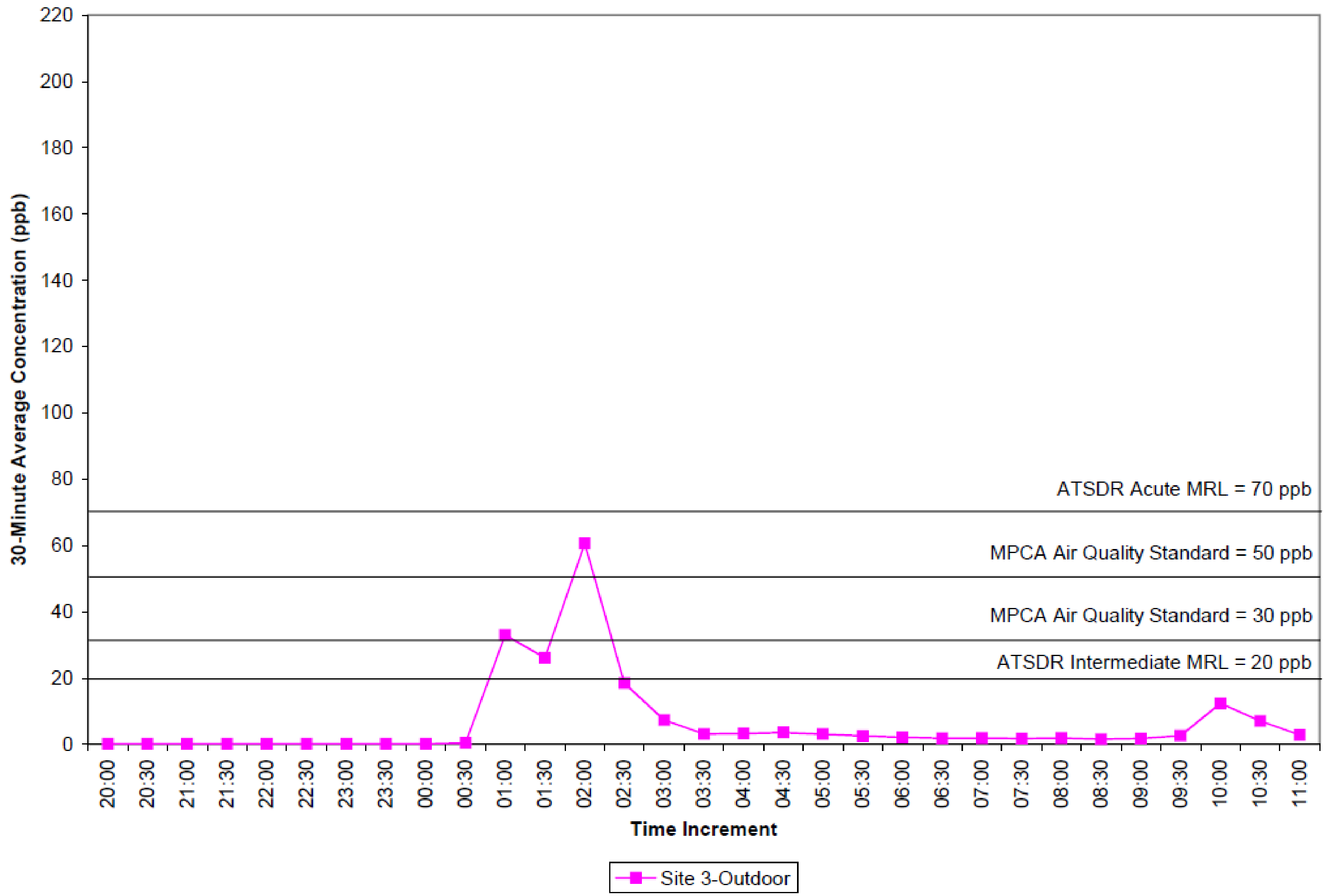


Figure 4-10. 30-Minute Average H_2S Concentration at Site 3 on July 22–23, 2008

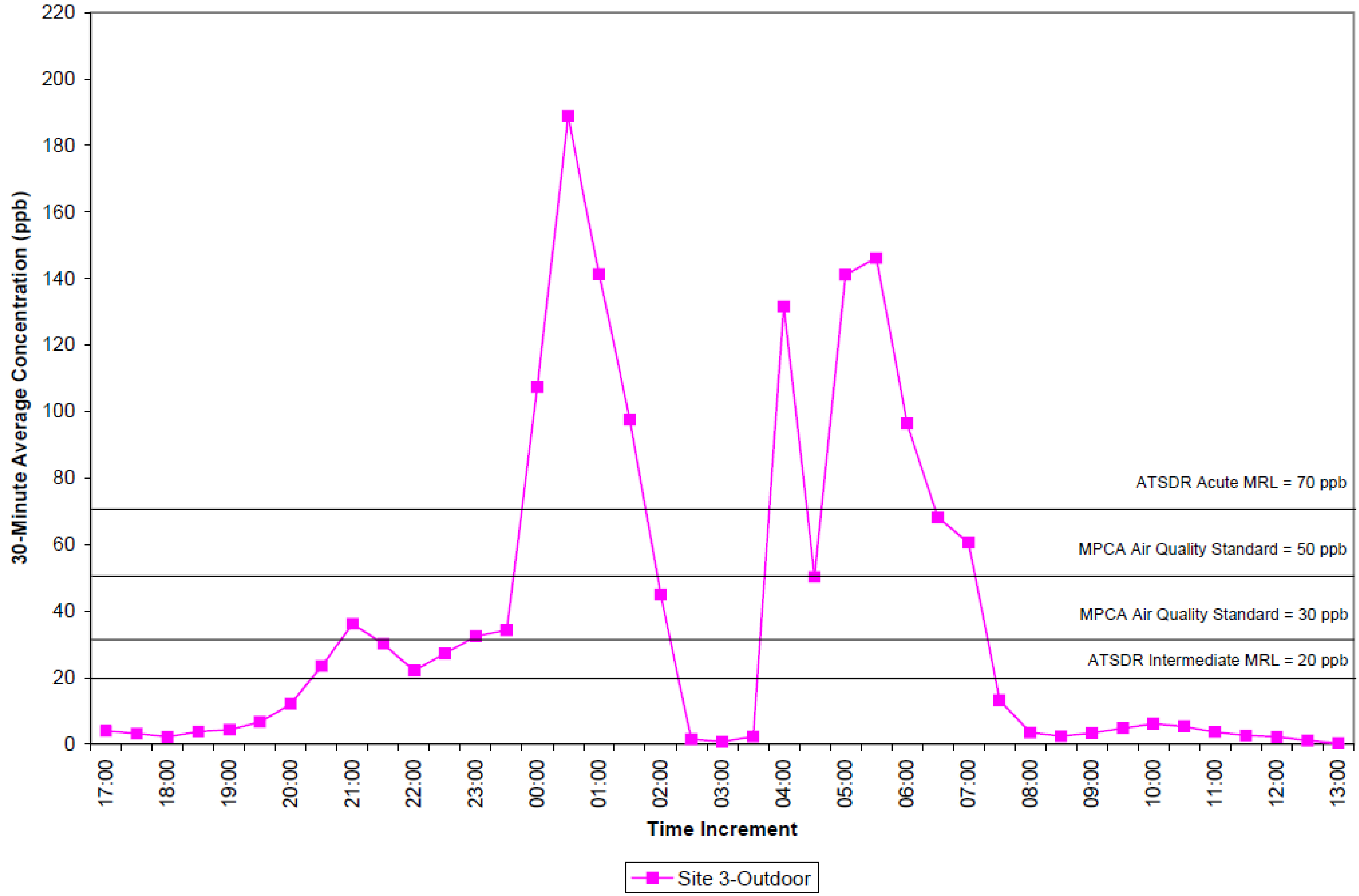


Figure 4-11. 30-Minute Average H_2S Concentration at Site 3 on July 28, 2008

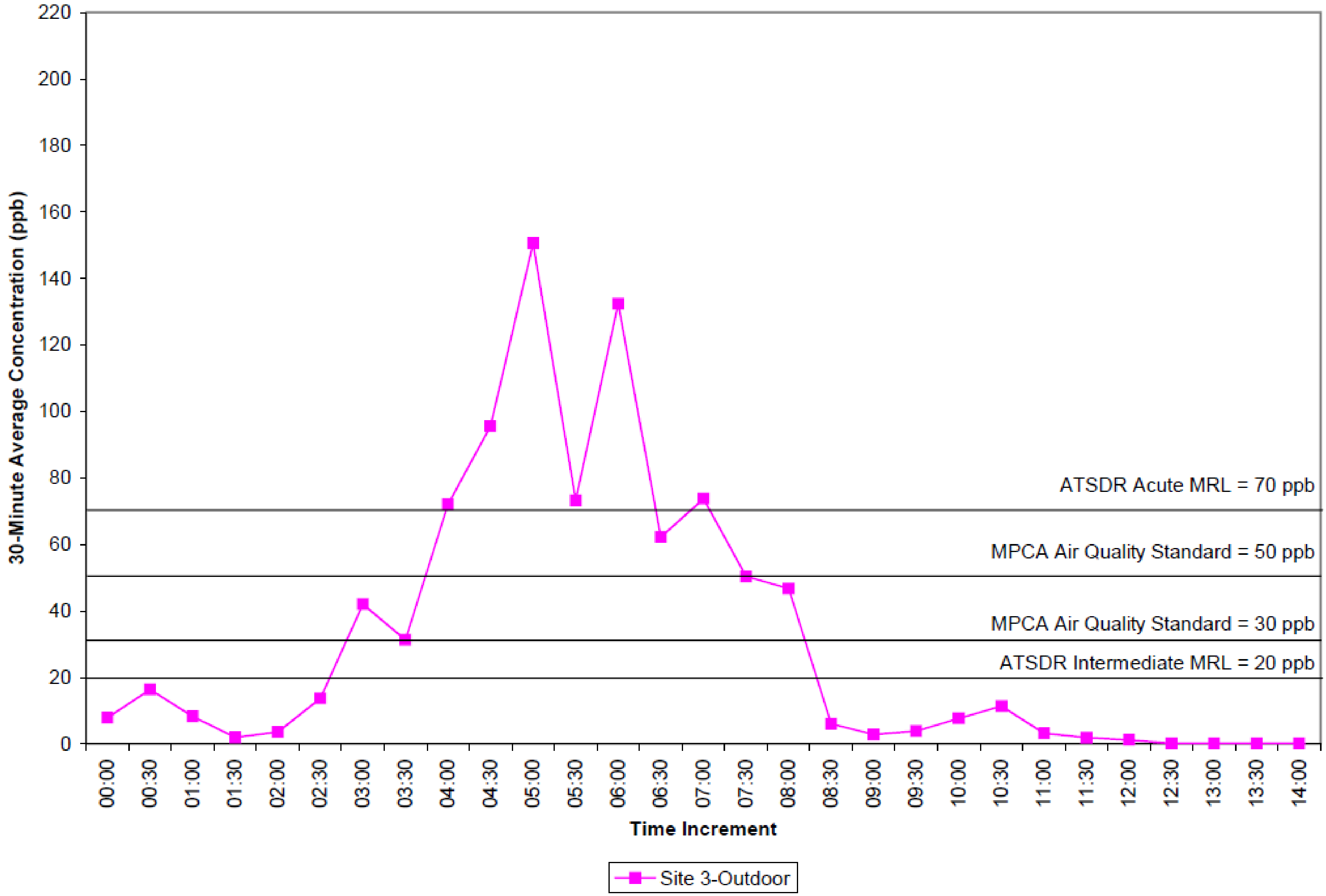


Figure 4-12. 30-Minute Average H_2S Concentration at Site 3 on July 28–29, 2008

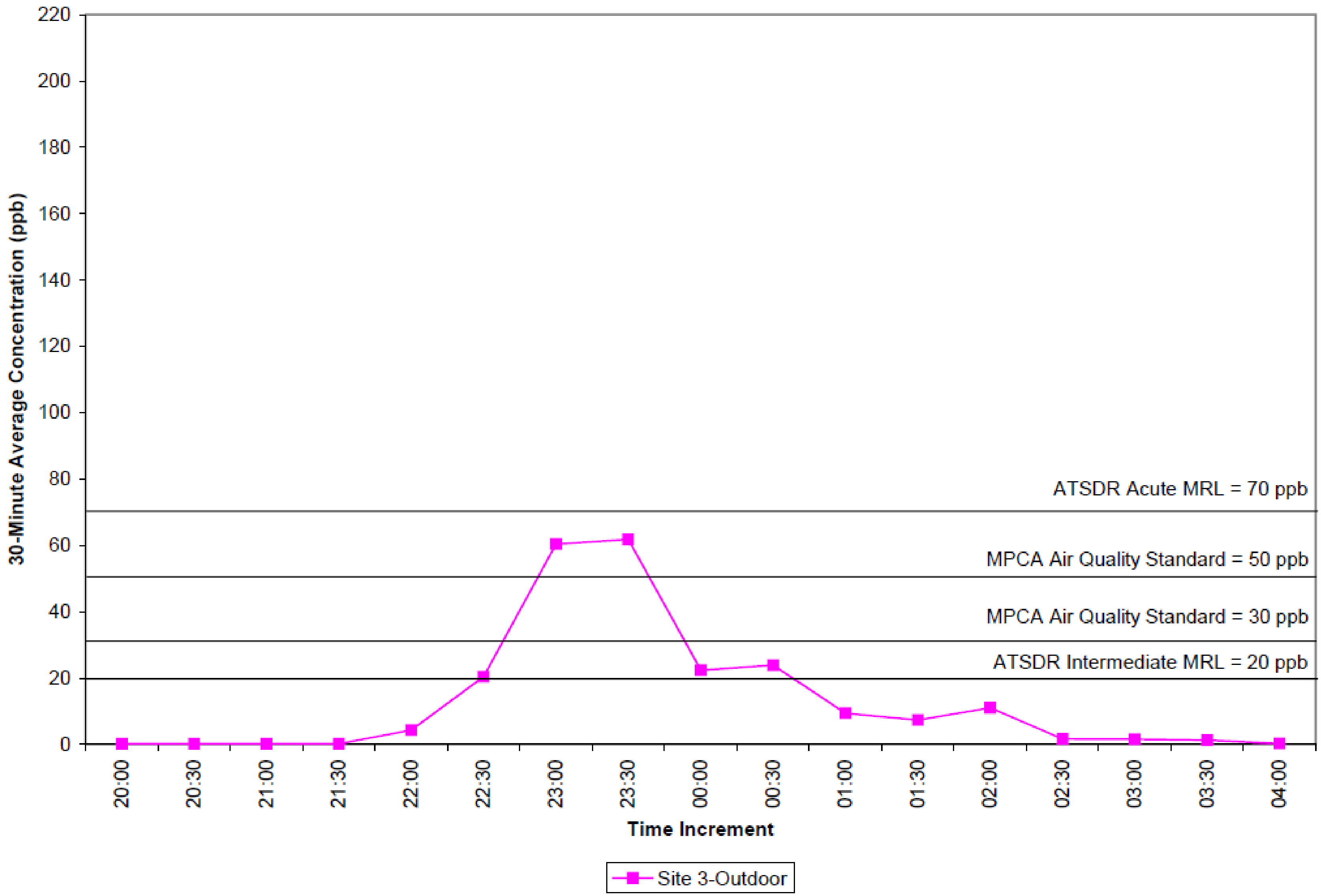


Figure 4-13. 30-Minute Average H_2S Concentration at Site 3 on July 30, 2008

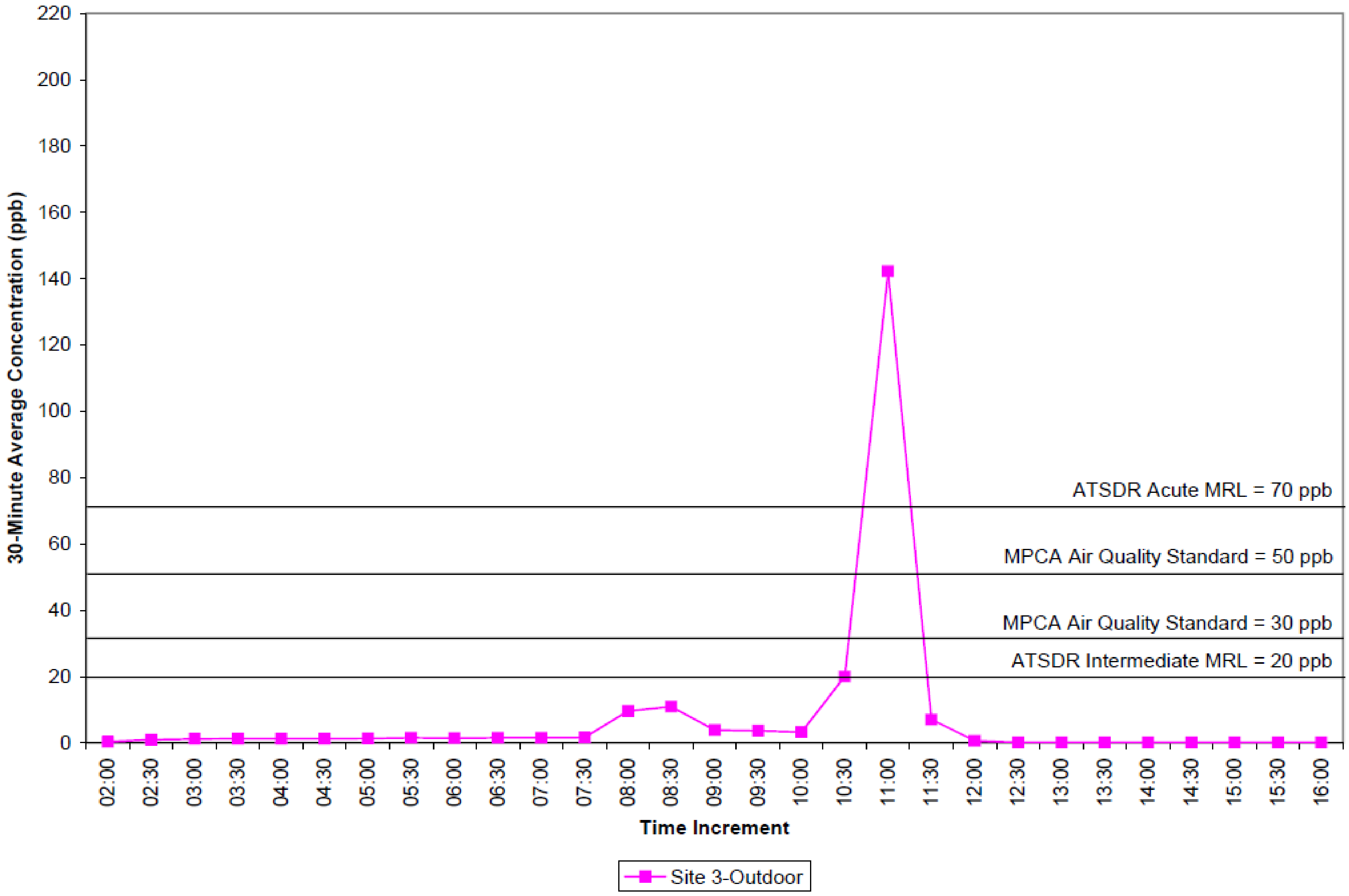


Figure 4-14. 30-Minute Average H_2S Concentration at Site 3 on July 31, 2008

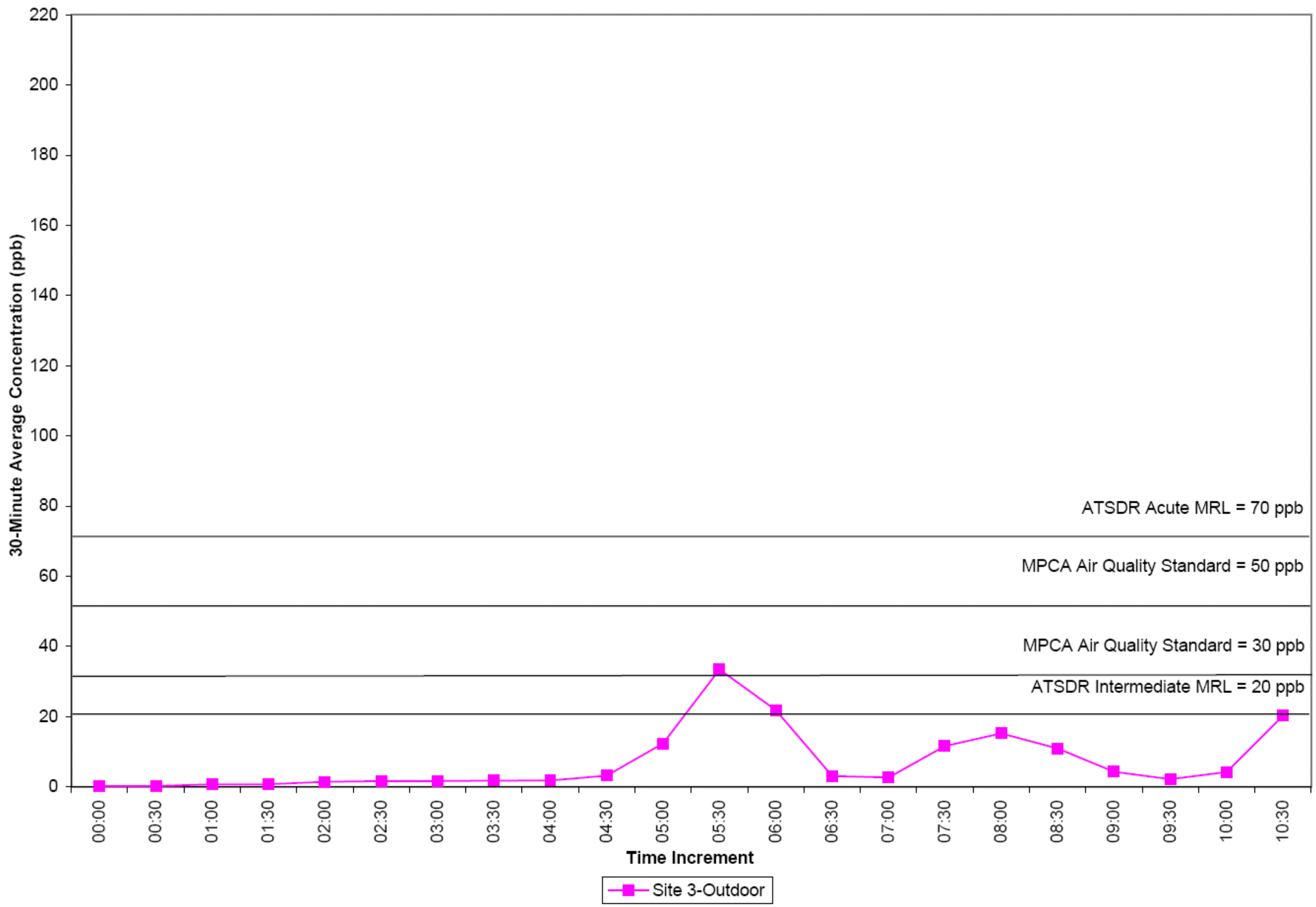


Figure 4-15. 30-Minute Average H_2S Concentrations at Site 1 Outdoor

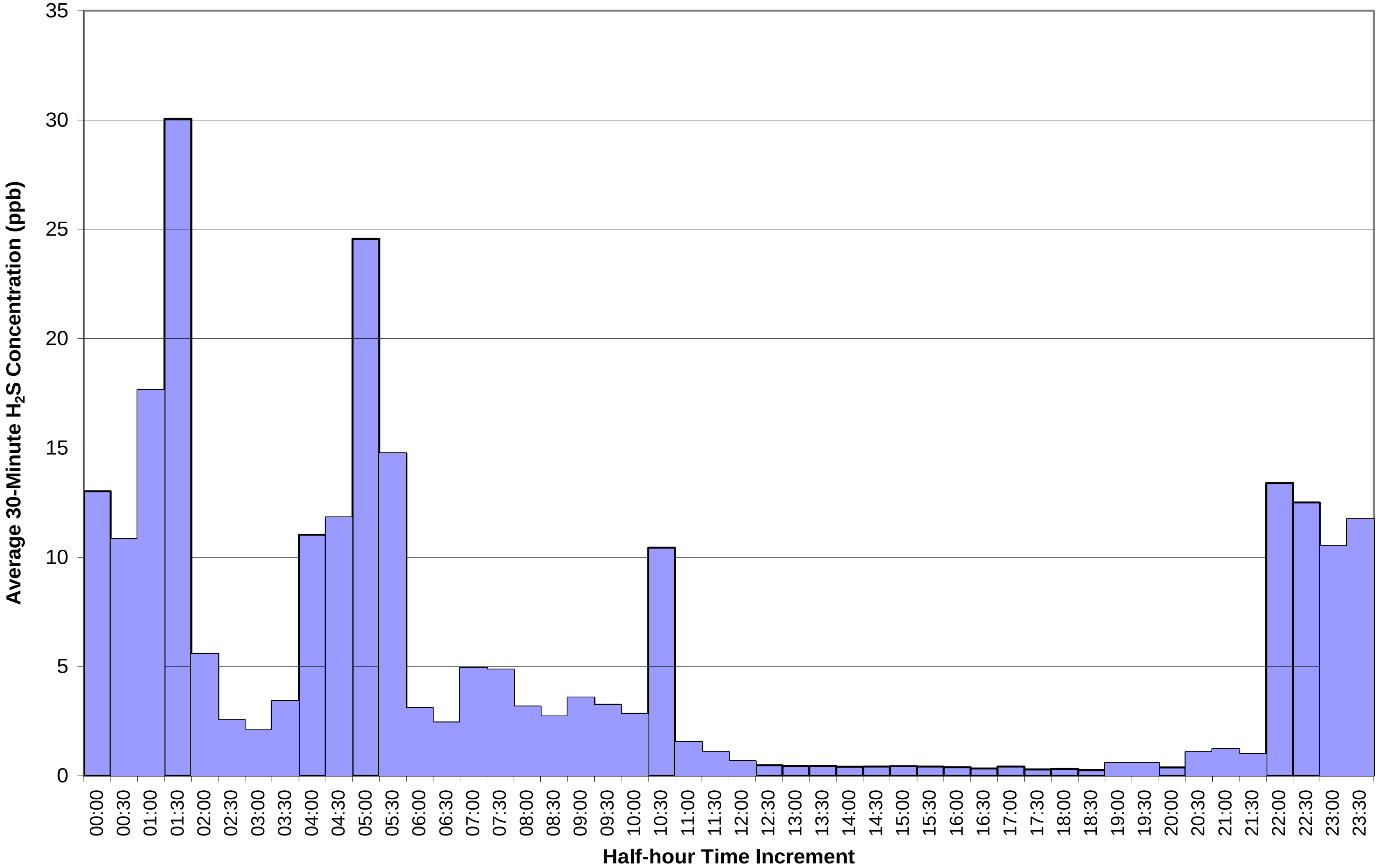


Figure 4-16. 30-Minute Average H_2S Concentrations at Site 1 Indoor

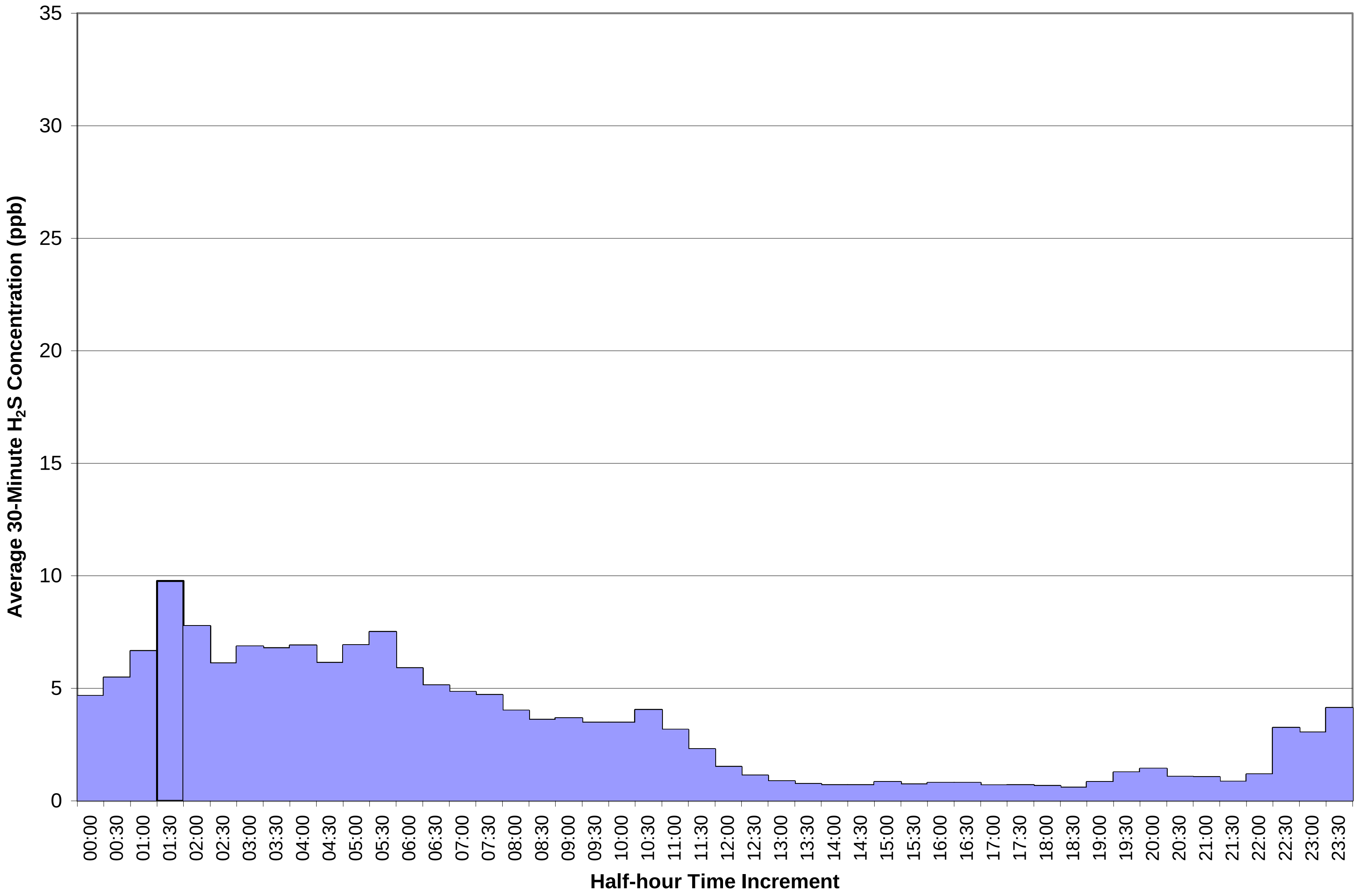


Figure 4-17. 30-Minute Average H_2S Concentrations at Site 2 Outdoor

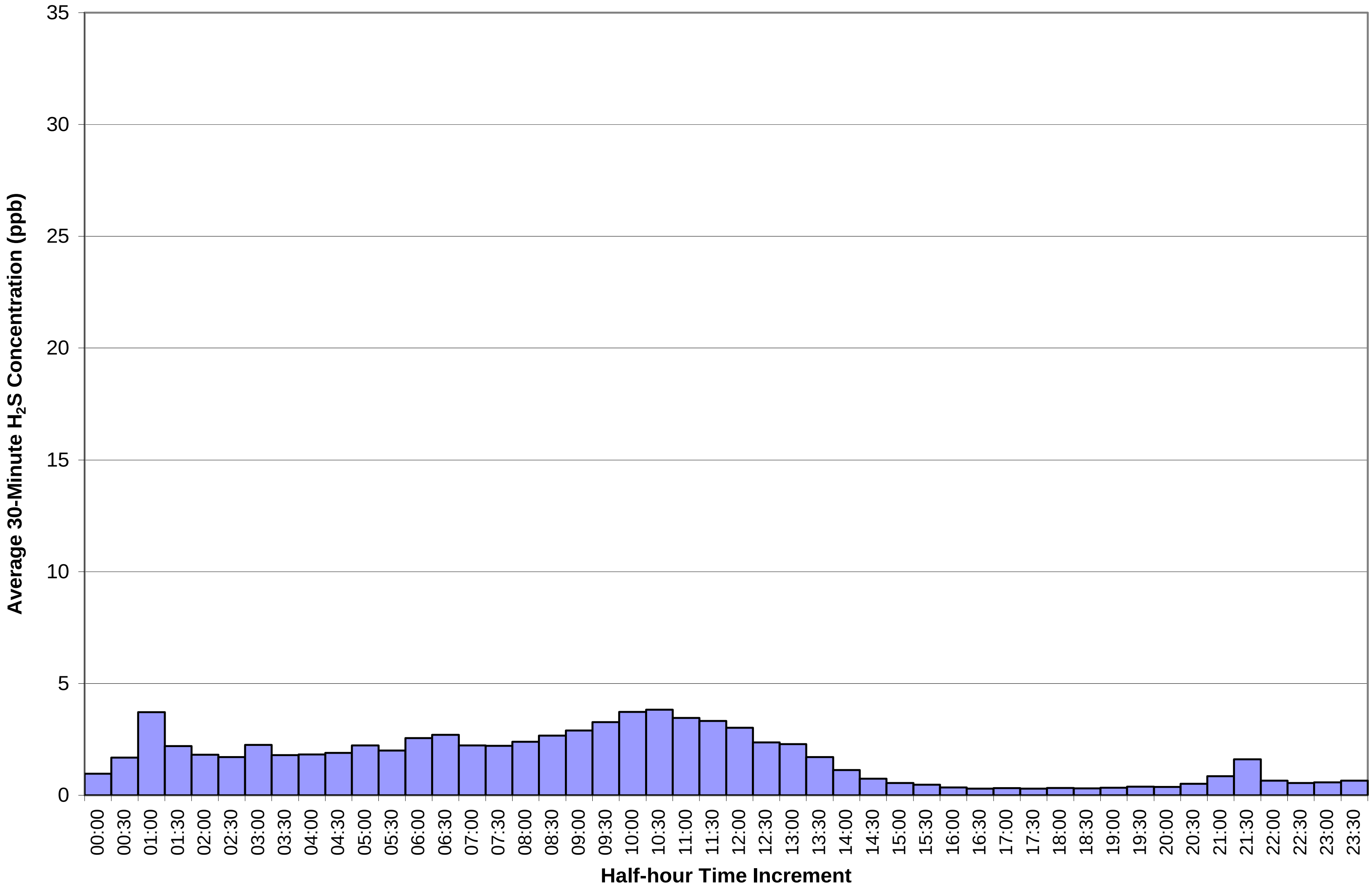


Figure 4-18. 30-Minute Average H_2S Concentrations at Site 2 Indoor

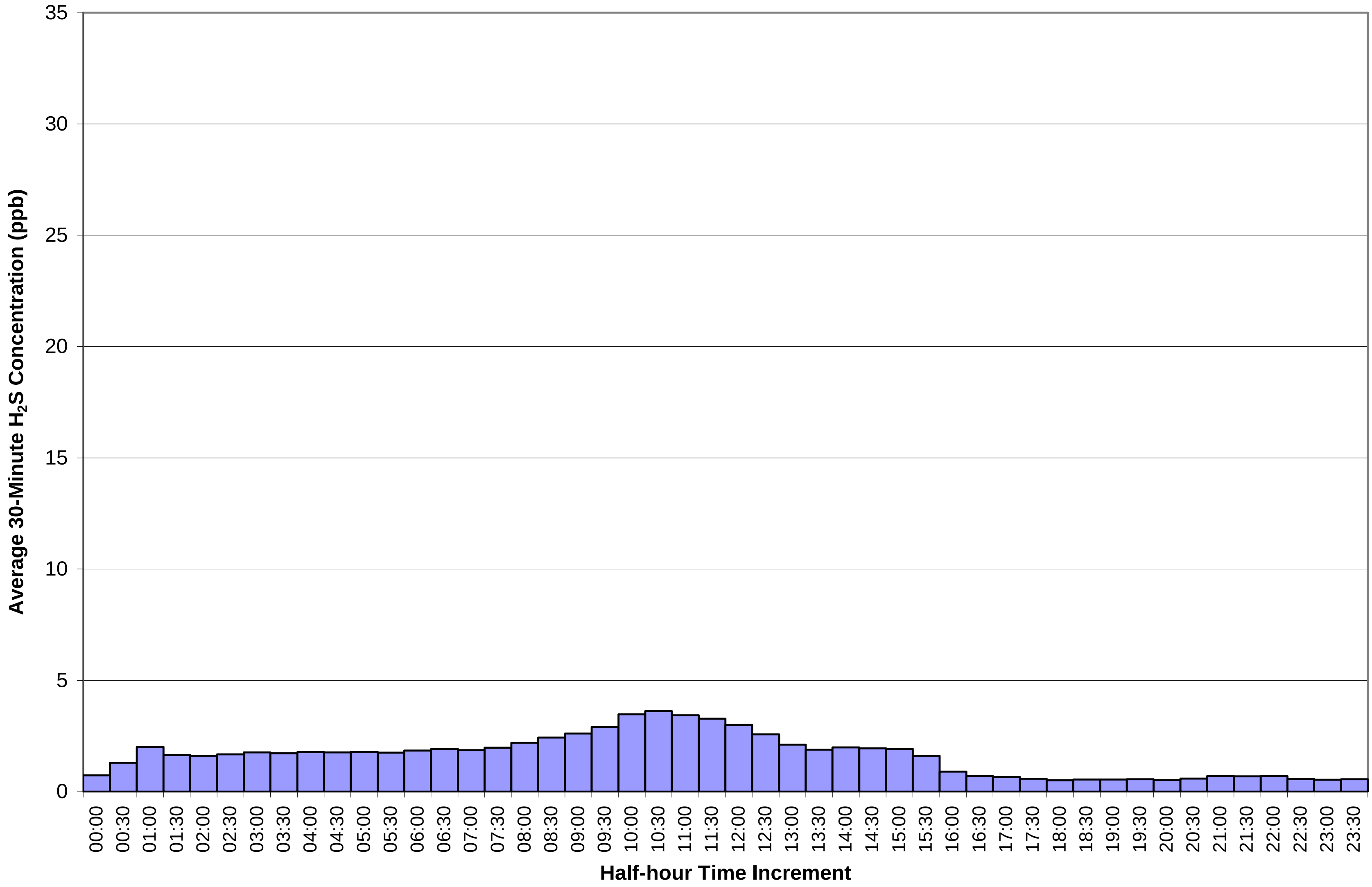
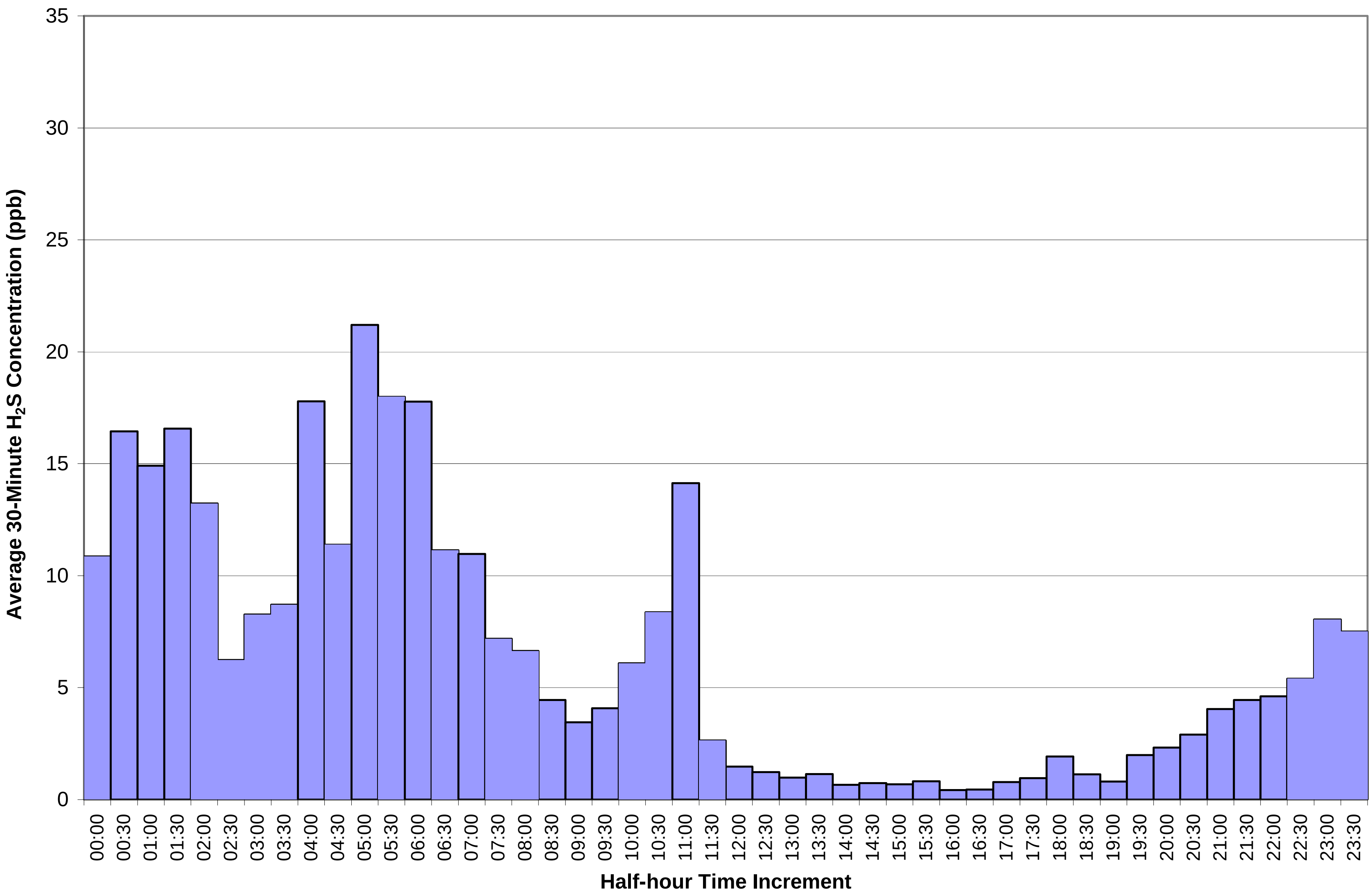


Figure 4-19. 30-Minute Average H_2S Concentrations at Site 3 Outdoor



4.2 Meteorological Parameters

As described in Section 2.2.2, an on-site system located at Site 1 collected meteorological measurements. Site 1 used a measurement height of approximately 10 feet (3.05 meters) above grade. Typically in its EI field reports, ATSDR presents and compares meteorological data collected at its own EI monitoring sites to meteorological data collected from the nearest airport station. For this EI, however, MPCA meteorological data are presented and compared to the EI data for the following reasons: 1) the MPCA station had no stall rate (see Section 4.2.1) and was located in close proximity to the EI meteorological station (see MPCA Site 1 on Figure 2-1), 2) the MPCA station was specifically positioned to evaluate meteorological conditions at the Excel Dairy fenceline, 3) to facilitate comparisons of EI and MPCA data of times outside of the EI monitoring period, 4) the Thief River Falls Municipal Airport meteorological station is approximately 10 miles west of the Excel Dairy, and 5) the airport station is positioned 10 meters above ground level while the MPCA station was positioned approximately 6 feet above ground level. Though the measurement technologies used by ATSDR and MPCA differ slightly, the two data sets correlate well and both present good data sets for comparison purposes. Data were obtained from the MPCA's meteorological station for the same time period as data were collected during the EI (i.e., July 9–31, 2008), and comparisons of these meteorological measurements are detailed below.

4.2.1 Wind Direction and Speed

Surface wind observations include two primary components: wind speed and wind direction. Wind speed is a scalar value, which was measured in meters per second (m/s). Wind direction describes the direction from which the wind is blowing and is measured in degrees, where 0E is from due north, 90E is from due east, 180E is from due south, and 270E is from due west.

Summarized in Figure 4-20 are the wind speed and direction data for Site 1 in a format known as a wind rose. The wind rose displays the statistical distribution of wind speeds and wind directions. This figure indicates that 38.86% of the wind observations were classified as calm for Site 1. As shown in the figure, prevailing winds at 10 feet above ground level at Site 1 were out of the northwest. The average wind speed measured at Site 1 was 1.26 meters per second (2.8 miles per hour). For comparison and reference, Figure 4-21 shows a wind rose constructed using meteorological data obtained for the MPCA meteorological monitoring station for the same time period as this EI. As shown in the figure, the frequency of calm winds was 6.48% at the state meteorological station during the investigation period. These differences are most likely the result of equipment design (e.g., EI station had stall rates[1] while MPCA station did not) and measurement system siting. For instance, the two systems were almost a mile apart; Site 1 is situated southwest of the facility whereas the MPCA station is northeast of the facility; and the MPCA station was situated in a fairly wide open space while Site 1 is right near a house, a road, and a stand of trees.

[1] A **stall rate** is the minimum wind speed required to provide sufficient force to physically cause the cup assembly of the anemometer to rotate, facilitating measurement. For the ATSDR wind speed sensor, the stall rate is approximately 1 meter per second. See Section 2.2.2 for additional information on the meteorological equipment used by ATSDR during this EI.

Figure 4-20. Wind Rose for the Site 1 Meteorological Station

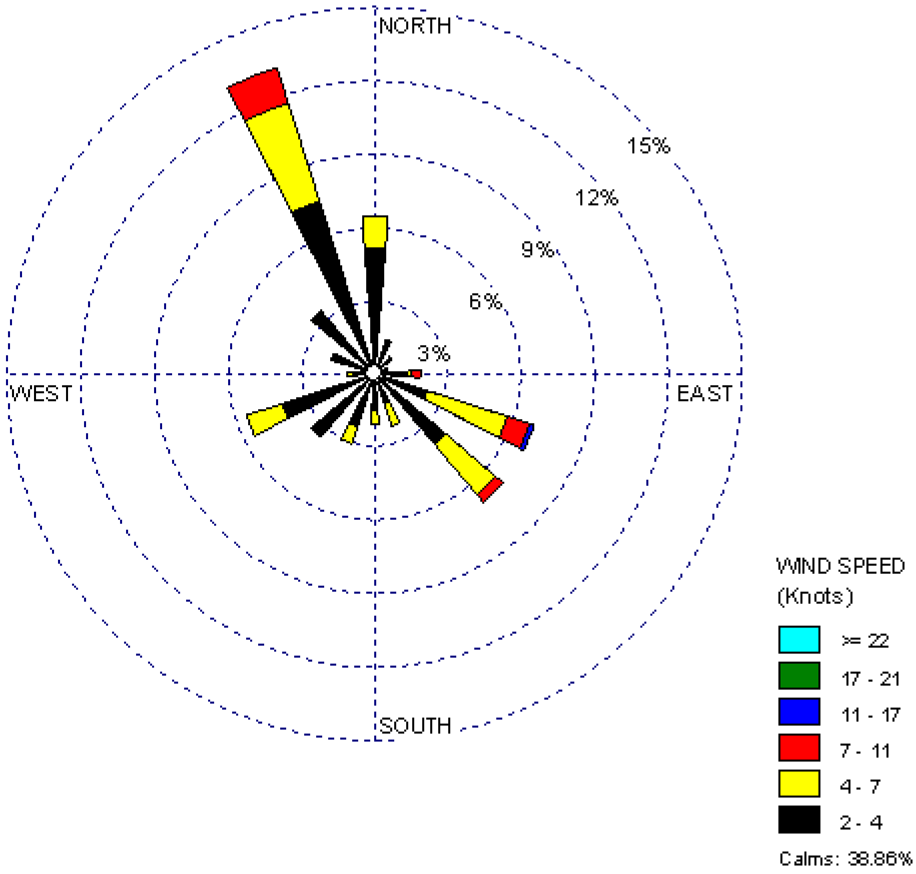
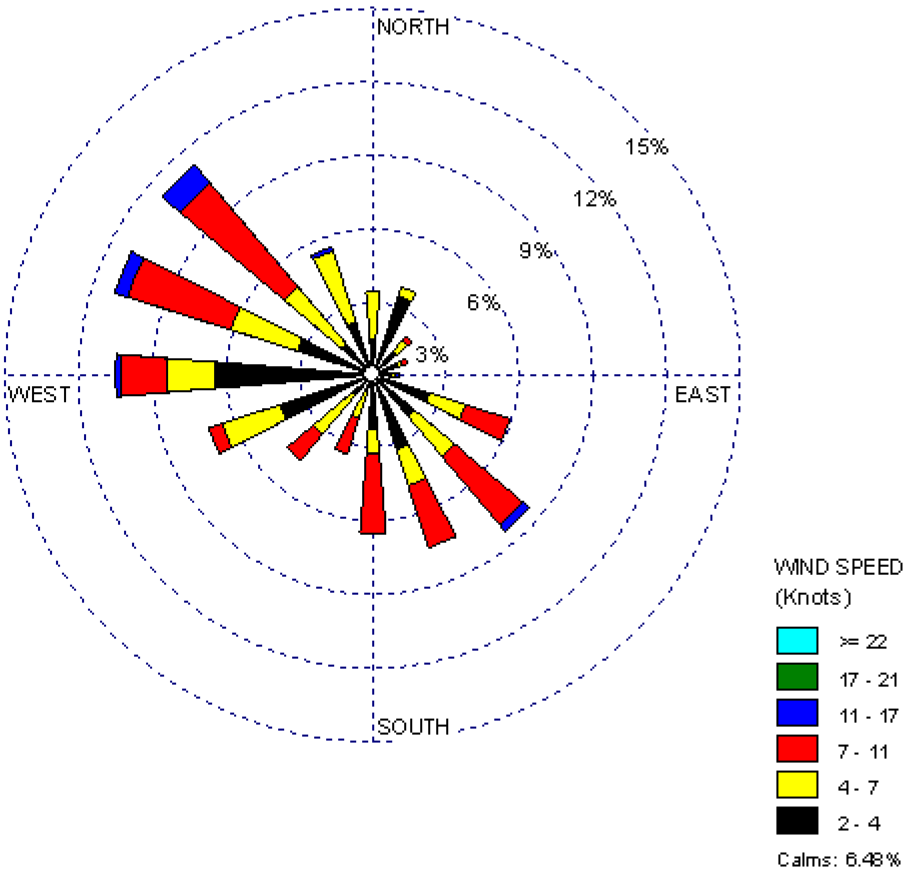


Figure 4-21. Wind Rose for MPCA's Meteorological Station



4.2.2 Temperature

Table 4-5 summarizes temperature measurements at Site 1 and the MPCA meteorological station. As shown in the table, temperature was evaluated by 8-hour time intervals at Site 1 and for the overall EI time period (i.e., July 9 to July 31) for both meteorological sites. Maximum 8-hour interval daytime temperatures at Site 1 were in the mid 80s (°F), while maximum overnight temperatures were more than 10 degrees lower. Minimum daytime and overnight temperatures did not vary much, with temperatures in the low to mid 50s (°F). As expected, average temperature measurements were lower in the early morning hours, with the temperature about 10 degrees cooler than compared to the rest of the day. Overall, temperatures were consistent at both meteorological stations during the EI period, with average temperatures in the mid to high 60s (°F).

Table 4-5. Temperature Data Summary

*Site**	*Time Period*	*Minimum Temperature (°F)*	*Maximum Temperature (°F)*	*Average Temperature (°F)*	*Standard Deviation (°F)*	*Total Number of Observations*
Site 1	0000-0759	52.49	71.08	59.93	3.99	10,560
	0800-1559	55.97	82.95	69.44	6.11	10,327
	1600-2359	56.66	84.38	71.47	6.29	10,560
	Overall	52.49	84.38	66.93	7.51	31,447
MPCA Station	Overall	51.58	87.60	69.28	8.78	1,104

*Site 1 measurements are based on 1-minute average observations, and MPCA measurements are based on 30-minute observations.

4.2.3 Humidity

Humidity measurements collected at Site 1 are presented in Table 4-6 by 8-hour time intervals and by the overall investigation period. As expected, relative humidity measurements were significantly higher in the early morning hours compared to the rest of the day. Humidity data are not available for the MPCA meteorological station, however.

Table 4-6. Humidity Data Summary

*Site**	*Time Period*	*Minimum Humidity (%)*	*Maximum Humidity (%)*	*Average Humidity (%)*	*Standard Deviation (%)*	*Total Number of Observations*
Site 1	0000-0759	68.25	100.25	91.62	6.62	10,560
	0800-1559	33.25	100.25	72.73	15.04	10,327
	1600-2359	33.75	96.75	68.30	15.49	10,560
	Overall	33.25	100.25	77.59	16.50	31,447

*Site 1 measurements are based on 1-minute average observations.

5.0 Data Characterization

This section will interpret the ambient air monitoring data and meteorological data using wind direction analyses (Section 5.1) and correlation analyses (Section 5.2). Both of these analyses were conducted separately using meteorological data collected at the EI meteorological station and the MPCA meteorological station. The results are presented below by type of analyses and meteorological station.

5.1 Wind Direction Analysis of H_2S by Site

Comparisons were made of 30-minute measurements of wind direction to 30-minute measurements of ambient air concentrations of H_2S detected at the three EI outdoor monitoring sites where H_2S was measured. Specifically, for the time period of the EI (i.e., July 9 to July 31), calculations were made of average H_2S concentration as a function of wind direction, based on meteorological data collected at EI Site 1 (see Figures 5-1, 5-2, and 5-3) and MPCA's meteorological station (see Figures 5-4, 5-5, and 5-6). Wind directions were stratified into eight sectors, and 30-minute periods with calm winds were excluded from this analysis. As noted in each of the figures, the highest 30-minute average concentrations were often reported during periods of calm winds.

The concentration data in the six figures are shown on consistent scales to facilitate visual comparisons across the three outdoor monitoring sites. The following interpretations describe how ambient air concentrations of H_2S varied with wind direction measured at the EI and MPCA meteorological stations.

<u>Site 1</u>

Using EI meteorological data, average H_2S concentrations at outdoor Site 1 were highest when winds blew from the north (2.28 ppb), followed by when winds blew from the northeast (1.78 ppb; suggesting that the emissions came from the direction of the Excel facility) and east (1.45 ppb) (see Figure 5-1). Average concentrations for all other wind directions were less than 1.26 ppb.

When the same analysis is conducted using MPCA meteorological data, the average H_2S concentrations at outdoor Site 1 were highest when winds blew from the northeast (11.06 ppb; suggesting that the emissions came from the direction of the Excel facility), followed by when winds blew from the north (6.22 ppb) and east (2.83 ppb) (see Figure 5-4). Average concentrations associated with all other wind directions were less than 1.7 ppb.

<u>Site 2</u>

Analyses conducted using EI meteorological data (see Figure 5-2) and MPCA meteorological data (see Figure 5-5) indicate that average concentrations at outdoor Site 2 exhibited relatively minor variations for all wind directions, with all concentrations less than 2.0 ppb.

Site 3

Using EI meteorological data, average H_2S concentrations at Site 3 were highest when winds blew from the east (11.96 ppb) and the southeast (7.78 ppb)—directions that both suggest emissions are coming from the direction of the Excel facility (see Figure 5-3). Average concentrations for all other wind directions were much lower, with concentrations less than 2.8 ppb.

When the same analysis is conducted using MPCA meteorological data, the average H_2S concentrations at Site 3 were highest when winds blew from the south (15.69 ppb), followed by when winds blew from the southeast (14.59 ppb) and the east (6.19 ppb)—directions suggesting emissions came from the direction of the Excel facility (see Figure 5-6). All other wind directions were associated with much lower average H_2S concentrations, with concentrations less than 2.3 ppb.

Summary of Outdoor EI H_2S Monitoring Sites

Based on the evaluation of these wind direction profiles (see Figures 5-1 through 5-6), ATSDR notes the following:

- Analyses conducted separately using the EI meteorological data and the MPCA meteorological data found similar trends between wind direction and average H_2S concentrations.
- Higher H_2S concentrations at Site 1 appear to occur when winds are blowing from the direction of the Excel facility.
- Concentrations of H_2S at Site 2 are fairly consistent, regardless of wind direction.
- The 30-minute average concentrations at Site 3 are higher when winds are blowing from the direction of the Excel facility.
- Overall, these wind direction analyses provide insights into the H_2S levels measured during the EI. These analyses, combined with others (e.g., detailed air dispersion modeling), could provide a more detailed account of the H_2S emissions sources contributing to the measured concentrations.

Figure 5-1. Average 30-Minute H_2S Concentrations at Site 1 by Wind Direction at the EI Meteorological Station

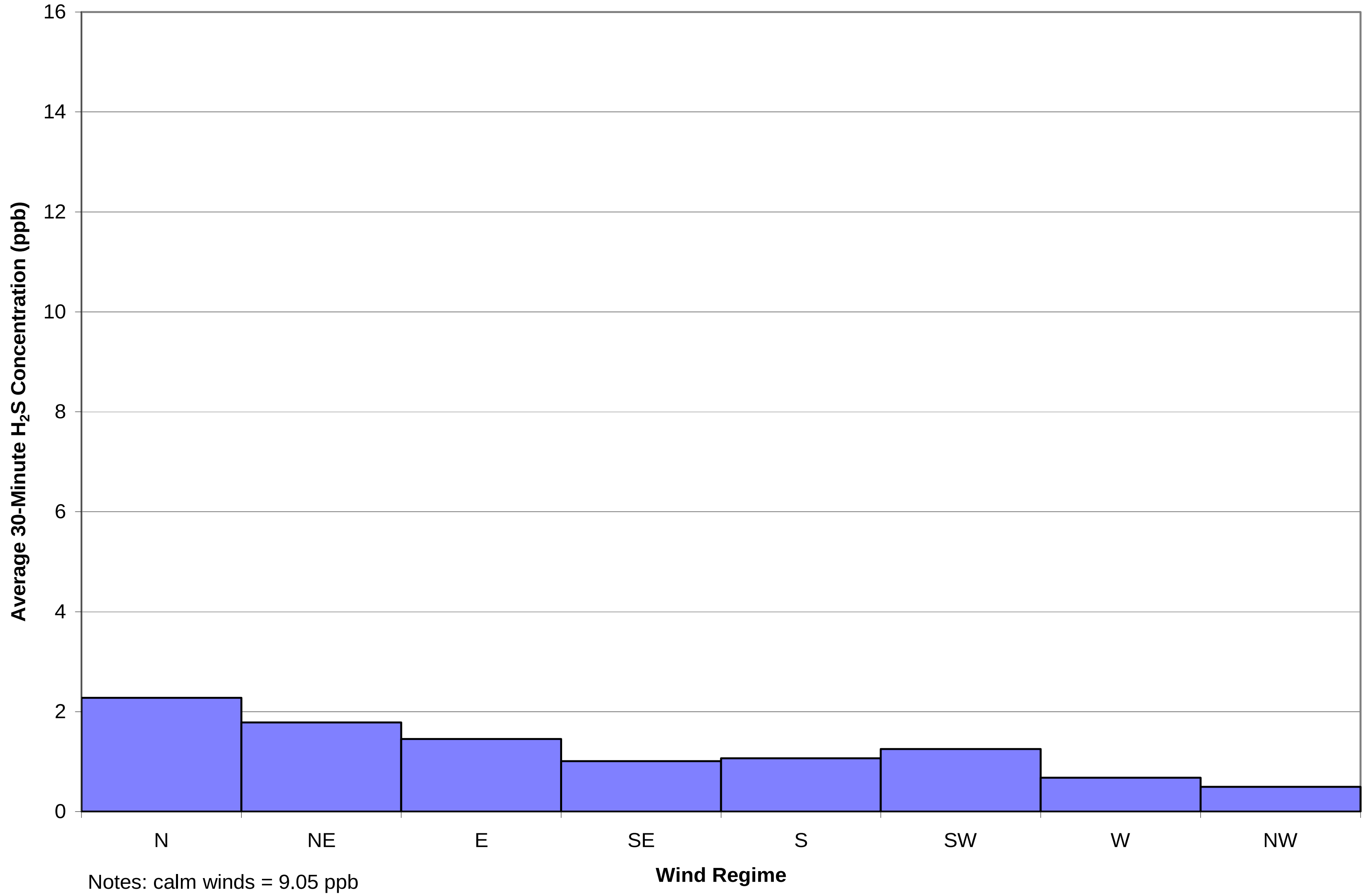
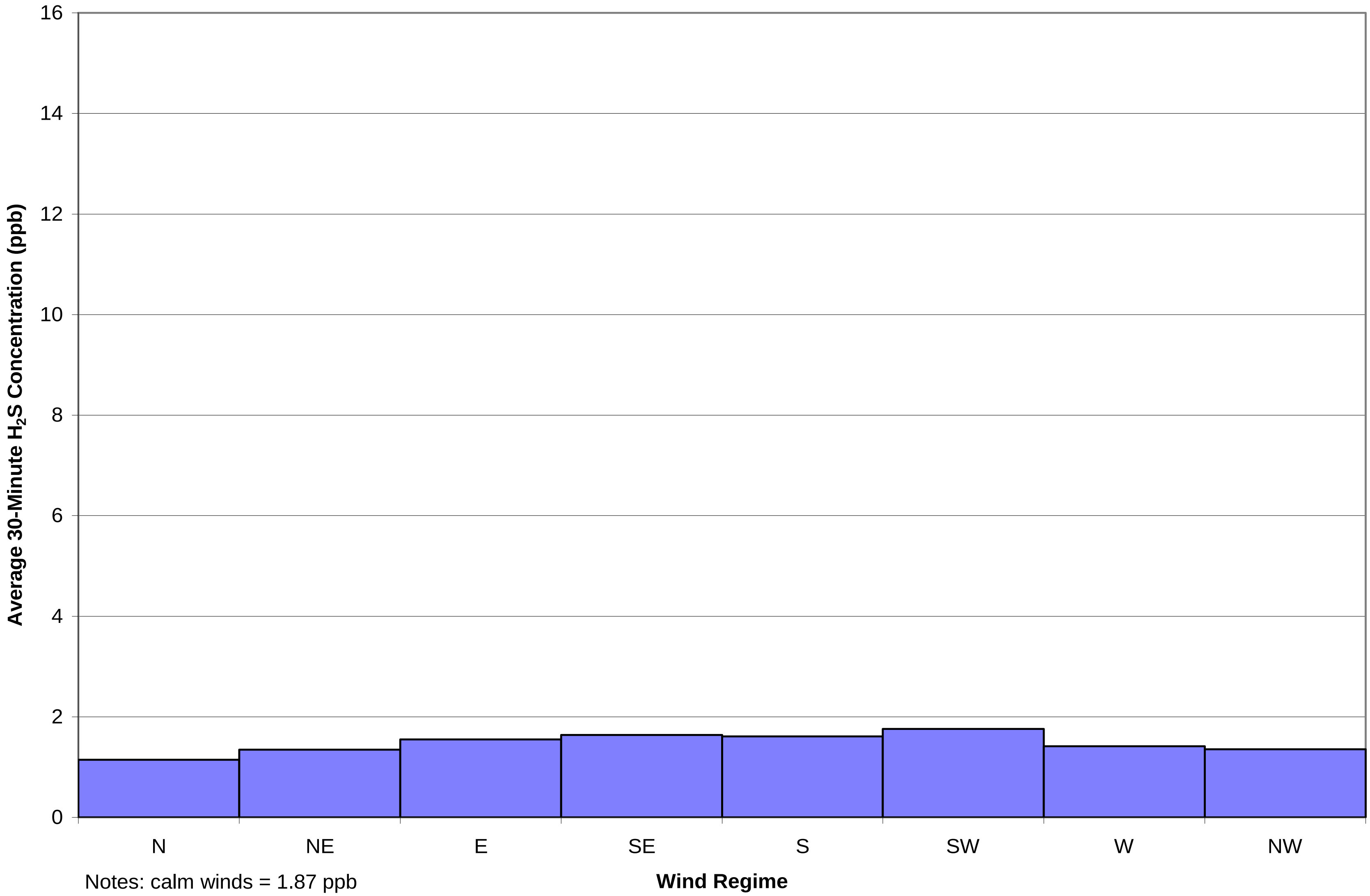


Figure 5-2. Average 30-Minute H_2S Concentrations at Site 2 by Wind Direction at the EI Meteorological Station



Notes: calm winds = 1.87 ppb

Figure 5-3. Average 30-Minute H_2S Concentrations at Site 3 by Wind Direction at the EI Meteorological Station

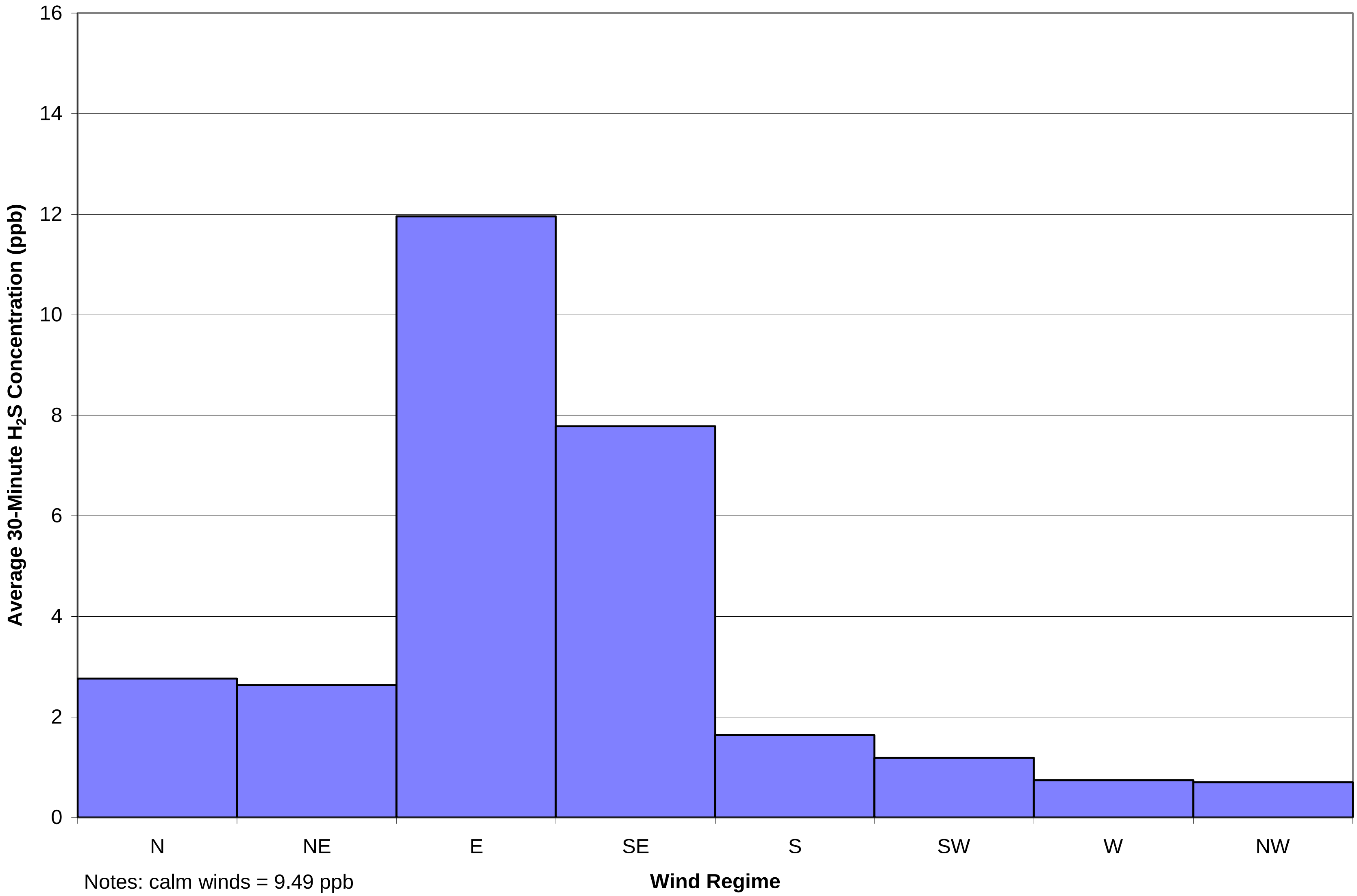
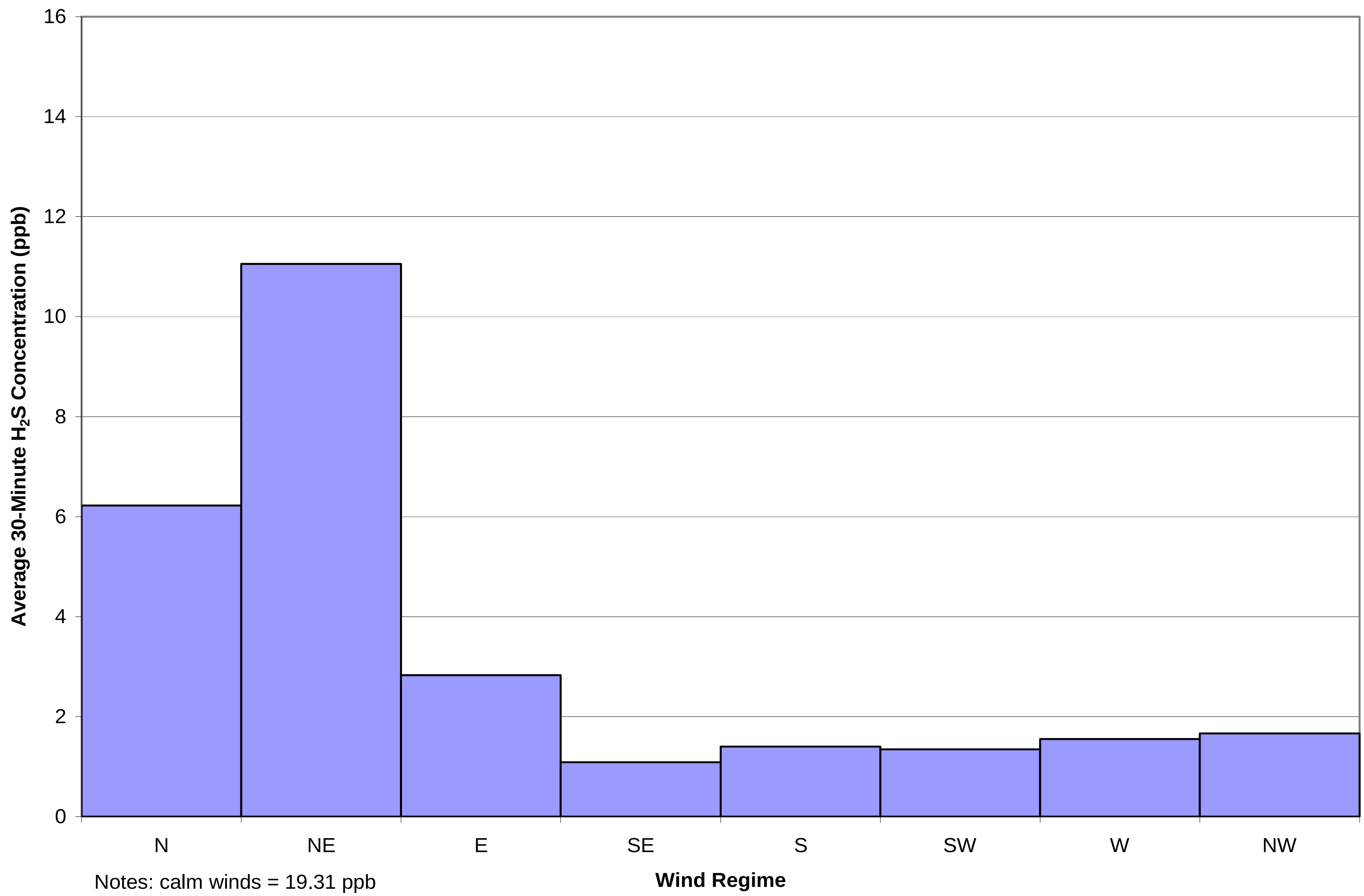


Figure 5-4. Average 30-Minute H_2S Concentrations at Site 1 by Wind Direction at the MPCA Meteorological Station



Notes: calm winds = 19.31 ppb

Figure 5-5. Average 30-Minute H_2S Concentrations at Site 2 by Wind Direction at the MPCA Meteorological Station

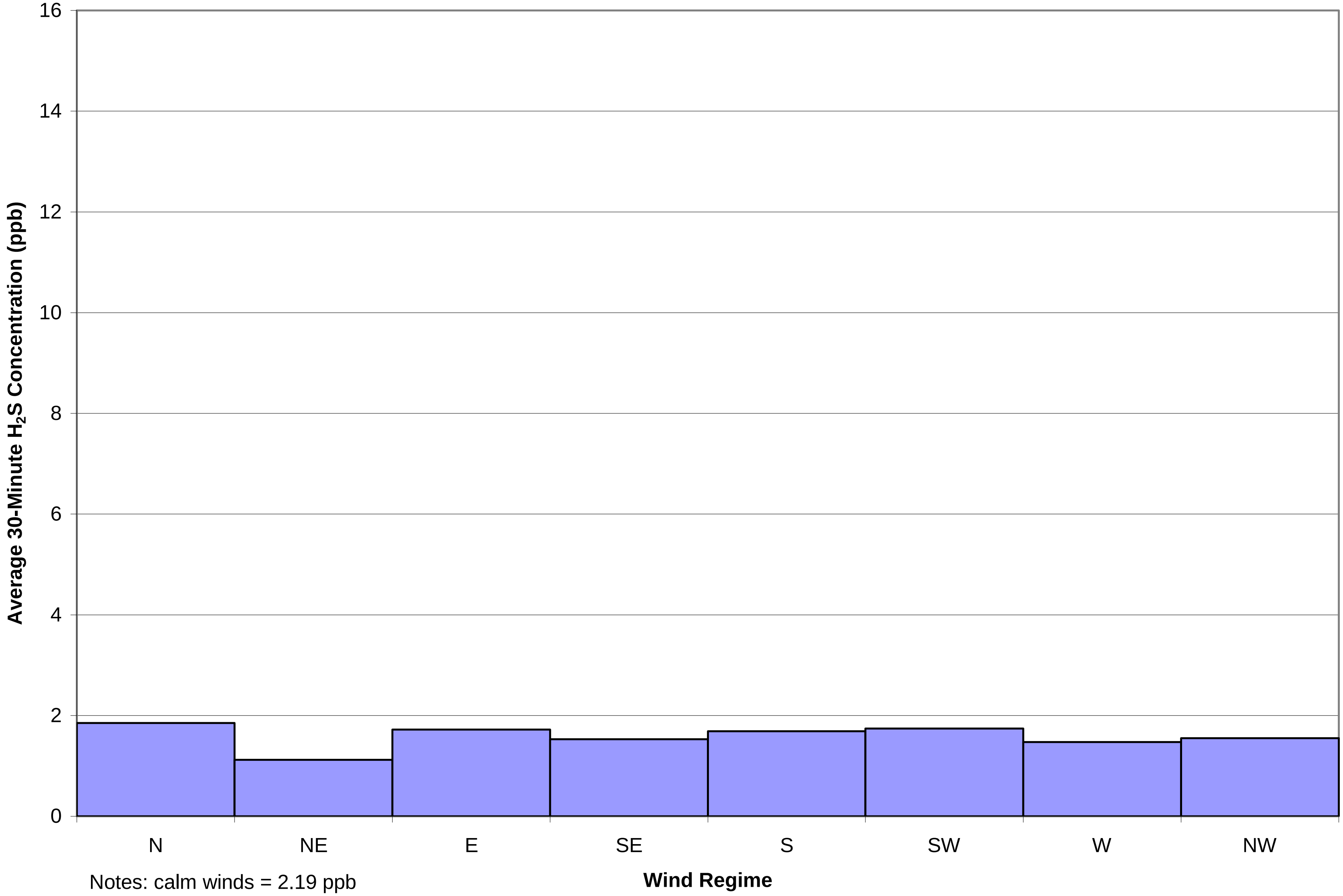
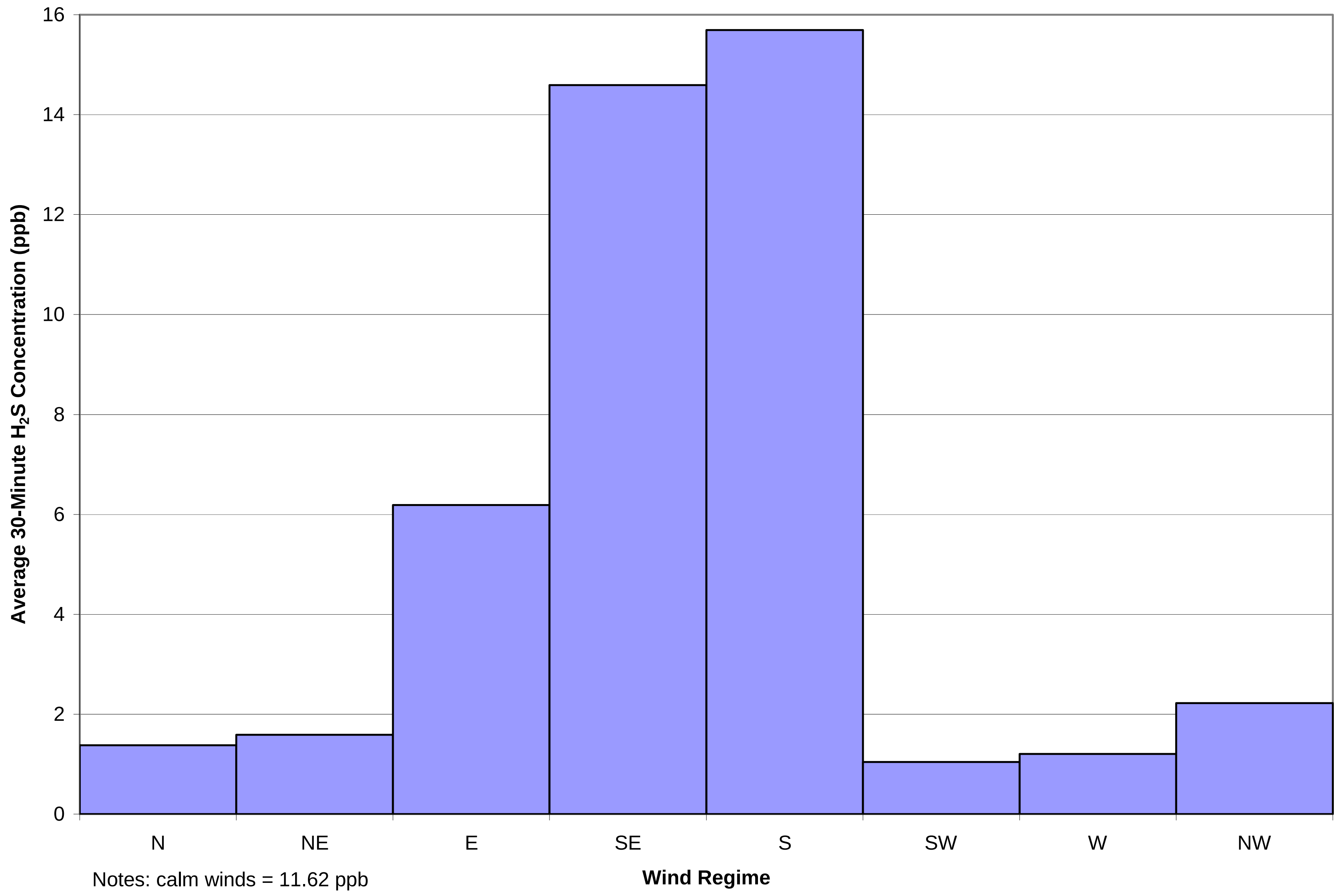


Figure 5-6. Average 30-Minute H_2S Concentrations at Site 3 by Wind Direction at the MPCA Meteorological Station



5.2 Correlation Analyses

Pearson correlation coefficients were calculated to investigate potential relationships between meteorological conditions and H_2S concentrations. These calculations were conducted for both the EI and the MPCA meteorological stations by comparing the 30-minute averaged meteorological data collected at each station to the 30-minute averaged ambient air monitoring data collected at each outdoor monitoring site.

For reference, Pearson correlation coefficients are used to measure the degree of correlation between two variables. By definition, Pearson correlation coefficients always lie between -1 and +1 and are interpreted as follows:

- A correlation coefficient of -1 indicates a perfectly "negative" relationship, indicating that increases in the magnitude of one variable are associated with proportionate decreases in the magnitude of the other variable, and vice versa.

- A correlation coefficient of +1 indicates a perfectly "positive" relationship, indicating that the magnitudes of two variables both increase and both decrease proportionately.

- Data that are completely uncorrelated have a Pearson correlation coefficient of or near zero.

Table 5-1 presents the results of the Pearson correlations conducted using the EI meteorological data for three meteorological parameters: temperature, relative humidity, and wind speed. As shown in the table, correlations between the H_2S concentrations and each of the three parameters were weak to none, ranging from -0.20 to -0.23 for temperature, 0.15 to 0.20 for relative humidity, and -0.04 to -0.19 for wind speed. This means that increases or decreases in temperature, relative humidity, and wind speed have little or no association with increases or decreases in H_2S concentrations.

Table 5-1. Pearson Correlations between 30-Minute Average H_2S Concentrations at the EI Outdoor Monitoring Sites and Meteorological Data Collected at EI Site 1: July 9 to July 31, 2008

Site	***Number of Observations***	***Temperature***	***Relative Humidity***	***Wind Speed***
Site 1	705	-0.20	0.18	-0.19
Site 2	1026	-0.23	0.20	-0.05
Site 3	705	-0.23	0.15	-0.11

Presented in Table 5-2 are the results of the Pearson correlations conducted using the MPCA meteorological data for three meteorological parameters: temperature, relative humidity, and wind speed. As shown in the table, correlations between the measured H_2S concentrations and each of the three parameters were weak to none, ranging from -0.21 to -0.27 for temperature and -0.02 to -0.22 for wind speed. [Note: humidity measurements may not have been collected at the MPCA meteorological station and are not therefore included in this report.] This means that increases or decreases in temperature and wind speed have little or no association with increases or decreases in H_2S concentrations.

Table 5-2. Pearson Correlations between 30-minute Average H_2S Concentrations at the EI Outdoor Monitoring Sites and Meteorological Data Collected at MPCA Site 1: July 9 to July 31, 2008

Site	***Number of Observations***	***Temperature***	***Wind Speed***
Site 1	705	-0.23	-0.22
Site 2	1026	-0.21	-0.02
Site 3	705	-0.27	-0.16

Pearson correlations were also prepared by comparing H_2S measurements to temperature, relative humidity, and wind speed on a daily basis (i.e., rather than over the entire EI duration as presented in Table 5-1 and Table 5-2). The purpose of this exercise was to evaluate correlations during periods of elevated H_2S measurements. The overall findings from this analysis include the following:

- Except for a few instances, weak to no correlations were observed between H_2S measurements seen during excursions (i.e., two consecutive 30-minute average concentrations above ATSDR's acute MRL of 20 ppb) at Site 1 and Site 3 and temperature, relative humidity, and wind speed.
- On days when no excursions occurred, strong negative correlations were often calculated between H_2S concentrations and temperature at Site 1, Site 2, and Site 3. Meaning, average H_2S concentrations tended to decrease as temperature increased, and concentrations tended to increase as temperature decreased.
- On days when no excursions occurred, strong positive correlations were often calculated between H_2S concentrations and relative humidity. This means that average H_2S concentrations tended to increase as relative humidity increased and concentrations tended to decrease as relative humidity decreased.
- With the exception of observations on July 24, H_2S concentrations had strong negative correlations with wind speed at Site 1 and Site 3, and a moderately negative correlation at Site 2. Meaning, concentrations tended to increase as wind speed decreased, and concentrations tended to decrease when wind speed increased. On July 24, however, H_2S concentrations had a strong positive correlation with wind speed. Thus, on this date of the EI period, concentrations increased when wind speed increased, but decreased when wind speed decreased. Because this is an atypical pattern among H_2S concentrations and wind speed, further in-depth analysis was conducted to examine what was occurring on July 24 to cause this unusual pattern. Based on an evaluation of surface weather conditions (Unisys 2008), it appears that a cold front passed through the study area on July 24. As a result, wind direction shifted from southeasterly to southerly, southwesterly, westerly, and finally northwesterly throughout the day. The approximate time of cold frontal passage was estimated between

11:00 am and 2:00 pm. This cold front likely cleared out the air in the site vicinity, resulting in decreasing H_2S concentrations from 12:00 to 3:00 pm.

6.0 Conclusions

ATSDR, with assistance from ERG, conducted an exposure investigation to measure the levels of H_2S in residential areas near the Excel Dairy. The EI consisted of a 3-week air monitoring program conducted from July 9 to July 31, 2008, in Thief River Falls, MN. The EI consisted of a program of continuous outdoor and indoor air monitoring of H_2S because it was identified as a contaminant of concern by residents and government agencies (i.e., EPA, MDH, and MPCA).

The Excel Dairy EI was developed to address six DQOs designed for the data generated during the monitoring program. All of the EI DQOs, presented in Table 6-1, were met except for measurement completeness (i.e., 80% data capture) at outdoor Site 1. At outdoor Site 1, over 30% of all H_2S measurements were invalidated due to a malfunctioning data logger during the first week of monitoring. After the problem was identified, the data logger was replaced and no other problems were encountered at outdoor Site 1. Nonetheless, the program's overall completeness DQO was reached, with a data capture of 87.58% (see Table 3-3)

Table 6-1. Operational and Technical DQOs for the Excel Dairy EI

Element	***Objective***
Where to conduct monitoring (siting)	All monitoring locations must be in close proximity to the potentially impacted population.
When to conduct monitoring (duration)	Daily from 0000 to 2359 hours across 3 continuous weeks.
Frequency of monitoring (measurement intervals)	Continuous for H_2S to allow assessment of short duration excursions and calculations of hourly and daily average concentrations.
Measurement completeness	80% data capture or greater
H_2S measurement precision	+/- 20% relative standard deviation (RSD)
H_2S measurement accuracy	+/- 15% difference

6.1 Overview of Findings

Technical conclusions and observations are presented below by parameter.

6.1.1 Hydrogen Sulfide

Overall Findings: H_2S was monitored at all three monitoring locations. The monitoring devices placed in indoor environments at Site 1 and Site 2 detected H_2S frequently, but typically at much lower concentrations than detected in outdoor environments. Nonetheless, while 30-minute average H_2S concentrations at indoor Site 2 were all below ATSDR's lowest comparison value of 20 ppb (i.e., intermediate MRL), some average concentrations detected at indoor Site 1 exceeded this MRL.

The highest 30-minute average H_2S concentrations ranged from 14.18 ppb at indoor Site 2 to 214.72 ppb at outdoor Site 1. The highest 30-minute average concentrations at all sites except indoor Site 2 exceeded ATSDR's intermediate MRL of 20 ppb. The highest 30-minute average concentrations detected at outdoor Sites 1 and 3 exceeded the acute MRL of 70 ppb. ATSDR also compared H_2S concentrations measured during the EI to MPCA's air quality standards for the state of Minnesota of 30 ppb and 50 ppb: some of the 30-minute average H_2S concentrations detected at Site 1 (i.e., indoor and outdoor) and Site 3 exceeded both of the state air quality standards.

Excursions of Elevated H_2S Measurements: "Excursions"—defined for the purposes of this EI as instances where two or more consecutive 30-minute average H_2S concentrations exceeded 20 ppb (ATSDR's intermediate MRL)—were identified and plotted graphically for each EI monitoring site. In summary, ATSDR found the following:

- While no concentrations at Site 2 exceeded 20 ppb during two or more consecutive 30-minute periods, 30-minute averages—often over sustained periods—were identified at Site 1 (indoor and outdoor) and Site 3.
- At Site 1, elevated H_2S concentrations at the outdoor site corresponded with increased concentrations at the indoor site.
- Excursions occurred more often at outdoor Site 3 than outdoor Site 1.
- Except for a few instances, graphs depicting these excursions for Sites 1 and 3 (see Figures 4-1 through 4-14) demonstrate that H_2S concentrations were considerably lower during the daylight hours when compared to those measured after sundown and before sunrise.

Diurnal Variations: Evaluations of diurnal variations in H_2S concentrations confirmed the findings of the excursion graphs: ambient air concentrations of H_2S were considerably higher after sundown and before sunrise compared to those measured during the daylight hours. Various mechanisms may contribute to the observed diurnal variations observed. Winds during the day disburse gas throughout the air, which results in lower ambient H_2S concentrations. During nighttime and early morning hours, however, winds are typically calmer, which usually results in less efficient dilution and dispersion of the H_2S gas and in ambient concentrations that are higher than during daytime hours. In addition, increased dispersion occurs as mixing heights rise during the day. Further, photochemical reactions occur during the day that break down H_2S.

Wind Analyses: In addition, wind analyses were conducted by comparing average H_2S concentration data from all three EI outdoor monitoring sites to meteorological data collected by ATSDR and MPCA at their separate monitoring stations. Overall, the findings were similar when using both meteorological data sets. Average H_2S concentrations at Site 2 were fairly consistent across all different wind directions, with no increased concentrations associated with any particular wind direction. Average H_2S concentrations at outdoor Sites 1 and 3 tended to be higher when winds were blowing from the direction of the Excel facility. The highest 30-minute average concentrations were often reported during periods of calm winds. While these wind direction analyses provide insights into the H_2S levels measured during the EI, they need to be combined with other efforts (e.g., detailed air dispersion modeling) to provide a more detailed account of the H_2S emissions sources contributing to the measured concentrations.

6.1.2 Meteorological Parameters

During the EI, a monitoring system was established at Site 1 to collect continuous meteorological measurements. Average winds were often calm (38.86%), typically out of the northwest, and had an average speed of 1.26 meters per second (2.8 miles per hour). In general, maximum daytime temperatures were in the mid 80s (°F), while overnight temperatures were in the low to mid 50s (°F). Relative humidity measurements were higher in the early morning hours compared to the rest of the day.

Little or no association was observed between H_2S concentrations measured during the overall EI period and changes in temperature, relative humidity, and wind speed. When analyses were conducted on a daily basis, weak to no correlations were observed between H_2S measurements seen during excursions at Site 1 and Site 3 and temperature, relative humidity, and wind speed. When no excursions occurred, however, in general strong negative correlations were often calculated between H_2S concentrations and temperature and wind speed, whereas strong positive correlations were often calculated between H_2S concentrations and relative humidity.

Data collected from the EI meteorological site were compared to data collected from MPCA's meteorological station, located near the Excel facility, during the same time period (July 9–31, 2008). Despite the differences in these stations that were noted previously (e.g., different stall rates, differences in siting), the data were consistent with regards to temperature and wind speed.

6.2 Limitations

ATSDR acknowledges that all scientific investigations, such as this Excel Dairy EI, have limitations. The limitations for this EI include:

- This EI focused on only one pollutant, H_2S, because of community health concerns and as requested by MDH and the US EPA. ATSDR recognizes that gases produce by dairy operations most likely are composed of a mixture of compounds.

- Monitoring was conducted at fixed, stationary monitoring locations; however, people move around, and do not remain in one place all day. Therefore, the monitoring data collected at the fixed locations are not directly equivalent to actual exposures that may have occurred, particularly for longer averaging periods (i.e., 24-hour averages and longer).

- The monitoring data collected during this program represent air quality conditions during July 9 to July 31, 2008. ATSDR selected the monitoring period to correspond with typical facility operations and representative emissions levels from the Excel Dairy facility and to provide short-term H_2S measured data at residential locations to complement the longer term MPCA fenceline monitoring program.

- No pre-site survey was conducted for this EI. Instead, the sample locations and sampling requirements were determined because they represented houses within the closest proximity to the Excel facility and because the residents in some cases were individuals who reported concerns about odors emanating from the lagoons and manure pit to MDH. These residents requested monitoring at their residences.

- Over 30% of all H_2S measurements at outdoor Site 1 were invalidated during the first week of the EI due to a malfunctioning data logger.
- Because two monitor locations (Sites 1 and 2) were originally planned for this EI, the monitors at outdoor Site 3 were not put in operation until the second week of the EI. Site 3 was added the second week of the EI program based on conditions on-site and the professional judgment of the EI Field Staff.
- While a low unit (i.e., detection range of 0–90 ppb) operated at outdoor Site 3 from July 16 through July 31, a mid unit (i.e., detection range of 76–1,500 ppb) was not brought on line until July 20. As a result, H_2S concentrations above 90 ppb could have occurred prior to July 20, but they would not have been captured at EI outdoor Site 3.

7.0 Authors and Technical Assistance

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9.0 Appendix A: Exposure Investigation Protocol

Exposure Investigation Protocol

Airborne Exposures to Hydrogen Sulfide

Excel Dairy
Thief Rivers Falls, MN

Cost Recovery Number A0LG

June 2008

Prepared by:

Debra Gable
ATSDR/DHAC/EISAB

Introduction

Purpose of Exposure Investigation

In order to better assess potential human exposure to airborne concentrations of hydrogen sulfide (H_2S) in ambient and indoor air at two residential properties near the Excel Dairy Farm near Thief Rivers Falls, Minnesota, the Agency for Toxic Substances and Disease Registry (ATSDR) will conduct an Exposure Investigation (EI). During this EI, an ambient and limited indoor air monitoring program will be conducted over a three week period to obtain representative concentration data of hydrogen sulfide, as well as meteorological parameters at two residential properties. The information collected through this exposure investigation will be used in conjunction with air monitoring data collected by the Minnesota Pollution Control Agency (MPCA) to better determine potential human exposure to airborne concentrations of hydrogen sulfide near the Excel Dairy Farm.

Exposure Investigation Objectives

This EI has two objectives. The first objective is to characterize concentrations, including peak concentrations and time-weighted average values, of hydrogen sulfide in residential areas near the Excel Dairy Farm.

The second objective is to provide information to evaluate if exposures are occurring at levels of health concern for residents and particularly to children and the elderly in the community.

Exposure Investigation Definition

An exposure investigation is defined as the collection and analysis of site- specific information and biologic tests (when appropriate) to determine whether people have been exposed to hazardous substances.

An exposure investigation is an approach ATSDR uses to fill data gaps in evaluating community exposure pathways. Its purpose is to better characterize past, present, and possible future exposures to hazardous substances in the environment and evaluate possible health effects related to those exposures.

Exposure investigations must meet four criteria. They are

1. Can an exposed population be identified?
2. Does a data gap exist that affects your ability to determine if a health hazard exists?
3. Can an exposure investigation be designed that will address this data gap?
4. Will the EI results impact the public health decision for the site?

An exposure investigation is NOT a study. Rather, it is a biased attempt at identifying the individuals most highly exposed and sampling their exposure. The results of an EI are a public health service directed to individual participants and are not generalizable to other populations.

Background

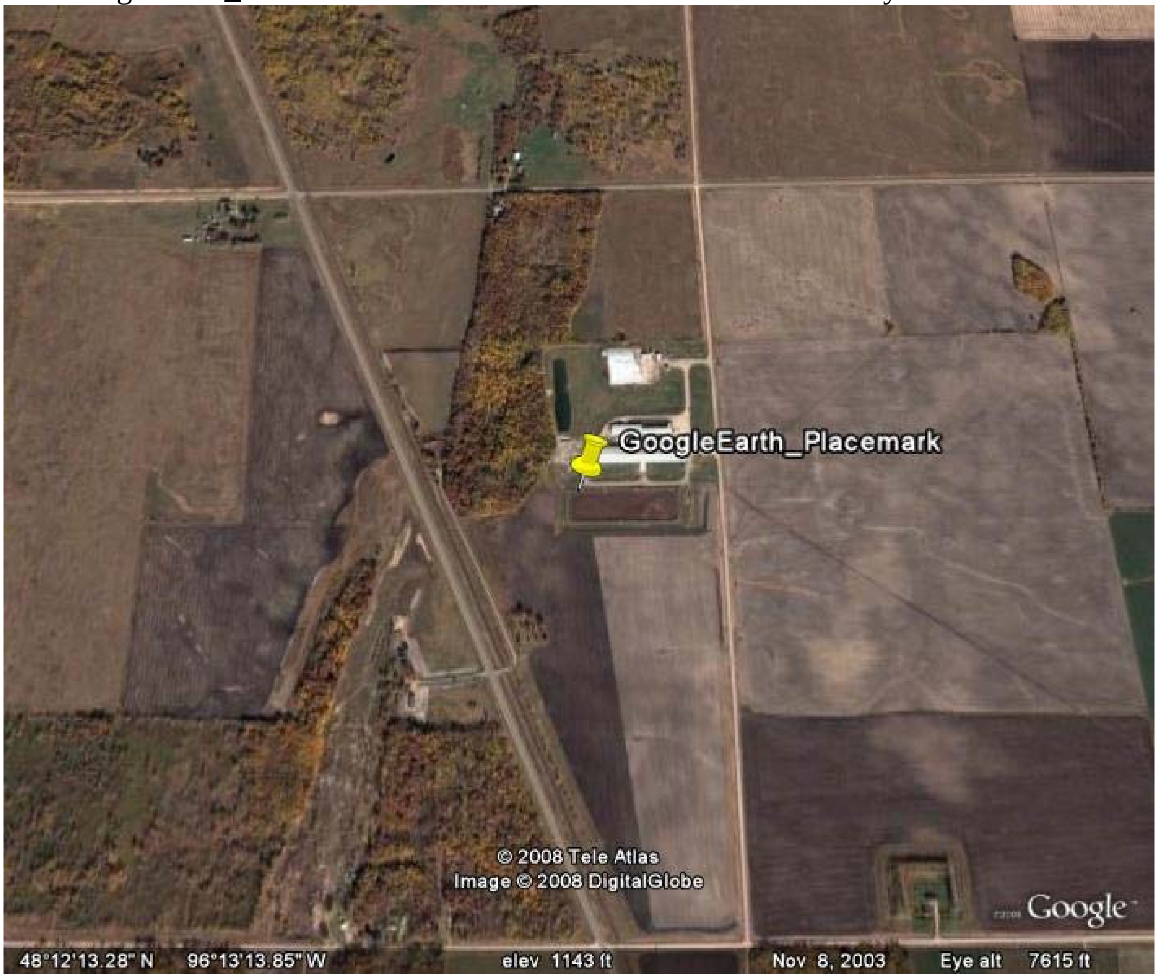
On June 10, 2008, the U.S. EPA Region 5 Air and Radiation Division (ARD) received an e-mail communication from a citizens' group advising ARD that on June 8, 2008, Minnesota health officials advised several families to evacuate their homes the prior week after hydrogen sulfide (H2S) fumes from Excel Dairy, a large dairy feedlot, reached unhealthy levels. The barn currently has 1500 cows, and is planning to increase the size to 2000 cows (see Figure 1).

On June 11, 2008, a local citizen contacted ARD. The caller reported that there are 12 families who live near the dairy. The caller indicated that he and his family (including children ages 3 and 5) have been sleeping at his parents' house. The citizen reported that the prior owner/operator of the dairy had gone out of business in 2002. Excel Dairy constructed a new, larger barn and began operating the new dairy in the fall of 2007. From the commencement of operation, the caller reported there had been strong odors (Colledge, 2008).

Marshall County public health officials reported to the Minnesota Department of Health (MDH) that approximately 12-15 families within ½ mile of the Excel Dairy are potentially affected by hydrogen sulfide gas (H_2S). Citizens have telephoned various agencies to complain. They have also rented a Jerome meter to measure H_2S and have developed a protocol to take readings every two minutes at one of two properties that appear to be the worst affected. The citizens have videotaped their activities. Citizens have faxed copies of the calibration of the Jerome meter done by Arizona Instruments, LLC, as well as copies of their data sheets. They have recorded many periods of hydrogen sulfide readings in the hundreds of parts per billion (ppb), and some readings over 1 part per million (ppm). The highest two minute reading was 6.8 parts per million. The highest 10 minute period was over 5 ppm, and the highest 30 minute period was over 1.8 ppm.

Figure 1. Google Earth Photo of the Excel Dairy and Nearby Areas.

The GoogleEarth_Placemark indicates the location of the Excel Dairy.



The (MPCA) has a continuous air monitor (CAM) measuring H_2S to the west of the dairy manure lagoons, in between the lagoons and one of the houses mentioned above (see Figures 2 and 3 for photographs of the basin). The CAM has been in operation since May 19, 2008. The upper detection limit of the CAM is 90 ppb. From May 19 at 12:30 hours to June 16 at 7:30 hours (27 days and 19 hours), the following high readings of H_2S (over 30 ppb) have been recorded:

Date	30 min. periods > 30 ppb	30 min. periods > 90 ppb
5-23	9	
5-24	21	13
5-25	4	2
5-28	4	
5-29	22	12
5-31	6	
6-2	1	
6-3	23	17
6-4	24	14
6-6	9	2
6-8	20	8
6-9	9	
6-11	24	9
6-12	5	3

The MPCA also has a CAM to the northeast of the facility, which has very few measurements of H_2S above 30 ppb and none above 90 ppb. This CAM also is recording meteorological data that can be used to confirm direction that the wind is blowing.

This CAM recorded 4 half hour periods over 30 ppb on June 8, 3 on June 9, 1 on June 12 and 2 on June 13. No periods above 90 ppb were recorded (Messing, June 18, 2008).

Figure 2. Photo of Excel Dairy Basin

Figure 3. Excel Dairy Aerator.

Rationale for the Exposure Investigation

The hydrogen sulfide data collected by the citizen group indicates a problem but does not provide definitive measurements of possible exposures. The MPCA CAMS are in place for compliance monitoring as close to the facility fencelines as feasible. They indicate violations of MPCA air quality standards for hydrogen sulfide (no more than two 30 min. periods of H_2S above 30 ppb in 5 days, or two 30 min. periods of H_2S above 50 ppb in any year). The purpose of the data collected by MPCA is to determine adherence to state regulations but not to measure actual human exposures or to assess health risks.

There is currently no MPCA monitoring data for levels above 90 ppb of H_2S. There is no air monitor to the southwest of the lagoons where the highest readings were obtained with the Jerome meter.

To help address these data gaps, ATSDR will loan MPCA two H_2S monitors with a detection range of 53-1500 ppb for deployment on or near the facility boundary. In addition, the Minnesota Department of Health has requested ATSDR to conduct an exposure investigation to measure hydrogen sulfide at two residential locations near the Excel Dairy.

The ATSDR exposure investigation is designed to assess potential human exposure to airborne concentrations of hydrogen sulfide to residents near the dairy. ATSDR will place H_2S monitors (single point monitors, SPMs) at two residences close to the Excel Dairy. One residential property at which an SPM will be placed is approximately 200 yards from the dairy fenceline. At each residential location, two SPMs will be co-located and continuously measure ambient concentrations of H_2S for three weeks. One of the ambient H_2S SPMs will have a detection range of 2-90 ppb and the second SPM will have a detection range of 53-1500 ppb so that the effective detection range of H_2S will be 2-1500 ppb. A SPM at each residential location will also measure indoor concentrations with a detection range of 2-90 ppb.

The data from ATSDR's Exposure Investigation and the MPCA monitoring program will be used to evaluate potential nearby community exposures. The ATSDR, the MDH, the MPCA, and the U.S. EPA Region 5 have coordinated efforts to provide data for both the community exposure assessment and regulatory compliance assessment.

Investigators/Collaborators

Agency for Toxic Substances and Disease Registry

The EI Principal Investigator and EI Lead for field activities for this project will be Ms. Debra Gable. In the capacity of EI Principal Investigator, Ms. Gable will serve as the primary liaison between ATSDR and ERG. She will be responsible for providing direction on the overall goals and approaches of the EI to ensure that the objectives of the monitoring project are met. Ms. Gable will develop, review, and/or provide comments on the EI Protocol, Monitoring Protocol and Health and Safety Plan, progress reports, and the Draft and Final EI Field Reports. Ms. Gable will be responsible for obtaining consent agreements from potential program participants identified. In the capacity of Technical Monitor, Ms. Gable will be responsible for overseeing overall coordination and logistics, approving project costs, approving changes to the Monitoring Program, and will serve as a technical advisor and Field Scientist.

LCDR Michelle Colledge will serve as the Site Lead for the public health consultation. She will be responsible for development of the health consultation (health report) and coordination of consultation activities. LCDR Colledge will also be the primary contact with other interested agencies (i.e., federal, state, and local).

Eastern Research Group, Inc.

The Project Director for this EI will be Mr. Dave Dayton. He will report directly to the ATSDR EI Manager. In the capacity of Project Director, Mr. Dayton will be responsible for the overall quality of the work conducted by ERG. He will oversee all activities associated with the monitoring project, from planning through reporting. As well as managing the monitoring project, Mr. Dayton will also be very involved in the actual technical effort including securing equipment, equipment checkout, equipment deployment, data downloading, and equipment recovery.

The ERG Field Scientists for this EI will be Mr. Dave Dayton, Mr. Scott Sholar, and Mr. Chris Lamie. In the capacity of Field Scientist, they will perform the pre-deployment check out of the measurement and sample collection systems, deploy them, perform daily sites visits, perform data downloading, and conduct the equipment recovery efforts.

Description of Target Population

Demographics

Thief River Falls is a small town of approximately 8,400 people in Pennington County in northwest Minnesota, near the North Dakota border. Most of the population of Thief River Falls is white (96.6%), have at least a high school diploma (79.1%), and own their homes (66.4%). The median family income in 1999 (dollars) is $40,908. In 1999, 12.4% of the population lived below the poverty line (U.S. Census Bureau, 2000).

Age, Gender and Ethnicity of the Target Population

In Thief Rivers Falls there are 4,416 women (52.5%) and 3,994 men (47.5%). The median age is 37.9 years. Approximately 77.6% of the population is 18 years or older and 18.8% older than 65 years (U.S. Census Bureau, 2000).

Race/ Ethnicity

Most of the population of Thief Rivers Falls is white (96.6%).

Special Populations

Pregnant women, children, the elderly, and people with chronic health conditions are considered as populations that may have increased susceptibility within the general target population. To address this concern, the EI will include two homes and at least one home where children are known to live.

Description of the Potentially Affected Population and Community Health Concerns

The issues cited in the citizens complaints reported to the MN Department of Health included reports of significant odors emanating from the dairy farms and in particular the lagoons and manure pit. As a result, excessive emissions of hydrogen sulfide gas may migrate into nearby residential areas. The citizen complaints contain numerous descriptions of health impacts related to conditions of significant gas odors. Community health effects reported include: headaches, nausea, eyes and respiratory tract irritation. There are approximately 12 households that appear to be impacted by gases from the dairy (Messing, 2008).

Criteria for Choosing the Target Area

The primary health concerns of the residents near the Excel Dairy as expressed to ATSDR are associated with dairy farming operations such as the lagoons and manure pit. To address community concerns, ambient and selected indoor air monitoring will be located at two residential properties near the dairy. One of the residential properties is located about 200 yards from the fenceline of the dairy. A met station will also be placed at one of the residences. These EI locations have been chosen at the request of the MDH.

Exclusion Criteria

Biologic sampling will not be conducted.

Rationale for Environmental Sampling

This EI will focus on the ambient and limited indoor air monitoring of hydrogen sulfide. Hydrogen sulfide was selected for monitoring during this EI because this compound presents a high potential to be emitted from dairy farms and because elevated concentrations of H_2S have been measured by both the MPCA and citizens in the area.

Confidentiality

The only personal identifiers collected during the EI will be adult names and property addresses for correlation with sampling results. Names will be used to ensure a point of contact for reporting results of testing. These personal identifiers will not be included in any data sets produced for the study and will not be used for any other purpose.

Risks/Benefits Information

There are minimal risks associated with this exposure investigation. The primary risks are that property owners/occupants could be slightly inconvenienced during set-up, checks, and demobilization of equipment. To reduce any inconvenience associated with the operation of the EI, field personnel will adhere to predetermined timeframes as agreed by participants to access property. The second risk is that electric power will be required to operate sampling equipment. A single 110 power source will be needed for most sampling locations. Field personnel will provide all supplies and equipment needed to access electrical power and will ensure all equipment are secured.

The potential benefits for this EI are that participants will learn whether they and/or their children are being exposed to the measured EI target compounds at levels of health concerns. The results of the EI are expected to provide ATSDR or other agencies, information to evaluate public health concerns of community members in Thief River Falls. The results of this EI may also be used to inform decisions by the local health department, the MDH, the MPCA, and other public health agencies and environmental agencies.

Informed Consent Procedures

If participants indicate a willingness to allow air monitoring/sampling near or on their property, ATSDR personnel will explain what the exposure investigation will entail, and will obtain written, informed consent [Appendix A]. It will be stressed that participation in the EI is strictly voluntary, and if they choose to participate, participants may withdraw from the investigation at any time without penalty.

Methods

The methodologies to be followed in this EI are provided in the attached Monitoring Protocol Health and Safety Plan [Appendix B]. Detailed information regarding the EI include monitoring/sampling methods, equipment siting, staging, data collection, monitoring, monitoring schedules, project schedule, quality assurance and control, and the site health and safety plan. A summary of sample collection methods for hydrogen sulfide and meteorological parameters are given below.

Hydrogen Sulfide

Measurements of H_2S will be made using Zellweger SPMs owned by ATSDR. Primary calibration of these instruments is performed at the factory. Two-point internal optical calibration performance checks will be conducted (i.e., initially before deployment, weekly onsite, and again after equipment recovery). The linear detection range for instruments used to monitor outdoor and indoor low levels is 2-90 ppbV. However, the instruments will be calibrated from 0-90 ppbv. The linear range or instruments used to monitor outdoor mid-range levels is 52-1,200 ppbV and high-range level is 1.1-30 ppmV. Ambient air is drawn through a humidifier filled with distilled water and into the instrument through a length of Teflon tubing (i.e., 0.250 inch outside diameter), outfitted with an inverted glass funnel connected at the inlet end. Measurement of the H_2S detected is automatic, and the resulting data are stored in the DAS. The distilled water will be changed in each humidifier every other day.

A portable H_2S Analyzer (e.g., Jerome 631X) will also be deployed to the field to make measurements for safety during the EI.

Meteorological Parameters

Measurements of meteorological parameters will be made using a stand alone meteorological monitoring system, attached to a secured tripod assembly. This system incorporates a cup anemometer to measure wind speed, a directional mast and vane to measure wind direction, a wound bobbin assembly to measure relative humidity, and a temperature probe to measure ambient temperature. Measurements will be made at a height of approximately 10 feet above grade. Resulting data are stored in the DAS.

Data Acquisition

Electronic signals from the H_2S and meteorological measurement systems will be collected and stored using HOBO Micro Station DASs with 4-20 mA adapters and BoxCar Pro 4.3 software. Each DAS is capable of collecting 6 channels of amperage input simultaneously, and offers internal storage for 1 million data points per system.

Data Quality Objectives

The project Data Quality Objectives (DQOs) provide the answer to the critical question of how good data must be in order to achieve the project goals. DQOs are used to develop the criteria that a data collection design should satisfy including where to conduct monitoring, when to conduct monitoring, measurement frequency, and acceptable measurement precision and accuracy. Considering the targeted compounds, information obtained during the site selection survey, and specifications associated with the monitoring and sample collection systems that will be utilized, DQOs for this EI are presented in Table 1. For a more detailed account of the DQOs and quality assurance/quality control see Appendix B: Monitoring Protocol Health and Safety Plan.

Table 1. Data Quality Objectives

Element	Objective
Where to Conduct Monitoring	All sites must be located in close proximity to the potentially impacted populous.
Number of Sites Required	2 outdoor/indoor monitoring sites will provide a representative and direct relationship to the potentially impacted populous (i.e., private residences).
When to Conduct Monitoring	Daily – from 0000 to 2359 hours
Frequency of Monitoring	Continuous for H2S so that short duration excursions can be assessed, and hourly and daily average concentration can be calculated.
Overall Completeness	80 % data capture
Acceptable Measurement Precision for SPMs	+/- 20 % relative standard deviation (RSD)
Acceptable Measurement Accuracy for SPMs	+/- 15 % RSD

Reporting of Results

Reporting Results to Participants

ATSDR will evaluate the results of this EI for health significance. EI measured concentrations of hydrogen sulfide will be compared to ATSDR's minimal risk levels (MRLs) for hydrogen sulfide (ATSDR, 2006) as follows:

ATSDR Acute MRL: 70 ppb

ATSDR Intermediate MRL: 20 ppb

For a list of other comparison values that may be used during the evaluation, see Appendix C (Memo. Criteria for Hydrogen (H_2S): Air Monitoring Data Near the Excel Dairy (Messing, June 25, 2008)). Upon completion of the investigation ATSDR will send a copy of the EI report to each exposure investigation participant.

Final Report

At the conclusion of this investigation, ATSDR will prepare a written summary in the form of an exposure investigation along with an overall public health interpretation. If contaminants are found at levels of health concern, appropriate local, state, and/or federal environmental and health agencies will be notified. The report will be available to community residents, the MDH, the MPCA, the Excel Dairy Farm, and other federal, state, and local environmental and public health agencies. Depending on the findings, recommendations for follow-up activities may include additional sampling, educating community members on mitigating exposures, and/or further study.

Limitations of Exposure Investigation

This EI has three main limitations. The first is that the EI will only capture ambient and a few selected indoor air quality locations during a three week period. This time frame may not be long enough to fully evaluate characteristic exposures to community members/residents. However, by choosing three weeks in July as the monitoring period, the EI will collect data during what may be one the worst case scenarios and if necessary, provide a rapid response to a potentially health adverse community situation.

The second limitation of the EI is that only a few of the numerous potential contaminants will be measured. All efforts in this EI have been made to measure those contaminants considered most likely to be of health concerns based on information provided by community members, environmental departments, and currently available information of facilities in the immediate vicinity of the Excel Dairy Farm.

The third limitation of the EI is that the EI and sample design were developed without the EI team having the opportunity to conduct a pre-survey site trip in which sample locations and sampling requirements would have been determined. A pre-survey was precluded due to the rapid response necessitated by site conditions. However, considerable site information was shared with ATSDR by the MDH, the MPCA, and U.S. EPA Region 5. If site conditions change or if additional EI procedures are determined to be needed during the course of the EI, the scope of the EI program may be revised.

References

Colledge, Michelle, 2008.Excel Dairy briefing notes. E-mail dated 6/12/2008.

Minnesota Department of Health. Proposed Excel Dairy Exposure Investigation, Draft 1. Dr. Rita Messing. June 18, 2008.

Bureau of the Census. Census 2000 Demographic Profile Highlights for Thief River Falls, MN. Last accessed June 30, 2008.

ATSDR, 2006. Toxicological Profile for Hydrogen Sulfide.

Minnesota Department of Health. Memo. Criteria for Hydrogen Sulfide (H2S); Air Monitoring Data Near Excel Dairy. Dr. Rita Messing. June 25, 2008.

Attachments

Appendix A: Consent Form

Appendix B: Monitoring Protocol Health and Safety Plan

Appendix C: Memo. Criteria for Hydrogen Sulfide (H2S); Air Monitoring Data Near Excel Dairy

Appendix A: Consent Form

Consent for Environmental Testing

Excel Dairy
Thief River Falls, Minnesota

We are from the Agency for Toxic Substances and Disease Registry (ATSDR). We would like to invite you to be part of an Exposure Investigation to learn what levels of hydrogen sulfide (H_2S) may be present in outdoor, and in some cases, indoor air in your community. We have asked you to help in this investigation because your home/school/property or business is located in areas near the Excel Dairy that may have high levels of the chemicals we want to measure. We want to test the outside, and in some cases, indoor air of several areas of your property for 3 weeks.

Procedure

We will place air measuring equipment, about the size of a briefcase, on your property. The air equipment will be on your property for 3 to 4 weeks. We will set-up the air monitoring equipment. It will take a few hours to set-up. Some of the equipment contains a small pump that draws in air for measuring. The pump sounds like a fish tank air pump. We will need to plug the equipment into one or two of your electric outlets.

Once a day, we will schedule a time to visit your home to check that the air monitors are working properly. These visits will be scheduled at a time that is good for you. These checks will take about 30 minutes. We will give you a phone number to call if the air monitors stop working properly or if you want us to take them away.

Benefits

Being part of this project will benefit you because you will find out if any of the chemicals we measure are in the outdoor, and in some cases, indoor air near your home or property. Also, by being part of this project you will also help your community find out if any of the chemicals we measure are in the outdoor, and in some cases, indoor air in your community.

Risks

You may be bothered by the air monitors on your property. You may also be bothered by us or our contractor checking the equipment. We will arrange a time with you for us to be on your property so that we bother you as little as possible. You may also have a small increase in your electric bill since we will need to use your power outlets.

Participation

You are free to choose whether or not to be part of this project. If you agree to help us, you may change your mind any time and drop out of the project. If you do this nothing will happen to you. You must sign this form to be part of the project.

Results

We expect to mail you the results of the air test within nine to twelve months of when we remove the air measuring equipment.

Confidentiality

We will protect your privacy as much as the law allows. The reports we write about this project will group all of the results together. We will not use your name or address in any of our reports. Still we are only including a small number of people in this project and it might be possible for someone to know that you were part of this. We will keep the forms with your personal information in a locked cabinet at ATSDR. We may share the results of the project with other federal, state, or local government agencies. They will also protect your information in the same way.

Contacts

If you have any more questions, you may contact Debra Gable at ATSDR at 770.488.1552.

Consent

This exposure investigation has been explained to me. My questions have been answered. I agree of my own free will to allow the air monitoring described in this paper.

I, (print) ____, agree to have air monitoring on my property.

Signature: ____ Date: _______________

Address: ____

Street

____

City State Zip Code

Phone #: ___________________________________

Witness: ____

(signature)

Appendix B: Monitoring and Health and Safety Plan

EXPOSURE INVESTIGATION

Monitoring and
Health and Safety Plan

Excel Dairy
Thief River Falls, Minnesota

Contract No. GS-10F-0036K
200-2005-F-13562

Prepared by:

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Morrisville, North Carolina 27560

June 2008

APPROVED BY

Ms. Debra Gable
Exposure Investigation Manager
Technical Monitor
Agency for Toxic Substances
and Disease Registry ______________________________

Mr. Dave Dayton
Project Director
Eastern Research Group, Inc. ______________________________

DISTRIBUTION LIST

Copies of this plan and all revisions will be provided to the following individuals:

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Lexington, MA 02421

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ACRONYMS

Acronym	Definition
ATSDR	Agency for Toxic Substances and Disease Registry
DAS	Data Acquisition System
DQO	Data Quality Objectives
EI	Exposure Investigation
ERG	Eastern Research Group, Inc.
HASP	Health and Safety Plan
HAP	Hazardous Air Pollutant
HAZWOPER	Hazard Waste Operations
H_2S	Hydrogen Sulfide
MDL	Method Detection Limit
PPE	Personal Protective Equipment
QA	Quality Assurance
QC	Quality Control
RSD	Relative Standard Deviation
SPM	Single Point Monitor

A – EXPOSURE INVESTIGATION OVERVIEW

SECTION 1
PROBLEM DESCRIPTION

1.1 Background

In order to better assess potential human exposure to airborne concentrations of hydrogen sulfide (H_2S) in ambient and indoor air at two residential properties near the Excel Dairy Farm near Thief River Falls, Minnesota, the Agency for Toxic Substances and Disease Registry (ATSDR) will conduct an Exposure Investigation (EI). During the EI, an ambient and limited indoor air monitoring program will be conducted over a three week period to obtain representative concentration data of H_2S, as well as meteorological parameters at two residential properties. The information collected through this EI will be used in conjunction with air monitoring data collected by the Minnesota Pollution Control Agency (MPCA) to better determine potential human exposure to airborne concentrations of H_2S near the Excel Dairy Farm.

1.2 Problem Definition

This EI has two objectives. The first objective is to characterize concentrations, including peak concentrations and time-weighted average values, of H_2S in residential areas near the Excel Dairy Farm.

The second objective is to provide information to evaluate if exposures are occurring at levels of health concern for residents and particularly to children and the elderly in the community.

1.3 Project Objectives

In order to better assess potential human exposure to H_2S, and to characterize indoor and ambient air at specific sites in Thief River Falls, Minnesota, the ATSDR will conduct an EI. During this EI, an ambient air monitoring program will be conducted to obtain representative concentration data for H_2S indoor and outdoor, and meteorological parameters, over a 3-week period. ATSDR will be assisted with the monitoring program by Eastern Research Group, Inc.

Hydrogen sulfide will be measured during the EI because it presents a high potential to be emitted from the local stationary source located in close proximity to the monitoring sites.

SECTION 2
PROJECT ORGANIZATION

2.1 Agency for Toxic Substances and Disease Registry

The EI Manager and Technical Monitor for this project will be Ms. Debra Gable. In the capacity of EI Manager, Ms. Gable will serve as the primary interface between ATSDR and ERG. She will be responsible for providing direction on the overall goals and approaches of the EI to ensure that the objectives of the monitoring project are met. Ms. Gable will review and provide comments on the Monitoring Protocol and Health and Safety Plan, progress reports, and the Draft and Final EI Reports. She will also be the primary contact with other interested agencies (i.e., federal, state, and local) and be responsible for obtaining consent agreements from potential program participants identified. In the capacity of Technical Monitor, Ms. Gable will be responsible for overseeing overall coordination and logistics, and serve as a technical advisor and Field Scientist.

2.2 Eastern Research Group, Inc.

The Project Director for this EI will be Mr. Dave Dayton. He will report directly to the ATSDR EI Manager. In the capacity of Project Director, Mr. Dayton will be responsible for the overall quality of the work conducted by ERG. He will oversee all activities associated with the monitoring project, from planning through reporting. As well as managing the monitoring project, Mr. Dayton will also be involved in the actual technical effort including securing equipment, equipment checkout, equipment deployment, data downloading, and equipment recovery.

The ERG Field Scientists for this EI will be Mr. Dave Dayton, Mr. Scott Sholar, and Mr. Chris Lamie. In the capacity of Field Scientist, they will perform the pre-deployment check out of the measurement and sample collection systems, deploy them, perform daily sites visits, perform data downloading, and conduct the equipment recovery efforts.

SECTION 3
PROJECT DESCRIPTION

3.1 Siting

Siting will be the responsibility of ATSDR. ATSDR will contact potential participants (i.e., private) located in the Thief River Falls area, and inform them of what is involved in general program participation. ATSDR will secure signed consent forms from each of the host sites. ATSDR will not release any vital information pertaining to the participants, except to agencies, and only with prior consent from each participant. After the sites have been selected, and participation consent has been obtained, ATSDR and ERG will contact the participants directly to schedule site events (i.e., deployment, operation, and recovery).

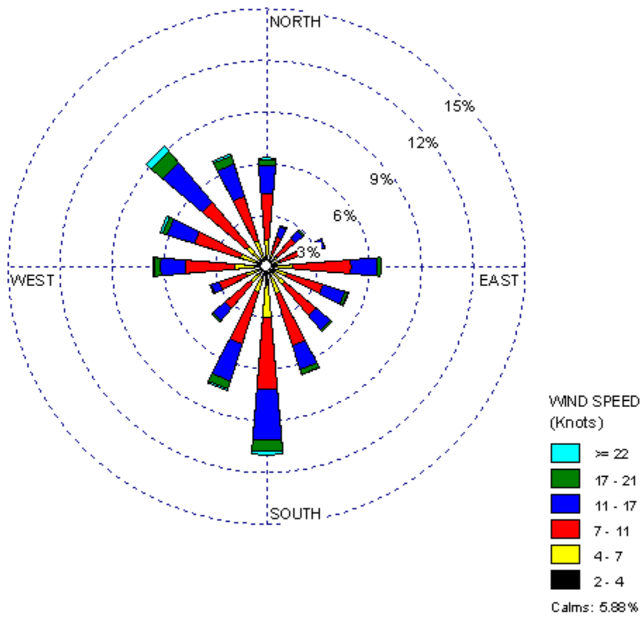
It must be noted that ERG will not assume any liability for damages or injuries resulting from locating/operating the ambient air monitoring equipment that will be used during the monitoring program. Should liabilities be encountered they will be project/contract borne.

3.2 Pre-Site Survey

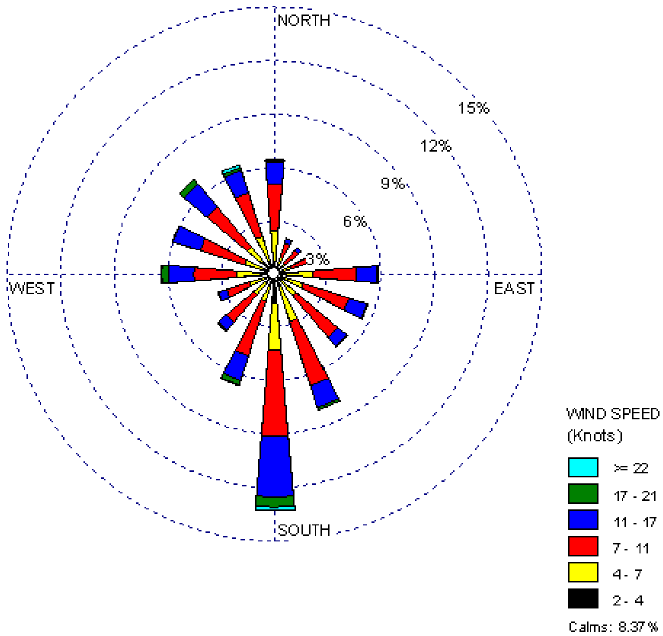
As the Thief River Falls is a rapid response EI, no pre-site survey will be conducted. ERG will deliver to the study area everything that it anticipates will be required to conduct monitoring. To aid in site characterization, annual and summertime average wind roses presenting data from National Weather Service station located in close proximity to the sites were prepared. These wind rose assessments are used to establish the typical wind flow patterns for the study area, and the relationship to monitoring sites. The annual and summertime average wind roses are presented in Figure 1.

Figure 1. 2006-2007 Annual and Summertime Average Wind Roses

Thief River: Annual Average Wind Rose



Thief River: Summer Average Wind Rose



3.3 Staging

Continuous measurement systems for this project will be provided by ATSDR. These systems include 6 single point monitors (SPM) for H_2S, a hand held monitor for H_2S, a meteorological monitoring system, and 5 data acquisition systems (DAS). All of the systems/equipment supplied by ATSDR are resident at ERG's laboratory facility in Research Triangle Park, North Carolina. The systems/equipment will be set up and rigorously checked to insure that everything is functioning correctly. For the SPMs and hand held H_2S monitors, ERG will perform post-recovery calibration and mid-point Quality Control (QC) checks to qualify precision and accuracy. Pre-deployment calibration and QC checks cannot be performed as a purchased H_2S standard will not arrive prior to the date that monitoring is to begin as specified by ATSDR. Long historical experience using the SPM equipment presents that this approach will not affect the quality of the data collected. Each site specific DAS will be set up, configured, and tested. ERG will design and fabricate any specialty hardware needed to support effective deployment and/or operation of the systems in the field. When all design, fabrication, and checkout activities are completed, ERG will pack the equipment for transport to the study area.

3.4 Deployment

ERG will transport the equipment to the study area and site locations. ATSDR and ERG will set up each of the chemical measurement systems and the meteorological measurement system in accordance with the site specific approaches developed during planning efforts. Table 1 presents the equipment configuration that will be employed at each site. Once the equipment is set up, each system will be tested to ensure that no damage occurred during transport. When the H_2S measurement systems are determined to be operating correctly, internal optical 2-point calibration checks will be initiated, and then the systems will be brought on-line. The wind direction sensor will be positioned using a digital compass. The meteorological system will be brought on-line once it is determined considered to be operating correctly.

Table 1. Measurement Descriptions by Site

Site Number	Site Description	Measurement Type
1	Private Residence	Continuous H_2S Indoors/low Continuous H_2S Outdoors/low Continuous H_2S Outdoors/mid or high
2	Private Residence	Continuous H_2S Indoors/low Continuous H_2S Outdoors/low Continuous H_2S Outdoors/mid or high Continuous meteorological

3.5 Monitoring

From the point that the H_2S and meteorological monitoring systems are brought on-line, monitoring will be conducted continuously for duration of 3-weeks. ATSDR and ERG will have at least one staff member resident in the study area throughout the monitoring program. A Field Scientist will visit the sites daily to assess the functional status of the chemical and meteorological measurement equipment and correct any problems identified. Field Scientists will download data from the H_2S monitors, reload chemcassetes, and perform the 2-point internal optical calibration checks weekly. For the meteorological monitoring system, Field Scientists will download data weekly and perform a visual check of the meteorological sensors daily.

There are presently two redundant or backup SPMs planned for this study. In the event that there is a failure of one of the primary H_2S monitors a back up SPM will be substituted. Primary systems will be repaired as quickly as possible and then returned to the network. If there is a failure of one of the meteorological parameters monitoring sensors, it will be repaired as quickly as possible and returned to the network.

3.6 Recovery

When the 3-week duration of the monitoring effort has been completed, Field Scientists will visit each site and perform the internal optical 2-point calibration checks for the SPMs and download data for the last time. After these activities have been completed, Field Scientists will breakdown and pack all equipment, and return that equipment to the ERG Laboratory in Research Triangle Park, North Carolina. To the greatest extent possible, the monitoring sites will be returned to the condition they were in prior to installing the equipment. ERG will set up the H_2S monitors at the ERG Laboratory and perform post-recovery calibration and QC checks to qualify precision and accuracy. Equipment belonging to ATSDR and/or ERG will be serviced, packed, and properly stored for use in future ATSDR monitoring programs.

3.7 Reporting

After data collection activities have been completed, an EI Report will be written. The report will address the following items:

- Introduction / Background;
- Site descriptions;
- Monitoring Approach and Methodology;
- Quality Assurance (QA) and QC; and
- Results.

A Health Consultation reflecting data collected during this EI will be prepared separately.

3.8 Proposed Project Schedule

The proposed schedule of major program events is presented in Table 2. If the schedule has to be revised, it will happen in 1-week increments.

Table 2. Schedule of Major Program Events

Event	Activity	Date
Siting	Site selection and agreements obtained with host residents (ATSDR responsibility).	On-going
Management	Preparation, review, revision (as needed) and acceptance of the Monitoring Plan.	June 16 – July 3
Staging	Acquire/obtain instrumentation and related ancillary equipment and materials. Fabricate all support systems and equipment.	June 16 – July 3

Table 2. Schedule of Major Program Events (Continued)

Event	Activity	Date
Staging	Set up and perform a functional checkout on all instrumentation at the ERG laboratory.	June 16 – July 3
Staging	Breakdown and pack all instrumentation, equipment, materials, and supplies, and prepare them for transport to the sites.	July 2 – July 3
Deployment	Transport equipment to sites.	July 7 – July 9
Deployment	Install/set up all equipment. Check out and bring systems on line.	July 9 – July 10
Monitoring	Week 1 – Check and service equipment daily. Perform sample collections as scheduled. Ship samples to ERG laboratory the same day they are collected.	July 10 – July 17
Monitoring	Week 1 – Download data, electronically transfer data to ERG Reporting Task Manager, and perform optical calibration checks.	July 17
Monitoring	Week 2 – Check and service equipment daily. Perform sample collections as scheduled. Ship samples to ERG laboratory the same day they are collected.	July 18 – July 25
Monitoring	Week 2 – Download data, electronically transfer data to ERG Reporting Task Manager, and perform optical calibration checks.	July 24
Monitoring	Week 3 – Check and service equipment daily. Perform sample collections as scheduled. Ship samples to ERG laboratory the same day they are collected.	July 25 – Aug 1
Monitoring	Week 3 – Download data, electronically transfer data to ERG Reporting Task Manager, and perform optical calibration checks.	Aug 1
Recovery	Breakdown and pack equipment for transport, return residences to their pre-deployment status.	Aug 1 – Aug 2
Recovery	Transport equipment to Research Triangle Park.	Aug 2 – Aug 5
Recovery	Set up instruments at the ERG laboratory, perform instrument calibrations and post-deployment QC checks.	Aug 18 – Aug 22
Recovery	Perform any required service on ATSDR owned equipment and store for future application. Return or dispose of any unconsumed materials/supplies (as appropriate).	Aug 25 – Aug 28
Reporting	Prepare the Draft EI Report.	Sept 1 – Sept 30
Reporting	Receive review comments.	Oct 4
Reporting	Finalize EI Report.	Nov 1

SECTION 4
QUALITY ASSURANCE AND CONTROL

4.1 Data Quality Objectives

The project Data Quality Objectives (DQOs) provide the answer to the critical question of how good data must be in order to achieve the project goals. DQOs are used to develop the criteria that a data collection design should satisfy including where to conduct monitoring, when to conduct monitoring, measurement frequency, and acceptable measurement precision and accuracy. Considering the targeted compounds, information obtained during the site selection survey, and specifications associated with the monitoring and sample collection systems that will be utilized, DQOs for this EI are presented in Table 3.

Table 3. Data Quality Objectives

Element	Objective
Where to Conduct Monitoring	All sites must be located in close proximity to the potentially impacted populous.
Number of Sites Required	2 outdoor/indoor monitoring sites will provide a representative and direct relationship to the potentially impacted populous (i.e., private residences).
When to Conduct Monitoring	Daily – from 0000 to 2359 hours
Frequency of Monitoring	Continuous for H2S so that short duration excursions can be assessed, and hourly and daily average concentration can be calculated.
Overall Completeness	80 % data capture
Acceptable Measurement Precision for SPMs	+/- 20 % relative standard deviation (RSD)
Acceptable Measurement Accuracy for SPMs	+/- 15 % RSD

4.2 Measurement Accuracy

Measurement accuracy for this project is defined as the ability to acquire the correct concentration measurement from an instrument or analysis with an acceptable level of uncertainty, while it is sampling a known concentration gas stream.

To determine the measurement accuracy associated with the SPM instruments used on this EI, a QC sample will be measured. The difference between the concentrations obtained from each instrument compared to the known concentration of the corresponding QC check standard will be calculated and expresses as RSD. Measurement accuracy checks will be performed post-recovery (i.e., after the systems returned from the field).

4.3 Measurement Precision

Measurement precision is defined as the ability to acquire the same concentration from different instruments with an acceptable level of uncertainty, while they are sampling the same gas stream. For this EI, measurement precision will be assessed as follows:

- *H_2S across instruments by type*—As part of the pre- and post-deployment QC checks, the eleven H_2S instruments will simultaneously perform 10 concentration determinations each. The average concentration from the 10 determinations will be calculated on an instrument specific basis. The eight averages will then be compared to each other and expressed as RSD.

SECTION 5
SPECIAL TRAINING REQUIREMENTS

Field personnel involved in this project have been trained in their tasks and have from 4 to 34 years of experience in the duties they will be performing. ERG staff will be subject to surveillance from the ERG QA Officer (Dr. Raymond Merrill) with appropriate corrective action enforced, if necessary. No additional special personnel will be required to augment the ERG personnel. ERG provides employee training through both specialized, in-house training classes, and by on-the-job training by their supervisors and co-workers. There are no unusual hazards and no special safety training or equipment other than standard personal protective equipment (PPE) will be required. Safety and hazard communication training have been completed by ERG laboratory staff. The ATSDR Project Manager and ERG Project Director are 40-hour Hazardous Waste Operations (HAZWOPER) certified.

SECTION 6
DOCUMENTS AND RECORDS

A field project notebook will be used to record the monitoring systems' operational parameters. Analysis documentation will include the use of bound laboratory notebooks to record experimental conditions, data, and pertinent observations. Hard copies of instrumentation records including calibration, QC checks, and any raw data will be archived in a Project Masterfile.

The project final summary report will include all applicable raw data and records. A summary of any outliers or findings will be presented in the report. The report will undergo a technical review before submission. After submission, the report will be available from the ATSDR Records Room and filed at ERG for a period of no less than three years. The file will also include electronic copies of all data used in the development of the report.

SECTION 7
MONITORING APPROACHES

7.1 Hydrogen Sulfide

Measurements of H_2S will be made using Zellweger SPMs owned by ATSDR. Primary calibration of these instruments is performed at the factory. Two-point internal optical calibration performance checks will be conducted (i.e., initially before deployment, weekly onsite, and again after equipment recovery). The linear detection range for instruments used to monitor outdoor and indoor low levels is 2-90 ppbV. However, the instruments will be calibrated from 0-90 ppbv. The linear range or instruments used to monitor outdoor mid-range levels is 52-1,200 ppbV and high-range level is 1.1-30 ppmV. Ambient air is drawn through a humidifier filled with distilled water and into the instrument through a length of Teflon tubing (i.e., 0.250 inch outside diameter), outfitted with an inverted glass funnel connected at the inlet end. Measurement of the H_2S detected is automatic, and the resulting data are stored in the DAS. The distilled water will be changed in each humidifier every other day.

A portable H_2S Analyzer (e.g., Jerome 631X) will be deployed to the site to make measurements for safety during the EI.

7.2 Meteorological Parameters

Measurements of meteorological parameters will be made using a stand alone meteorological monitoring system, attached to a secured tripod assembly. This system incorporates a cup anemometer to measure wind speed, a directional mast and vane to measure wind direction, a wound bobbin assembly to measure relative humidity, and a temperature probe to measure ambient temperature. Measurements will be made at a height of approximately 10 feet above grade. Resulting data are stored in the DAS.

7.3 Data Acquisition

Electronic signals from the H_2S, ammonia, and meteorological measurement systems will be collected and stored using HOBO Micro Station DASs with 4-20 mA adapters and BoxCar Pro 4.3 software. Each DAS is capable of collecting 6 channels of amperage input simultaneously, and offers internal storage for 1 million data points per system.

SECTION 8
DATA VALIDATION AND USABILITY

8.1 Verification and Usability Processes

A two-step process of verification and validation will be performed for data review. This process will begin with an objective review of whether or not the data collection plans and protocols were followed and whether the basic operations, calculations, and statistical evaluations were performed correctly. Ongoing QA review that started with the development of this Monitoring Plan will be reviewed to verify that the sampling and analytical methodology planned for this project was accomplished or that changes were identified documented and met project quality objectives. Only data collected by the EI Field Scientists will be reviewed and validated.

The second step will be to validate the technical usability of the data by determining whether the procedures followed were appropriate for the actual situations encountered, and whether the results make sense in the context of the study objectives. This validation will be done by comparing the original study objectives and data quality objectives with the actual circumstances encountered by the Field Scientists.

8.2 Verification Methods

Evaluation of the Experimental Design—the first step in validating the data set is to assess if the project, as executed, meets the requirements of the sampling design.

Sample Collection Procedures—Actual sample collection procedures will be documented in the field notebook and on applicable data sheets, and checked against any applicable requirements contained in this Monitoring Plan. Deviations from the Monitoring Plan will be classified as acceptable or unacceptable, and critical or noncritical.

8.3 Validation Methods

Calibration—Documentation of equipment calibration (i.e., where applicable) will be assessed to ensure that the values obtained are appropriate for data collection. Errors and omissions will be discussed in the final summary report. The documentation will be checked to ensure that the calibrations: (1) were performed at the specified intervals, (2) included the proper number of calibration points, and (3) were performed using appropriate approaches/standards for the reported measurements. Results generated during periods when calibration requirements are met will be considered conditionally valid and ready for Quality Control Validation review.

Data Reduction and Processing—The data processing system will be checked by using example raw data for which calculated values are already known. The example data are input into the system and the calculated results are compared to the known. Hand calculations will be used to check the data processing system. Findings from these audits will be included in the final report. Data will be considered conditionally valid if manual calculations are reconciled with automated data processing results.

QC Results and Procedures—QC measurements and QC procedures performed during the experimental program will be checked against the monitoring program requirements. Omissions will be discussed in the final summary report. Quality control results will be reviewed. Results that meet the DQOs and all other validation are considered valid. All results outside specified parameters will be discussed with the ATSDR EI Manager for corrective action.

SECTION 9
HEALTH AND SAFETY PLAN

9.1 Purpose

The purpose of this Health and Safety Plan (HASP) is to inform field personnel of known or potential health and safety hazards that may be encountered during ambient air monitoring activities planned for Thief River Falls, Minnesota. Accordingly, this HASP describes the possible hazards and the procedures required to minimize the potential for exposure, accidents and/or injuries during the scheduled work activities. This HASP has been reviewed by ATSDR and the ERG Laboratory Health and Safety Coordinator.

9.2 Scope

In order to better assess potential human exposure to selected chemical species in ambient air in the greater Thief River Falls area, ATSDR will conduct an Exposure Investigation (EI). During this EI, an ambient air monitoring program will be operated to obtain representative concentration data for H_2S and meteorological data, over a 3-week period.

9.3 Physical Hazards Assessment

Possible dangers associated with project activities include physical hazards related to heat stress; slips, trips, or falls; electrical hazards; excessive noise; lifting; and animals, poisonous plants, and poisonous insects. Brief descriptions of these potential physical hazards and measures for preventing, or mitigating the consequences of, the hazards follow:

1. Heat Stress C Ambient temperatures may be high enough to induce heat stress if field staff do not take appropriate preventive measures. Low winds and high humidity also contribute to heat stress, and both of these conditions may persist in Thief River Falls during the summer. Field staff must be familiar with the signs and symptoms of heat stress as presented below, and be aware of measures necessary to prevent its occurrence. Field staff can prevent heat stress using good common sense and awareness. Sampling team members should wear appropriate clothing and drink ample quantities of water and electrolyte solutions (water and drinks such as Gatorade should be purchased ahead of time). Flexible working and resting schedules should be used as needed depending upon conditions. If ambient temperatures exceed 90°F, field personnel should make efforts to limit their time in hot sunny areas and rotate where possible into cooler areas. If such heat waves persist, field personnel should monitor their heart rates on a regular basis. The resting pulse rate should not exceed 110 beats per minute. If employees note than their one-minute pulses exceed 110, they should stop work and contact the field team leader immediately and reduce work loads accordingly.

   - *Heat Rash*. Heat rashes may result from continuous exposure to excessive heat and humidity. Fieldworkers with heat rashes will be instructed to seek medical attention if symptoms persist.

   - *Heat Cramps*. Heat cramps are caused by heavy sweating with inadequate electrolyte replacement. Symptoms include muscle spasms and pain in the hands, feet, and abdomen. Fieldworkers with heat cramps will be instructed to seek medical attention if any of the symptoms persist.

   - *Heat Exhaustion*. Heat exhaustion occurs when one=s body loses the ability to maintain proper temperature. The signs of heat exhaustion include shallow breathing; pale, cool, and moist skin; profuse sweating; dizziness; nausea; and fatigue. Fieldworkers will be trained in the recognition of these symptoms and will be provided electrolyte solutions to help prevent heat exhaustion. If symptoms of heat exhaustion persist, the employees will be instructed to immediately move to a cool location and contact emergency medical services.

   - *Heat Stroke*. Heat stroke, with an estimated mortality rate of 50 percent, is the most severe form of heat stress. The signs and symptoms of heat stroke include red, hot, and dry skin; body temperatures exceeding 105°F; lack of perspiration; strong, rapid pulse; nausea; dizziness; confusion; and unconsciousness. If signs of heat stroke occur, victims will be instructed to immediately retreat to a cool place and contact the nearest medical facility (see Emergency Response Procedures). The affected person may return to work only after obtaining the approval of a doctor.

2. Slips, Trips, and Falls C Testing at the site is expected to occur primarily at ground level. Field personnel will use good safety sense in evaluating walking and working surfaces. It is expected that ATSDR will select monitoring sites such that neither testing personnel nor the general public will be injured by tripping or falling over test equipment. If work must be done above ground level (e.g., on rooftops, etc.), field personnel must take measures to ensure the safe access to these areas, including the use of safe equipment and remaining at a safe distance (at least 10 feet) from a building=s edge. All ladders or stairways must meet OSHA standards. Where possible, roofs should be accessed from windows or stairways. Field team leaders will review applicable OSHA rules with team members prior to assigning employees to work on roofs.

3. Electrical **C** Prior to installing equipment in the field, field staff will verify that all electrical equipment and cords are in good working condition. If additional extension cords are needed after arriving on site, the field team leader will purchase a high quality extension cord that works well under the testing conditions. Field workers will be instructed to immediately report to their team leaders any signs of malfunctioning electrical equipment.

4. Lifting Hazards C When carrying and lifting equipment, field staff should practice good lifting techniques and avoid carrying heavy loads.

5. Animals, Poisonous Insects, and Poisonous Plants C field staff should be alert for and stay clear of wild and unsupervised animals, poisonous insects and poisonous plants (e.g., poison ivy). Particularly, team members should also be aware of multiple poisonous spiders (e.g. brown recluse and black widow). As Thief River Falls is a rural/agricultural area, snakes could also be encountered.

   - Field staff will wear thick leather gloves, long pants, and long sleeve shirt. When entering the room that houses the monitoring equipment turn on all lights, if lights not available use a flash light to look around the sampling area before opening sampling container. Be aware of your surroundings; do not just blindly wander in the monitoring locations. Observation is critical to avoidance. Learn to check around with a sweeping glance for anything that seems out of place, your subconscious may notice a camouflaged animal. All monitoring equipment will be kept in a large sealed container; the vents will be screened to reduce the chance of animals and insects from entering the container.

- Tap the monitoring container before opening the container. Snakes and other animals have many sensing devices to warn them of your presence. Make plenty of noise and movements while entering the monitoring room to announce your presence.

- If a field staff is bitten by a snake, rodent, or spider, they should be taken to a medical facility immediately for treatment. Give the medical staff as much detailed information about the animal as possible. Describe the size, shape, and color of the animal.

9.4 Chemical Hazards Assessment

No chemicals will be used by the field staff for this EI effort. However, the sites have the potential for high concentrations of H_2S. As a result, field personnel will use a portable H_2S monitoring system while approaching these sites and during work on these sites. If a monitoring device alarms indicating unsafe levels of H_2S all personnel will leave the site immediately.

9.5 Contacts for Local Emergency Services

Prior to the first field activity, the field team leader will provide each of its field staff with the pertinent emergency contact information for the study area. This information will include the phone number(s) and address for the following:

Thief River Falls Police (Chief)
102 1st St. West
Thief River Falls, MN
(218)681-6161 or 911

Marshall County Sheriff=s Office (Sheriff John Novacek)
208 E. Colvin Ave.
Warren, MN
(218)745-5411 or 911

Northwest Medical Center
120 S. LaBree Ave.
Thief River Falls, MN
(218)681-4240

Thief River Falls Fire Department
320 2nd St.
Thief River Falls, MN
(218)681-3943 or 911

9.6 Staff Concurrences

Prior to working on this ambient air monitoring program, ATSDR and ERG will require all of its associated field staff to read and understand this HASP.

STAFF CONCURRENCE SHEET

I have read, understood, and agree to comply with this Project Health and Safety Plan.

Signature	Printed Name	Date
Signature	Printed Name	Date
Signature	Printed Name	Date
Signature	Printed Name	Date
Signature	Printed Name	Date

Appendix C: Memo. Criteria for Hydrogen Sulfide (H2S); Air Monitoring Data Near Excel Dairy

Memo

MINNESOTA MDH DEPARTMENT OF HEALTH

Date: June 25, 2008 corrected July 21, 2008

To: John Linc Stine, Director
Environmental Health Division

From: Rita B. Messing, Ph.D., Supervisor
Site Assessment and Consultation Unit
Rita B. Messing 7/21/08

Subject: Criteria for Hydrogen Sulfide (H_2S); Air Monitoring Data Near the Excel Dairy

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(Note: 1 ppm = 1.42 mg/cu.m . 1 mg/cu.m = 0.7 ppm. Hydrogen sulfide measurements and standards are often reported in ppm or ppb, but occasionally standards are given in mg/cu.m.).

The purpose of this memo is to briefly describe some toxic effects of hydrogen sulfide, document criteria developed by different regulatory and health agencies, and summarize monitoring data around the Excel Dairy near Thief River Falls, Minnesota. Finally, a recommended action level range is provided.

I. Notes on Toxicity

Hydrogen sulfide (H_2S) is a gas that is heavier than air, and releases of H_2S can sometimes travel in relatively compact plumes close to the ground. It is not rare for people who enter confined spaces, such as manure pits, to be overcome and to die (NIOSH, 2008).

Perhaps of more relevance to the general public is an incident that occurred in Terre Haute, Indiana in May and June, 1964 (Public Health Service, 1964). Hydrogen sulfide was released from a chemical disposal lagoon on the other side of the Wabash River from the City. The Indiana State Board of Health requested that the Public Health Service (PHS) evaluate the air pollution, and the PHS conducted air monitoring. PHS epidemiologists also investigated odor complaints, reviewed mortality records for February thru May, 1964, reviewed emergency room records from the 2 Terre Haute hospitals, and studied absenteeism in one of the hospitals. The highest air measurements at the fence line were between 2 and 8 ppm. Hourly samples were taken at 5 different locations in the City. All but one hourly H_2S measurement in the city were less than 300 ppb (maximum obtainable). Levels of 100 ppb or higher were recorded 5 times in 185 measurements over 5 days. NIOSH (1977) has evaluated this event in their summary document for their occupational criterion for H_2S.

> "Conclusions of the study were that complaints were related to the concentrations of hydrogen sulfide in the air and that potential danger existed for susceptible individuals (notably infants, the aged, and the infirm). Worker populations are generally healthier than city populations and might prove less susceptible to the effects of hydrogen sulfide. Still, this study did suggest that hydrogen sulfide can irritate the eyes and respiratory system at concentrations below 1 ppm, and that it has adverse effects on sleep and appetite and poses a danger at low concentrations to individuals with heart or lung diseases."

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www.health.state.mn.us

The odor threshold for hydrogen sulfide is variable, ranging from 0.5 to 300 ppb. At high concentrations people lose the ability to smell H_2S, making it very dangerous (ATSDR, 2006). Occupational exposure limits protect against loss of smell that could lead to exposures to "knockdown" or even lethal levels of hydrogen sulfide.

EPA (2000) cites a memo from the State of Texas reporting persistent eye and throat irritation, headache and nausea experienced by 6 workers in a monitoring van exposed to a mean concentration of 90 ppb for 5 hours downwind from a refinery. Impaired lung function has been observed in asthmatics exposed to 2 ppm of hydrogen sulfide for 30 minutes (Jappinen, 1990; cited by ATSDR, 2006).

EPA (2003) reviewed a case report of a 20-month old child who lived next to a coal mine where a "burning tip" emitted H_2S for nearly a year. The maximum recorded level at the child's house was 0.6 ppm, but levels may have been higher previous to onset of monitoring. The child developed paroxysmal tonic deviation of the eyes. The abnormal eye movements resolved after a few months but progressive involuntary movements of the body developed, the child fell frequently, and had disturbance of muscular control needed for speech production. The child was admitted to the hospital, and a brain scan suggested toxic encephalopathy. Shortly after hospital admission the child's condition improved spontaneously; ten weeks after admission ataxia was resolved and involuntary movements were reduced. A brain scan was normal. EPA notes that in humans the period of rapid development of the nervous system (synaptogenesis) extends from late gestation to several years after birth, and that children of a certain age may be selectively susceptible to the neurological effects of H_2S, although "ascribing relevance of this apparent susceptibility to environmental levels of H_2S would be…conjectural." However, in conjunction with the evidence from animal studies of effects on H_2S on the development of the nervous system (see paragraph below), EPA concluded that a possibility of children's vulnerability to effects from high levels of exposure to H_2S may exist.

ATSDR (2006) has also reviewed evidence from animal studies that subchronic exposures of rats (6 hrs/day, 7 days/week for 10 weeks) at 30 ppm results in olfactory neuron loss (Brenneman et al., 2000; cited in ATSDR, 2006). Exposures from 20 ppm to 80 ppm to developing rats (5-21 days postnatally) results in subclinical alterations in neurochemistry and neuroanatomy (cf. ATSDR, 2006).

II. Criteria for Hydrogen Sulfide

A. Occupational Criteria for Hydrogen Sulfide (from ATSDR, 2006, unless noted with *)
TWA = time weighted average

IDLH—Immediately Dangerous to Life and Health (NIOSH)	100 ppm
C—Ceiling (Acceptable maximum peak for an 8 hr shift) (OSHA)	50 ppm
C-- Ceiling (Acceptable--15 min TWA-- concentration (OSHA)	20 ppm
STEL (short-term exposure limit; 15 min TWA) (ACGIH*)	15 ppm
PEL (Permissible Exposure Limit; 8 hr TWA) (MN OSHA*)	10 ppm
TLV (Threshold Limit Value; 8 hr TWA) (ACGIH*)	10 ppm
REL (Recommended Exposure Limit; 10 min TWA) (NIOSH)	10 ppm

Note that ACGIH STEL is below the OSHA 15 minute Ceiling, and that the NIOSH REL is more stringent than the MN OSHA PEL and the ACGIH TLV.

As noted by NIOSH (see above), occupational exposure limits are set to protect a healthy worker population. Additionally, workers who are paid may accept some health consequences of working, often have access to protective equipment, and may be able to take other measures to avoid exposures that are not practical for people exposed in their dwellings or on their property. Occupational standards are not protective for the general population, including children, the elderly, or people with health problems, including people with asthma or other respiratory problems, and people with compromised immune systems.

B. EPA Interim Acute Exposure Guideline Levels (AEGLs)

According to EPA (www.epa.gov/oppt/aegl/) "AEGLs are intended to describe the risk to humans resulting from once-in-a-lifetime, or rare, exposure to airborne chemicals. The National Advisory Committee for AEGLs is developing these guidelines to help both national and local authorities, as well as private companies, deal with emergencies involving spills, or other catastrophic exposures." Further, "Acute exposures are single, non-reptitive exposures for not more than 8 hours." AEGLs are *not* meant to be safe levels for repeated exposures of people.

Interim AEGL-1: "…airborne concentration… above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects. Effects are not disabling, and are transient and reversible upon cessation of exposure." (Asymptomatic effects could be biochemical changes, or reversible effects on body organs.)

10 min	750 ppb
30 min	600 ppb
60 min	510 ppb
4 hrs	360 ppb
8 hrs	330 ppb

Interim AEGL-2: "…airborne concentration… above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long lasting adverse health effects or an impaired ability to escape."

10 min	41 ppm
30 min	32 ppm
60 min	27 ppm
4 hrs	20 ppm
8 hrs	17 ppm

Interim AEGL-3: "…airborne concentration… above which it is predicted that the general population, including susceptible individuals, could experience life-threatening adverse health effects or death."

10 min	76 ppm
30 min	59 ppm
60 min	50 ppm
4 hrs	37 ppm
8 hrs	31 ppm

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C. Health-Based Criteria for Exposures to the General Population

ATSDR acute MRL (minimal risk level) 70 ppb
Exposures for 1 day up to 14 days
Basis: Jappinen study. LOAEL = 2 ppm.
UF = 30 (3 for minimal LOAEL; 3 for human variability, 3 database deficiencies: concern for 30 min duration of the original study). (*UF was misreported in 6/25/08 memo.*)

ATSDR intermediate MRL 20 ppb
Exposures for 15 days to 1 year
Basis: Brenneman study.
NOAEL = 10 ppm.
LOAEL = 30 ppm for olfactory neuron loss and nasal lesions. ATSDR noted the steep dose-response curve, with effects at 30 ppm and 80 ppm virtually identical.
$NOAEL_{adj}$ = 2.5 ppm—accounts for exposure for only part of a day.
UF = 30, including 3 for interspecies extrapolation; 10 for human variability.

EPA RfC (reference concentration; IRIS) 2 microg/cu.m (1.4 ppb)
Chronic exposure.
Basis: Brenneman study.
NOAEL = 13.9 mg/cu.m (10 ppm).
$NOAEL_{adj}$ = 3.48 mg/cu.m.
$NOAEL_{HEC}$ = 0.64 mg/cu.m. (accounts for differences in rat/human respiratory system).
UF = 300, including 3 for interspecies extrapolation; 10 for sensitive populations; and 10 for extrapolation from subchronic to chronic exposure.

MDH HRV (Health Risk Value) 10 microg/cu.m (7 ppb)
Subchronic exposure (up to 13 weeks).
Basis: Previous IRIS value with subchronic to chronic UF removed.

MPCA Hydrogen Sulfide Rules
30 ppb no more than 2 times in 5 days.
50 ppb no more than 2 times per year.
Basis: Odor.

III. Measured Levels of Hydrogen Sulfide Near the Excel Dairy

Marshall County public health officials reported to MDH that approximately 12-15 families within ½ mile of the Excel Dairy are potentially affected by hydrogen sulfide gas (H_2S). Citizens have telephoned various agencies to complain. They have also rented a Jerome meter to measure H_2S and have developed a protocol to take readings every two minutes at one of two properties that appear to be the worst affected. They video tape their activities. Citizens have faxed copies of the calibration of the Jerome meter done by Arizona Instruments, LLC, as well as copies of their data sheets. They have recorded many periods of hydrogen sulfide readings in the hundreds of parts per billion (ppb), and some readings over 1 part per million (ppm). The highest two minute reading was 6.8 parts per million. The highest 10 minute period was over 5 ppm, and the highest 30 minute period was over 1.8 ppm.

The Minnesota Pollution Control Agency (MPCA) has a continuous air monitor (CAM) measuring H_2S to the west of the dairy manure lagoons, in between the lagoons and one of the houses mentioned above. The CAM has been in operation since May 19. The maximum value recorded by the CAM is 90 ppb. From May 19 at 12:30 hours to June 19 at 10:00 hours the following high readings of H_2S (over 30 ppb) have been recorded:

Date	30 min. periods > 30 ppb	30 min. periods > 90 ppb
5-23	9	
5-24	21	13
5-25	4	2
5-28	4	
5-29	22	12
5-31	6	
6-2	1	
6-3	23	17
6-4	24	14
6-6	9	2
6-8	20	8
6-9	9	
6-11	24	9
6-12	5	3
6-18	4	

The MPCA also has a CAM to the northeast of the facility, which has very few measurements of H_2S above 30 ppb and none above 90 ppb. This CAM also is recording meteorological data that can be used to confirm wind direction. This CAM recorded 4 half hour periods over 30 ppb on June 8, 3 on June 9, 1 on June 12, 2 on June 13 and 2 on June 18. No periods above 90 ppb were recorded.

The citizen data indicate a problem but do not provide definitive measurements of possible exposures. The MPCA CAMs are in place for compliance monitoring as close to the facility fence lines as feasible. They indicate violations of MPCA air quality standards for hydrogen sulfide (no more than two 30 min. periods of H_2S above 30 ppb in 5 days, or two 30 min. periods of H_2S above 50 ppb in any year). Their purpose is not to measure actual human exposures or to assess health risks. The standards are useful for regulatory purposes and are based on odor.

IV. Conclusions

In a discussion on June 24 between Rita Messing and Hillary Carpenter, the following conclusions were reached:

1. The MPCA monitoring data indicate prolonged and repeated exceedances of 90 ppb of hydrogen sulfide.
2. Releases from the Dairy are uncontrolled so that the worst case hydrogen sulfide air concentration is unknown.
3. There is uncertainty in many of the air measurements. These include actual levels of hydrogen sulfide when CAMs register air concentrations in excess of 90 ppb, and uncertainties related to reliability of citizen monitoring.

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4. Data indicate possible repeated exposures to elevated levels of hydrogen sulfide.
5. Repeated exposures to hydrogen sulfide above 90 ppb arguably cause toxicity related symptoms in some people.
6. Exposures to hydrogen sulfide above 1 ppm are possibly dangerous to sensitive portions of the population; i.e., these exposures may cause symptoms requiring hospitalization.

V. Recommendation

State agency meetings are needed to set policy regarding response to possible exposures to high levels of hydrogen sulfide.

References for Toxicity Section

ATSDR, 2006. *Toxicological Profile for Hydrogen Sulfide.*

EPA, 2000. *Federal Register*, March 15 2000; Volume 65, Number 51, pp. 14185-14197.

EPA, 2003. Toxicological Review of Hydrogen Sulfide. EPA/635/R-03/005, www.epa.gov/iris

NIOSH, 1977. Criteria for a recommended standard for occupational exposure to hydrogen sulfide.

NIOSH, 2008. www.cdc.gov/niosh/face/

Public Health Service, 1964. The Air Pollution Situation in Terre Haute, Indiana with Special Reference to the Hydrogen Sulfide Incident of May-June, 1964. U.S. Department of Health, Education and Welfare, Public Health Service, Division of Air Pollution, June 19, 1964.

Cc: Larry Gust
Pamela Shubat
Hillary Carpenter
Tannie Eshenaur
Kathleen Norlien
Dale Dorschner

Appendix 2

DEPARTMENT OF HEALTH & HUMAN SERVICES
Public Health Service

Agency for Toxic Substances
and Disease Registry
Atlanta, GA 30333

MINNESOTA MDH DEPARTMENT OF HEALTH

September 19, 2008

Cheryl Newton
Acting Director, Air and Radiation Division
United States Environmental Protection Agency, Region 5
77 W. Jackson Blvd., MS ATSD-4J
Chicago, IL 60604

Gaylen Reetz
Director, Regional Division
Minnesota Pollution Control Agency
520 Lafayette Road
St Paul, MN 55155

Dear Ms. Newton and Mr. Reetz:

We are writing to inform you of the finding of a public health hazard associated with community exposures to hydrogen sulfide air emissions from the Excel Dairy, Excel Township, Marshall County, Minnesota (near Thief River Falls, MN). This conclusion is based on air monitoring data collected by the Minnesota Pollution Control Agency (MPCA) and by the Agency for Toxic Substances and Disease Registry (ATSDR) during an Exposure Investigation (EI). A more formal and complete Exposure Investigation report, including more detailed descriptions of methodologies and results, will be available later this year.

Background

The Excel Dairy under the ownership of The Dairy Dozen of Veblen, South Dakota has been permitted since 2006. The Dairy has a capacity of 1544 animal units or 1100 cows over 1,000 pounds (milked or dry) (Permit MN0068594). The Dairy has 3 free-stall barns, a sand separator building, a feed storage pad, and 3 earthen manure storage basins or lagoons. The lagoons are either uncovered or incompletely covered, and are thought to be the major source of odors and emitters of hydrogen sulfide (H_2S) at the facility. Approximately 12 families live within 1 mile of the Excel Dairy.

The Minnesota Department of Health (MDH) and the Minnesota Pollution Control Agency (MPCA) received complaints from citizens about odors, health effects and hydrogen sulfide (H_2S) emissions originating at the Dairy. Citizen health complaints included upper respiratory effects (such as nasal congestion and sore throats), itchy eyes, trouble breathing, nausea and headaches.

In response to these complaints, MPCA installed two continuous air monitors (CAMs) at the fence line to the northeast (May 6, 2008) and to the west (May 19, 2008) of the on-site manure lagoons at Excel Dairy. MPCA also installed meteorological equipment at the northeast site. Figure 1 shows the relationship of MPCA air monitoring equipment to the Dairy. Since the range of the MPCA H_2S monitors were from 0-90 ppb, air concentrations in excess of 90 ppb could not be quantified. As a result, the maximum concentrations at those locations are unknown.

Minnesota Ambient Air Quality Standards (MAAQS) require that there be no more than two 30 minute periods of H_2S above 30 ppb in 5 days, or no more than two 30 minute periods of H_2S above 50 ppb in any year (Minnesota Administrative Rules 7009.0080). Standards are applicable at the property boundary of the facility, and/or at locations to which the general public has access. Large livestock facilities are exempt from these requirements for a maximum of 21 days per calendar year during and for 7 days after manure is removed from barns or manure storage facilities. Operators of livestock facilities claiming this exemption are required to provide notice to either the MPCA or the county feedlot officer. The MPCA may not require air emissions modeling for a type of livestock system that has not had a hydrogen sulfide emission violation (Minnesota Statutes 116.0713). MDH has promulgated a subchronic Health Risk Value (HRV) for hydrogen sulfide of 7 ppb for a period of 13 weeks (Minnesota Administrative Rules 4717.8000-4717.8600).

Over a 4 month period (May-Sept), MPCA monitoring data showed the hydrogen sulfide levels exceeded 30 ppb for 15.5 hours (cumulative) at the northeast monitor location and for 172.5 hours (cumulative) at the west monitor location. Furthermore, despite the fact that the maximum concentrations for the MPCA data are not known, the average concentration over that period exceeded the subchronic HRV of 7 ppb.

The Minnesota Attorney General and the MPCA filed an Interim Order for injunctive relief against the Excel Dairy owner on June 20, 2008 to address operational shortfalls contributing to these ambient releases of hydrogen sulfide. As you are aware, these exceedences also prompted the Notice of Violation issued by USEPA to Excel Dairy owners on July 18, 2008.

Toxicity of Hydrogen Sulfide

Of all of the chemicals that are emitted from the storage, handling, and decomposition of animal wastes, hydrogen sulfide is one of the most important. This is due to the fact that large amounts of hydrogen sulfide gas are produced under anaerobic conditions and that is a gas that is heavier than air. As a result, it has the ability to accumulate in low-lying areas and when meteorological conditions lead to less air mixing. The odor threshold for hydrogen sulfide ranges from 0.5 to 300 ppb. Adverse health effects associated with short-term exposures to hydrogen sulfide include airway constriction in individuals who have asthma, decreased lung function, eye irritation, dizziness, nausea, and headache. Acute exposures to high concentrations (greater than 100 ppm) may result in pulmonary edema, physical collapse, and death (ATSDR, 2006). Although many of these effects from acute exposure are reversible, exposure to high concentrations for even a short period can lead to long-lasting neurological impacts.

Long-term or repeated episodic exposures to hydrogen sulfide are likely to result in the same types of reversible effects observed with acute exposures, such as irritation of nose and respiratory tract, headaches and nausea (cf. MDH, 2008, Collins and Lewis, 2000). There is only limited epidemiological data assessing the potential for irreversible effects from chronic exposures low level (below 1 ppm). However, several studies and case reports have observed neurological effects with such low level exposure (ATSDR, 2006).

ATSDR Exposure Investigation

A group of citizens acquired a Jerome 631-X meter (instrument for measuring hydrogen sulfide in air), and developed a protocol to document readings of hydrogen sulfide. This citizen group submitted data to MDH, showing many periods of hydrogen sulfide in the hundreds of parts per billion (ppb), and on one occasion citizens submitted data with periods in excess of 1,000 ppb of H_2S. These detections were reported as various locations near residences and areas outside of the Excel facility.

Based on a request from MDH to collect more data about community exposures to hydrogen sulfide, ATSDR approved the request for an Exposure Investigation (EI) on June 19, 2008. On July 9, 2008, ATSDR staff initiated sampling for hydrogen sulfide levels at three residential locations in proximity to the Excel Dairy (Figure 1). The sampling instruments, known as Single Point Monitors, were placed at both outdoor and indoor locations at these locations. The monitors detected the concentration of hydrogen sulfide continuously throughout the day for a 2-3 week period at each location. In addition, the two MPCA monitoring stations continued to collect data during the ATSDR EI at the fence line to the northeast and west of the onsite manure lagoons.

Although hydrogen sulfide is the target contaminant for the EI, it is acknowledged that over 80 chemicals are known to be emitted to air from dairy operations. In addition to hydrogen sulfide, chemicals that could contribute to odors and irritation include ammonia and other reduced sulfur compounds including dimethyl sulfide and dimethyl disulfide (Filipy et al., 2006).

Results from EI

In addition to the MPCA air standard for hydrogen sulfide (no more than two 30 minute periods of H_2S above 30 ppb in 5 days, or no more than two 30 minute periods of H_2S above 50 ppb in any year), the air monitoring data were compared to the ATSDR Minimal Risk Levels (MRLs) for acute or intermediate exposures. The acute MRL for hydrogen sulfide exposure is 70 ppb is based on respiratory effects in humans resulting from a 30 minute exposure. The intermediate MRL is 20 ppb, based on neurological effects in animals resulting from exposure over a 10 week period. Other comparison criteria are summarized in Table 1. Background concentrations of hydrogen sulfide in outdoor air are typically less than 1 ppb (ATSDR, 2006).

The data indicate that both ATSDR and MPCA health based guidelines were exceeded at all five ATSDR and MPCA sampling locations. At ATSDR sampling locations S1 and S3, where monitoring occurred over a 15 day period from July 16-July 31, ambient air concentrations reached levels up to 481 ppb, with many periods where air concentrations were over 100 ppb. Furthermore, many of these episodes of elevated hydrogen sulfide concentrations lasted for many hours. During a two week period, ambient concentrations of hydrogen sulfide at Site 3, the residence in closest proximity and most affected by site releases, exceeded the acute ATSDR MRL for over 8 hours (cumulative), but the average concentration over that time did not exceed the intermediate ATSDR MRL.

During this same period, the 30 min average concentrations at the MPCA Site 2 monitor (west of facility and closest to the manure lagoons) exceeded the acute ATSDR MRL for 10.5 hours. The MPCA air quality standards for H_2S were exceeded over 300 times at the MPCA monitoring stations before, during, and after the EI (May-Sept). Comparison of the MPCA data to longer duration criteria (e.g. ATSDR Intermediate MRL) is limited because the maximum concentrations were not quantifiable with their monitoring.

Child Health Considerations

Citizens have reported the presence of children on the Dairy site. During the EI, ATSDR and MDH staff noticed a toddler onsite in at a mobile home. It is unknown whether or not workers and their families live onsite. Manure lagoons are unrestricted and easily accessible to workers and their families. Therefore, children living on or near this site may be at risk for elevated exposures to hydrogen sulfide.

Conclusions

Although ATSDR did not conduct a formal health study to evaluate the health of people living on or near Excel Dairy, the symptoms described by the residents to ATSDR and MDH staff were consistent with the known acute health effects of hydrogen sulfide exposure. Based on the air monitoring data collected by during the EI and by MPCA, ATSDR and MDH conclude that inhalation exposure to hydrogen sulfide poses a *public health hazard* to area residents.

No data has been provided to ATSDR or MDH to determine the concentration of hydrogen sulfide exposure that individuals who work or live on the Excel Dairy property may experience. However, given their proximity to the source of emissions, the exposure of these individuals may be a significant health concern.

Recommendations

1) Excel Dairy should take action immediately to implement improved emission control measures that will significantly reduce the levels of exposure to hydrogen sulfide gas released from onsite operations.

2) MPCA and Excel Dairy should coordinate to implement an air monitoring program to verify the effectiveness of emission control measures in reducing the release of hydrogen sulfide gas.

3) Excel Dairy should restrict access to lagoons to reduce physical hazards and direct exposures to trespassers and children living on-site.

ATSDR and MDH are available to consult further with U.S. EPA and MPCA on remediation efforts at this site. If you have any questions, please contact Mark Johnson at the ATSDR Region 5 Office (312-886-0840) or Rita Messing at MDH (651-201-4916).

Sincerely,

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MDH, 2008. Memo from Rita B. Messing to John Linc Stine.

Table 1: Guidelines for hydrogen sulfide exposures

	Exposure Value	Exposure Period/Intent
State of Minnesota	30 ppb, no more than twice in 5 days	Ambient Air Quality Standard, not to be exceeded except for exceptions noted in Minnesota Laws.
State of Minnesota	50 ppb no more than twice per calendar year	Ambient Air Quality Standard, not to be exceeded except for exceptions noted in Minnesota Laws.
ATSDR	70 ppb	Acute Minimal Risk Level—value for up to 14 days of exposure. Exposures below this value are not expected to result in non cancerous adverse health effects
ATSDR	20 ppb	Intermediate Minimal Risk Level—value for between 15-365 days of exposure. Exposures below this value are not expected to result in non-cancerous adverse health effects
State of Minnesota	7 ppb	Health Risk Value (HRV) — Subchronic exposure (up to 13 weeks)
California EPA	30 ppb	Reference Exposure Limit (REL) —Acute exposure, up to 1 hr
AIHA	100 ppb	ERPG-1—The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor
USEPA	1.4 ppb	Reference concentration (RfC): concentration for a substance in air that EPA considers unlikely to cause noncancer health effects over a lifetime of chronic exposure.
WHO	14 ppb	Medium-term tolerable concentration: The level at which exposure could occur for up to 90 days without appreciable risk of adverse health effects.

Figure 1. Excel Dairy with ATSDR and MPCA Monitoring Stations.

Figure 2: Data trends for most adversely affected ambient air during the ATSDR Exposure Investigation- Residential Monitoring Site 3