

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:

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ATSDR/DHAC/EISAB

Introduction

Purpose of Exposure Investigation

In order to better assess potential human exposure to airborne concentrations of hydrogen sulfide (H₂S) 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

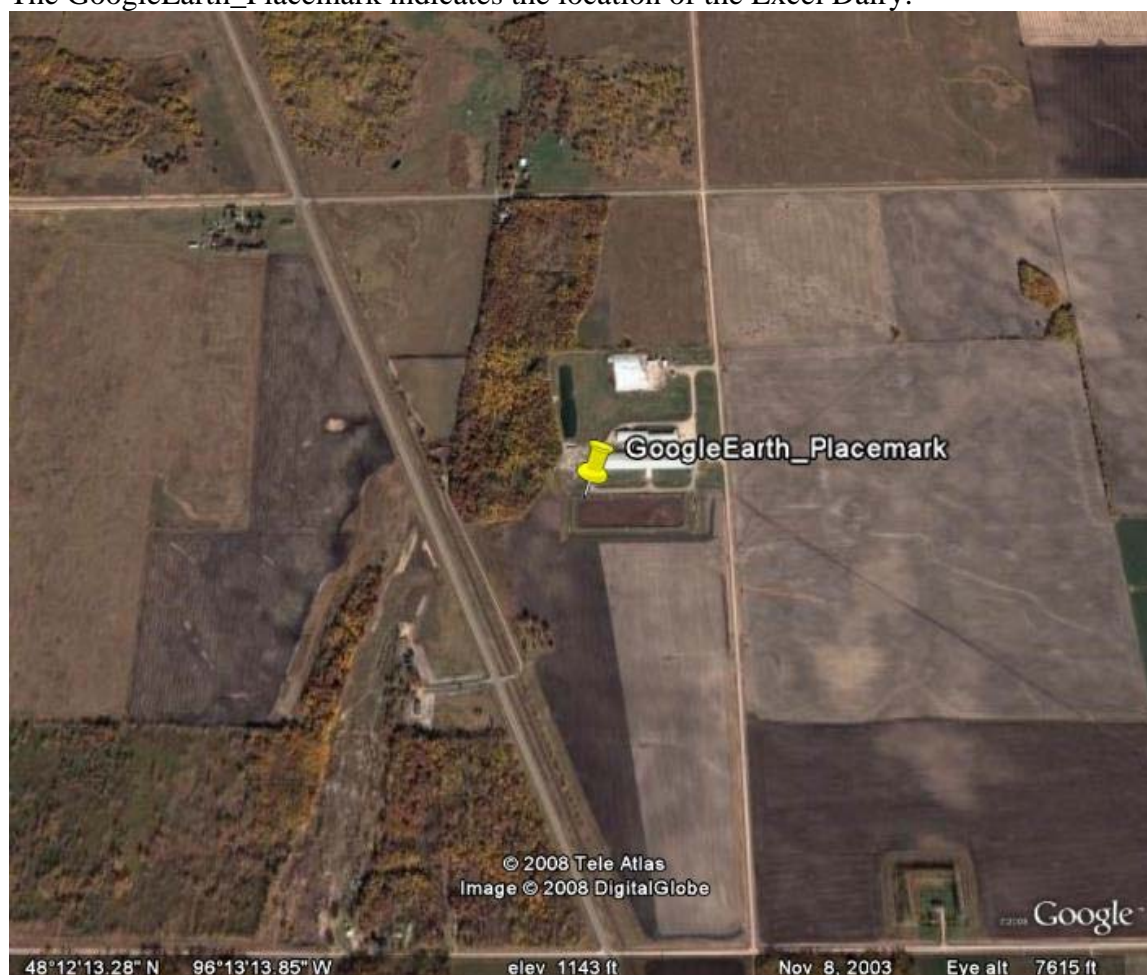
On June 10, 2008, the U.S. EPA Region 5 Air and Radiation Division (ARD) received an e-mail communication from a citizens' group advising ARD that on June 8, 2008, Minnesota health officials advised several families to evacuate their homes the prior week after hydrogen sulfide (H₂S) fumes from Excel 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 (H₂S). Citizens have telephoned various agencies to complain. They have also rented a Jerome meter to measure H₂S 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 H₂S 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 H₂S (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 H₂S 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 H₂S above 30 ppb in 5 days, or two 30 min. periods of H₂S 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 H₂S. 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 H₂S 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 H₂S 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 H₂S for three weeks. One of the ambient H₂S 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 H₂S 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 H₂S 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 H₂S 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 H₂S 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 H₂S 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 H₂S 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 H ₂ S 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 (H₂S): 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 (H₂S) 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**

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June 2008

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Mr. Dave Dayton
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DISTRIBUTION LIST

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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 ₂ S | 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 (H₂S) 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 H₂S, 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 H₂S 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 H₂S 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 H₂S, 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 H₂S 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.

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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

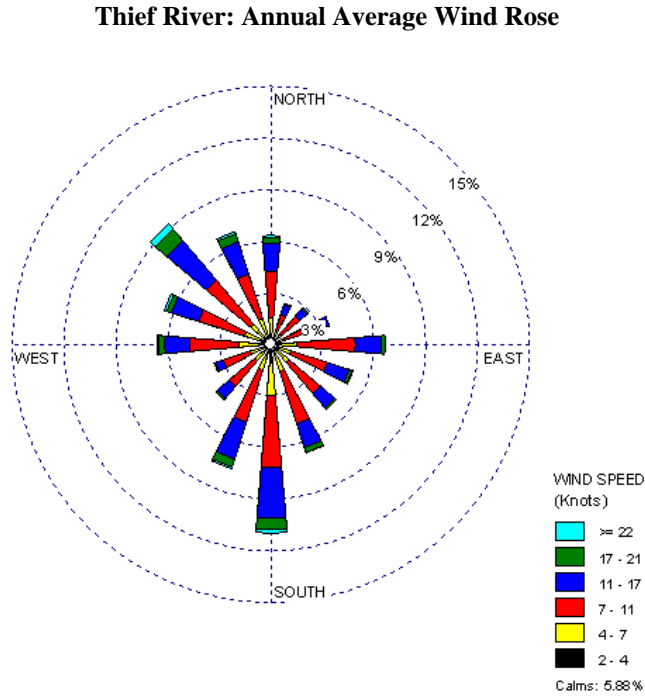
participation consent has been obtained, ATSDR and ERG will contact the participants directly to schedule site events (i.e., deployment, operation, and recovery).

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.

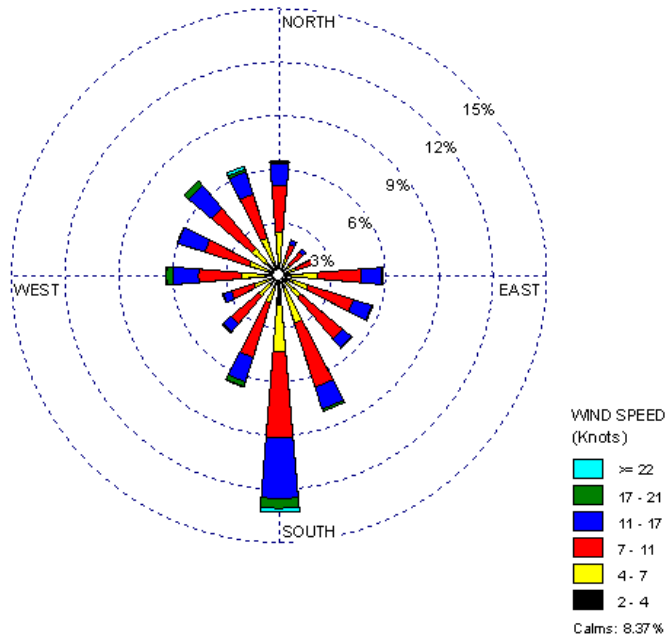
3.2 Pre-Site Survey

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: 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 H₂S, a hand held monitor for H₂S, 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 H₂S 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 H₂S 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 H₂S 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 ₂ S Indoors/low Continuous H ₂ S Outdoors/low Continuous H ₂ S Outdoors/mid or high |
| 2 | Private Residence | Continuous H ₂ S Indoors/low Continuous H ₂ S Outdoors/low Continuous H ₂ S Outdoors/mid or high Continuous meteorological |

3.5 Monitoring

From the point that the H₂S 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 H₂S 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 H₂S 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 H₂S 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 H ₂ S 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 expressed 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:

- *H₂S across instruments by type*—As part of the pre- and post-deployment QC checks, the eleven H₂S 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 H₂S 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 H₂S 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 H₂S 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 H₂S, 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 H₂S 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 that 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 H₂S. As a result, field personnel will use a portable H₂S monitoring system while approaching these sites and during work on these sites. If a monitoring device alarms indicating unsafe levels of H₂S 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 |
|-----------|--------------|------|

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

Memo



Date: June 25, 2008 corrected July 21, 2008
To: John Linc Stine, Director
Environmental Health Division
From: Rita B. Messing, Ph.D., Supervisor *Rita B. Messing 7/21/08*
Site Assessment and Consultation Unit
Subject: Criteria for Hydrogen Sulfide (H₂S); Air Monitoring Data Near the Excel Dairy

(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 (H₂S) is a gas that is heavier than air, and releases of H₂S 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 H₂S 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 H₂S.

"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."

John Linc Stine
 June 25, 2008 corrected July 21, 2008 Page 2

The odor threshold for hydrogen sulfide is variable, ranging from 0.5 to 300 ppb. At high concentrations people lose the ability to smell H₂S, 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 H₂S 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 H₂S, although “ascribing relevance of this apparent susceptibility to environmental levels of H₂S would be...conjectural.” However, in conjunction with the evidence from animal studies of effects on H₂S 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 H₂S 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/aepl/) "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-repetitive 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 (H₂S). Citizens have telephoned various agencies to complain. They have also rented a Jerome meter to measure H₂S 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 H₂S 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 H₂S (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 H₂S 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 H₂S above 30 ppb in 5 days, or two 30 min. periods of H₂S 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.

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