Public Health Assessment

Gopher State Ethanol, City of St. Paul

Ramsey County, Minnesota

September 19, 2003

Prepared by

The Minnesota Department of Health
Under Cooperative Agreement with the
Agency for Toxic Substances and Disease Registry

Foreword

This document summarizes health concerns associated with the Gopher State Ethanol, St. Paul, Ramsey County, Minnesota. It is based on a formal site evaluation prepared by the Minnesota Department of Health (MDH). A number of steps are necessary to do such an evaluation:

- Evaluating exposure: MDH scientists begin a site evaluation by reviewing available information about environmental contamination at the site, or emitted from the site. The first task is to find out how much contamination is present, where it is found, and how people might be exposed to it. Usually, MDH does not collect its own environmental sampling data; instead MDH relies on information provided by the Minnesota Pollution Control Agency (MPCA), the U.S. Environmental Protection Agency (EPA), and other government agencies, businesses, and the general public. MDH can also request additional data from the MPCA and EPA.

- Evaluating health effects: If there is evidence that people are being exposed—or could be exposed—to hazardous substances, MDH scientists will take steps to determine whether that exposure could be harmful to human health. The report focuses on public health i.e., the health impact on the community as a whole and is based on existing scientific information.

- Developing recommendations: In the evaluation report, MDH outlines its conclusions regarding any potential health threat posed by a site and offers recommendations for reducing or eliminating human exposure to contaminants. The role of MDH in dealing with individual sites is primarily advisory. For that reason, the evaluation report will typically recommend actions to be taken by other agencies—including EPA, MPCA or local government. However, if an immediate health threat exists, MDH will issue a public health advisory warning of the danger and will work to resolve the problem.

- Soliciting community input: The evaluation process is interactive. MDH starts by soliciting and evaluating information from various government agencies, the organizations responsible for cleaning up the site, and the community surrounding the site. Any conclusions about the site are shared with these groups and organizations that provided the information. Once an evaluation report has been prepared, MDH seeks feedback from the public. *If you have questions or comments about this report, you are encouraged to contact MDH.*

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Summary

The Minnesota Pollution Control Agency (PCA) requested the Minnesota Department of Health (MDH) investigate health concerns associated with emissions from the Gopher State Ethanol (GSE) facility. The GSE plant started out as the Minnesota Brewing Company (MBC) and expanded its facility in West 7th Street neighborhood of St. Paul, Minnesota to include ethanol and CO_2 production in the spring of 2000. MBC discontinued beer brewing at the facility in June 2002. GSE is on the north side of the Mississippi River Valley approximately 3 miles southwest of downtown St. Paul. This public health assessment evaluates the emissions of the entire Minnesota Brewing Company/Gopher State Ethanol/MG-CO_2 facility.

Beer, ethanol and CO_2 production at the MBC/GSE/MG-CO_2 facility resulted in odorous emissions that impacted neighborhoods miles from the facility. Although beer brewing has stopped, state and city officials have received hundreds of complaints of nauseating and irritating odors. Citizens have complained that the offensive odors have initiated or aggravated asthma attacks. Other health effects, such as shortness of breath, difficulty breathing, skin rashes, head aches, changes in sleeping and eating patterns have also been reported. The most obvious source was the 206 foot-tall Distilled Dried Grains Solids (DDGS) dryer stack. Emissions tests were performed for the DDGS dryer stack, TO, Distillation Scrubber, and Fermentation Scrubber (CO2 Scrubber). Initially, the DDGS stack was monitored for only methanol and ethanol. MDH specifically requested aldehyde and ketone emissions data to be collected from the DDGS dryer. The results showed the presence of numerous irritant and odorous VOCs. More specific data were subsequently collected to quantify 11 of the most common contaminants. Test results showed that GSE was a “major source” (greater than 100 tons/year, as defined in the U.S. Clean Air Act). A Thermal Oxidizer (TO) was installed to control emissions, and the U.S. Environmental Protection Agency (EPA) and the PCA began enforcement actions to ensure that GSE and 11 other ethanol plants in Minnesota would be appropriately permitted in accordance with the Clean Air Act requirements. The EPA also compared GSE emissions data presented in this report with emission data collected from other ethanol plants in Illinois and Indiana and determined other ethanol plants that dry their mash were also “major sources” and in violation of the Clean Air Act. The Amended Gopher State Ethanol Consent Decree requires more rigorous emissions monitoring and implementation of emission controls.

Chemical emission data from Gopher State Ethanol DDGS dryer stack were also used in an air dispersion model to estimate the highest one-hour and annual average air concentrations of 11 compounds. None of the estimated exposure concentrations exceeded health criteria, but the model did not include all the emission sources at GSE/MG-CO_2.

The TO experienced numerous operational problems including two fires and other mechanical failures resulting in only intermittent use and failure after less than one and a half years. When it failed, GSE shipped the DDGS off-site wet (wet process) for several months. A new TO was installed and began operation in January 2003, to control DDGS dryer gasses. The additional emissions from the cooling cyclone, CO_2 carbon beds, thin and stillage surge tank that were controlled by the original TO are not treated with the new TO. The first engineering tests were scheduled for March 2003; and performance tests scheduled for summer of 2003.

The St. Paul HAZMAT team has responded to two anhydrous ammonia releases at facility. One of the releases involved a “run-a-way” ammonia compressor that could not be shut off. Several people received medical attention. The HAZMAT team measured ammonia concentrations above health criteria 300 feet from the release site.

Particulate testing was conducted on the Grain Cooler Stack and the Baghouse Stack. Although test results suggest that these particulate sources are in compliance under “normal” operating conditions, residents around the plant have complained that they often find a small yellow particulate on their windowsills and cars. Recent improvements to plant operations have lowered particulate emissions.

Odor testing was also conducted at the DDGS dryer stack, cooling cyclone, distillation scrubber, fermentation scrubber, cooker room cupola, and No. 2. brew kettle. The 3 most odorous sources were the Carbon Bed Steam Regenerator, DDGS dryer, and Cooling Cyclone. Control equipment and process design improvements are being implemented to address these odor sources. However, residents still complain of odor problems and health effects. Remaining fugitive emissions are known to include irritants and odorous compounds, and could be the cause of ongoing complaints. The report discusses mechanisms by which odors, when especially accompanied by chemical irritants, may be associated with or cause health effects

Neighborhood citizens have also complained about noise. GSE has been cited by the MPCA and the City of St. Paul numerous times for operating above the permissible daytime and nighttime noise levels. Injunctive relief from noise was sought by the City of St. Paul, and the motion was denied in court. The City of St. Paul and the facility entered a settlement agreement to better define the noise sources and mitigate noise levels to meet the nighttime noise standard. Several compliance dates have not been met. GSE has been in compliance based on the most recent monitoring results.

Although substantial work has gone into reducing odors and noise, these issues have not been completely resolved and numerous complaints are still received from local residents. A long term commitment to identifying and controlling known sources of noise, irritant compounds, odorous gasses, particulates, and fugitive emissions is recommended.

There is a completed air exposure pathway, but air emissions and their toxicity are not sufficiently characterized. Therefore MDH has concluded that the facility poses an indeterminate health hazard.

Introduction

The Minnesota Pollution Control Agency (MPCA) has requested the Minnesota Department of Health (MDH) investigate health concerns associated with emissions from the Gopher State Ethanol (GSE) plant. It is the position of the MDH that the public was initially exposed to combined emissions from the brewery and ethanol plant. However, the brewery has ceased operations and is no longer in business. This public health assessment evaluates the emissions coming from the Gopher State Ethanol facility. This document examines contaminated media (water, air and soil), transport mechanisms, and routes of exposure (ingestion, inhalation and dermal contact) to determine the likelihood of individuals being exposed to contamination.

Data and information that form the bases for this public health assessment were collected during numerous site visits, phone conversations with City of St. Paul representatives, residents, MPCA site files, and technical reports provided to MDH. Health effects that might be associated with any exposures are also discussed.

Background

Site Description and History

The GSE plant started out as the Minnesota Brewing Company (MBC) and expanded its facility in St. Paul Minnesota to include ethanol production in the spring of 2000. GSE is located entirely within MBC's property in the West Seventh Street neighborhood. MBC is situated on the north side of the Mississippi River Valley approximately 3 miles southwest from downtown St. Paul. There has been extensive press coverage of GSE since it began production because of odor issues.

The site of the Minnesota Brewing Company/Gopher State Ethanol has been associated with brewing beer since 1855. In 1897, the St. Paul Brewing Company bought the brewery, which operated until 1900. Then the Brewery was sold to Jacob Schmidt, who renamed it the Jacob Schmidt Brewing Company ("Schmidt"). Beginning in 1955, another series of ownership changes occurred, ending with the acquisition of the company by G. Heileman Brewing Company ("Heileman") of LaCrosse, Wisconsin in 1972. Heileman announced plans to consolidate its operations, and its intent to close the St. Paul brewing operation in July 1990. News of the pending shutdown brought a number of offers to buy the brewery, but for various reasons, all attempts were unsuccessful. The brewery was scheduled to be scrapped in the summer of 1991.

With the aid of former employees and local government officials, public pressure was exerted on Heileman to consider the plight of the laid-off workers and the impact to St. Paul of the loss of this facility.

In the 18 months following the closing, a group of investors was able to convince Heileman to sell them the brewery. A sale was agreed upon in August 1991, and in a rare reversal of trends in the industry, the brewery was reopened two months later under the holdings of the Minnesota Brewery Company (MBC) (1). On January 26, 1997, in accordance with State of Minnesota Environmental Review Statutes and Rules, the MPCA sent an Environmental Assessment Worksheet (EAW) for the proposed Minnesota Brewing Company Ethanol Facility Modifications to interested parties and state agencies. In the EAW, Minnesota Brewing Company proposed to expand its existing brewing facility to include 18.0 million gallons per year (GPY) of dry mill ethanol production capacity. The facility already produced malt

beverages, both alcoholic and non-alcoholic, at the rate of 300,000 to 550,000 barrels (9.6-17.6 million GPY).

The environmental review process ended in a "negative declaration," i.e., a finding that an environmental impact statement would not be required, and that the facility could be permitted. The EAW also stated that odors would not be a problem. A hammermill, distillation and molecular sieve dehydration equipment, and storage tanks were added. Processing equipment including an evaporator and a spent grain dryer were enclosed in existing buildings. A new ethanol production building was constructed which contains the distillation columns. Existing idle boiler, grain receiving, and fermentation capacity were utilized for ethanol production. New storage tanks were added, including two 250,000 gallon denatured ethanol storage tanks, two 20,000-gallon ethanol day storage tanks, one 20,000-gallon tank for off-spec ethanol, and one 20,000-gallon denaturant tank. Gopher State Ethanol now has a capacity to produce 20 million gallons of ethanol per year from 8 million bushels (274,000 tons) of corn. New grain receiving and storage facilities were constructed for ethanol production. The Minnesota Brewing Company (MBC) converted approximately 40% of its fermentation capacity from beer production to fuel ethanol production. MBC appears to have sufficient fermentation capacity to brew one and one-half million barrels of beer at full production. The permit application for the GSE plant was prepared by Environmental Resource Group members who had previously prepared permits for the ethanol plants in Luverne and Preston, Minnesota. Both these plants have had odor issues prior to GSE (4).

Ethanol production at the Minnesota Brewery/ Gopher State Ethanol (GSE) location resulted in numerous additional emissions points impacting neighborhoods miles from the facility. The most obvious odor source is emissions from the 206-foot Distillers Dried Grain Solids (DDGS) stack. Since the inception of ethanol production at GSE, hundreds of complaints of nauseating and irritating odors have been received by state and city officials (see Appendix A). Citizens have complained that the offensive odors have initiated or aggravated asthma attacks. Other health effects, such as shortness of breath, difficulty breathing, skin rashes, head aches, and changes in sleeping and eating patterns have also been reported. These effects have been reported at city council meetings during public testimony, and MDH has received both verbal and written complaints to this effect. The complaints continue even after numerous mechanical and ventilation improvements have been made.

Ethanol Production

The following is a brief description of the six basic steps of ethanol production (2).

1) Grain Receiving and Storage
Corn is used as the feedstock, and is received and stored on site. A truck scale weighs delivery trucks entering and leaving the facility. Trucks off-load into a covered dump pit. Dust emissions are controlled with a vacuum system that pulls air into the pit with the corn while the trucks unload. The vacuumed air is sent to a fabric filter that removes particles. Corn is transported from the dump pit to storage bin by a bucket elevator.

2) Mash Preparation, Cooking, and Conversion
The mash preparation, cooking, and starch conversion processes are done in newly constructed ethanol building. From storage, the corn is cleaned, milled, and mixed with water to form mash. Nutrients and enzymes are added. The slurry is cooked and transferred to conversion tanks where additional enzymes are added. The mash remains in conversion tanks for 10-12 hours to convert starches into fermentable sugars.

3) Fermentation
The fermentation system is located in Cellars 34 and 35 at the facility. The system consists of several tanks that allow for continuous or batch operations. The existing fermentation capacity available for ethanol production is approximately 1,000,000 gallons. In either operating mode (batch or continuous), the amount of ethanol, carbon dioxide (CO_2), and by products produced are nearly identical. In continuous mode, the mash is moved through the fermentation tanks in sequence to maintain the proper liquid in each tank. In the batch mode, each tank is filled and emptied independently. With a fermentation time of approximately 40-50 hours, the sugar is converted to "beer" with an ethanol content of approximately 11 percent by volume. The exhaust gases from the fermentation tanks are collected, passed through a water scrubber (fermentation scrubber) to remove ethanol, and then processed to recover CO_2 in liquid form at the CO_2 plant. GSE has installed a post-scrubber for the fermentation scrubber and plans to test the unit for VOC removal by Spring 2003 (see Appendix B for GSE Mechanical Changes). In the MG-CO_2 plant, the raw CO_2 is passed through two carbon bed absorbers that remove organic impurities from the CO_2 gas. The carbon bed units are alternately regenerated with steam and were originally vented to the atmosphere every 5 hours. Odor studies found the emissions generated during carbon bed regeneration to be the most odorous of the emissions tested (3). In 2001 emissions from the carbon bed were sent to a condenser that removes some of the emissions and the non-condensables were sent to the original Thermal-Oxidizer (TO). The non-condensables from the condenser are now sent to the inlet feed of the MG-CO_2 plant but do not appear to be collected anywhere in the system. The condensable emissions are discharged to the sanitary sewer. The condenser is supposed to remove dimethyl sulfide, the primary odorous compound coming from the carbon bed during regeneration (4).

4) Distillation
The fermentation tank liquid and solids are transferred to the distillation area where ethanol is separated and recovered. The fermented mash is heated and introduced into the top of the column. As the beer moves through the column, it is stripped of alcohol by cross current contact with steam. The alcohol is vaporized by the steam and exits at the top of the distillation column for further purification in the rectifier column. In the final distillation step, ethanol and other VOCs dissolved in the water leaving the beer column pass through the rectifier where the ethanol is separated by a stripping column. The distillation process vents through a scrubber to the atmosphere. This emission point is very odorous, and efforts have been made to limit the odor. For a more detailed odor evaluation of this emission point, see the Olfactometry Section.

5) Dehydration
The ethanol vapor leaving the rectifier is superheated to 240°F and sent to molecular sieves for dehydration to concentrate the ethanol from 187 to 199.5 proof. The superheated vapor passes through a packed bed of molecular sieve desiccant, where water molecules are absorbed from the steam, and only anhydrous ethanol exits the bed.

The anhydrous ethanol is condensed, cooled and sent to a day tank where it is tested for product quality specifications before being pumped to an ethanol storage tank. The ethanol is denatured with five percent gasoline or other suitable hydrocarbon denaturant to make the product nonpotable. The denatured ethanol is then transferred to tank trucks for shipment to GSE customers.

6) Stillage Separation, Evaporation and Drying
The whole stillage is pumped to a pre-evaporator where over 90% of the remaining residual ethanol and water is removed. The resulting condensate is pumped into a storage tank to be used for mash

preparation. The partially concentrated whole stillage (beer minus the alcohol) from the pre-evaporator is centrifuged and separated into liquids (thin stillage) and solids (wet cake). The centrifuge vents are a significant fugitive source of corrosive and odorous gases that are released into the dryer building. Attempts to send these emissions to the original TO were not successful because all the emissions were not captured and the TO failed. GSE is now designing a centrifuge scrubber system to capture and treat the centrifuge fugitive emissions. The scrubber is scheduled to be installed and tested for chemical and odorous emissions in spring 2003. The thin stillage storage tanks have been identified as a significant fugitive emission source. GSE has installed a "green scrubber" to control these fugitive emissions. The liquid fraction is used for both mash preparation and "syrup" production. The syrup is mixed with partially dried mash wet cake for final drying. The wet cake is dried with hot air in the re-circulation dryer. The final dry product, Distillers Dried Grain Solids (DDGS), is conveyed to a storage building until it is loaded for shipment off-site as animal feed. The dryer is exhausted through multiple cyclones; these control particulate missions from the dryer. The gasses from the cyclones were being controlled in the original TO while it operated. The original TO became fully operational June 30, 2001 and ceased to operate in Summer 2002. GSE believes the cooling cyclone gasses contributed to the TO's unreliability, so the gasses are not being sent to the new TO. The new TO was installed in January 2003, and is the primary means of VOC and odor control on the DDGS dryer.

Site Visit

MDH has attended numerous site visits to the GSE facility. MDH also attended numerous visits to several residences near the facility. Site visits to the facility included tours of both the beer and ethanol plants. Tours included visual inspections of the various production stages of beer and ethanol production, and observations of a sampling event. One site visit included a roof top tour to view stack emission points. All site visits occurred during fall 2000 to winter 2002.

Demographics, Land Use, and Natural Resources Use

The MBC/GSE is in a heavily populated urban area with residential and commercial property on the north, east and west sides (See Figure 1). There are several private and public schools within one mile of the facility. The population in a one-mile radius from the site is approximately 12,960. The land north/northwest of the site is relatively flat for approximately 2,000 feet before rising 175 feet to the top of the river bluff. The southern river bluff is approximately 4,500 ft. from the site, and rises approximately 200 feet. Both river bluffs are heavily populated. South of the facility along the Mississippi River there is a bike trail that passes through the Harriet Regional Park. The river has a lot of barge traffic with some recreational use.

General Regional Issues

Because the site is located in the middle of a heavily populated city, there are air quality issues due to multiple point and non-point sources of air pollution. Within a mile of the site, there is a major highway (35E) and a large electric power utility.

Community Involvement and Public Comment Period

When GSE began producing ethanol in April 2000, citizens living miles from the facility began to complain of bad odors. Control equipment improvements have reduced odor complaints to within a mile of the facility. Residents have also complained of loud noise coming from the GSE facility at all hours

of the night. Citizens have petitioned the City of St. Paul to intervene on their behalf to stop the nuisance odors and noise. The City of St. Paul reached a settlement agreement with the GSE in September 2001. GSE agreed to meet the nighttime noise ordinance and address nuisance odors. The settlement established criteria and dates for noise compliance with a phased-in reduction in noise levels until there was to be complete compliance with the law by March 1, 2002, but the agreement provided no assurance for odor remediation. This deadline was not met by the facility. The City of St. Paul and a group of residents have filed a lawsuit seeking abatement of noise and odor nuisances emanating from the GSE facility.

Community members were given an opportunity to provide comments to this public health assessment from May to June 30, 2002. The public comments received by MDH (36 letters) can be found in Appendix C. Comments were summarized into 20 categories (table in Appendix C). In general, citizens are upset with GSE's negative impacts to their quality of life. They are not able to enjoy open windows or their yards because of oppressive odors and noise being generated at GSE. Many report suffering health effects like headaches, increased asthma symptoms, irritated noses, and throats. Residents are frustrated with GSE's broken promises to fix the problems. Many individuals believe their health is being compromised and regulatory agencies are not doing enough to solve noise and odor problems at GSE.

Agency For Toxic Substances and Disease Registry Involvement

MDH, under a cooperative agreement with the U.S. Agency for Toxic Substances and Disease Registry (ATSDR) , evaluated the public health significance of contamination associated with MBC/GSE emissions. More specifically, MDH and ATSDR cooperated to determine whether health effects are possible and to make recommendations to reduce or prevent possible health effects. ATSDR, located in Atlanta, Georgia, is a federal agency within the U.S. Department of Health and Human Services, Public Health Service. The ATSDR reviews and publishes public health assessments written by cooperative agreement states.

Evaluation of Contamination and Exposure

MDH has determined that a complete exposure pathway via ambient air exists for a complex mixture of VOCs found in the stacks tested at GSE. There is a completed air exposure pathway, but air emissions and their toxicity are not sufficiently characterized. Chemical data are lacking for many emission sources at the GSE facility. On the basis of MDH's review and evaluation of environmental information collected from the MPCA Site file, environmental reports provided to MDH, and site visits, MDH concludes that the November 2001 modeled air concentrations resulting from operation of the Thermal Oxidizer do not exceed any MDH Health Risk Values (HRVs). An HRV is the amount of a chemical, emitted to ambient air, to which the general public, including sensitive sub-populations, can be exposed with de minimus health risks. The dermal and ingestion pathways are considered to be negligible in this scenario. The air modeled concentrations did not include other emissions points or fugitive emissions that will likely increase exposure point concentrations.

The following sections contain chemical characterization data collected during stack tests for the Distilled Dried Grains Solids (DDGS) dryer stack, Thermal-Oxidizer (TO), Distillation Scrubber, and Fermentation Scrubber (CO_2 Scrubber). Fugitive emissions and particulate emissions are discussed in separate sections. The Screening Risk Assessment section evaluates the air modeling results presented by GSE's consultant.

Distilled Dried Grains Solids (DDGS) Dryer Stack

Initially, the Dryer Stack permit required only the monitoring of methanol and ethanol to meet its VOC stack emission limit of 7.7 lb/hr. Per MDH's request, MPCA asked GSE to investigate the presence of other VOCs, including aldehydes and ketones. On October 12 and 13, 2000, Pace Analytical performed compliance stack testing on the DDGS dryer stack using numerous U.S. Environmental Protection Agency (EPA) methods (5). Sampling was witnessed by Steven Sommer and Rhonda Land of the Minnesota Pollution Control Agency, and Charles Hall and Greg Chomycia of the U.S. EPA Region V.

The objectives of the sampling were to quantify emissions constituents and compare them to applicable air emissions regulations stipulated by Minnesota Rules and the facility permit. Table 1 lists the testing requirements for the DDGS Dryer Stack before the Consent Decree took effect. The tests were conducted at maximum throughput. Sampling included the following:

- Three one-hour samples for particulate
- Three one-hour samples for methanol/ethanol
- Three one-hour continuous monitoring periods for Total Hydrocarbons as Carbon (THC) and Nitrogen Oxides (NOx)
- Integrated gas sampling for Total Reduced Sulfur analysis (TRS), and Volatile Organic Compounds (VOCs)
- Sampling did not include carbon monoxide

During performance testing on October 12, 2000, a process problem forced the shut down of the dryer during the second run for approximately one hour. Testing was halted when the dryer shut down and resumed after the dryer was back on line. The dryer also shut down during testing on October 13, 2000, 35 minutes into Run 2 of the aldehyde and ketone testing. Testing for Run 2 was ended at that time, and samples were processed. Approximately one hour later, the dryer was back on-line and Run 3 was started (5).

The most significant finding of the October 2000 stack testing was that substantially more VOCs were emitted from the dryer than had previously been noted. The VOC test results indicated that the dryer stack was not in compliance with the VOC limit in the permit (Table 1). The average emission rate for THC is used to determine VOCs compliance. The total hydrocarbon analyzer is calibrated to propane. The results are mathematically converted to methane and carbon for standardization purposes. All the total hydrocarbon mean emission rates exceeded the emission cap of 7.7 lb/hr for the DDGS Dryer stack. Table 2 lists the summary results of the performance testing conducted on the DDGS Dryer Stack on October 12-13, 2000.

This sampling round also identified the presence of several chemical irritants:

Acetic Acid
Lactic Acid
Styrene
Acrolein
Crotonaldehyde (2-butenal)
Acetaldehyde
Glycerol
Furfural
Formaldehyde
Methyl Ethyl Ketone (2-butanone)

All of these compounds were selected for further monitoring because they were found in the highest concentrations in the DDGS Dryer exhaust. The presence of the organic acids might also indicate that

the Dryer Stack gas is corrosive. During a site visit, MDH observed that the condensate dripping from the stainless steel dryer stack appeared to be dissolving the concrete floor.

An additional 29 tentatively identified compounds were found in the dryer stack emissions. See Table 3 for a list of the compounds and their respective estimated concentrations and CAS numbers. Sparse toxicological information exists for many of these compounds. Most of the compounds were found in relatively low concentrations in the Dryer Stack gas. Note that these concentrations were measured inside the base of the 206-foot DDGS Dryer stack and there would be considerable dilution of these chemicals once released to the atmosphere.

GSE's consultant, Environmental Resources Group (ERG), challenged the validity of the October performance test results because they believed the analytical method used to calculate total hydrocarbons was not applicable to the DDGS Dryer stack. The MPCA classified the October performance testing results from Method 25 A as indeterminate based on the information presented by ERG's in February 2001 (6). However, the MPCA required that GSE quantify the following VOCs based on their significant concentrations reported in the October 2000, DDGS Dryer Stack test results and the Gopher State Ethanol Screening Risk Assessment:

Formaldehyde
Acetaldehyde
2-Furancarboxaldehyde
Acrolein
Benzene
Methanol
Ethanol
Glycerol
Styrene
Lactic Acid
Acetic Acid

Another compliance test was scheduled for March 2001. GSE's contractor Environmental Resource Group (ERG) contracted Pace Analytical Services, Inc. to perform another round of emissions compliance testing on the DDGS Dryer on March 31, 2001. These measurements were performed at the process maximum throughput. The testing was witnessed by Stuart Arkley of the Minnesota Pollution Control Agency. Testing consisted of the following measurements:

- Three independent 90-minute samplings for methanol/ethanol.
- Integrated gas sampling for benzene and styrene analysis concurrent with above.
- Three independent 30-minute samplings for aldehyde compounds concurrent with above.

The purpose of this round of Performance testing was to quantify the following compounds:

Acetic Acid
Lactic Acid
Ethanol
Methanol
Benzene
Glycerol
Styrene
Acrolein
Furfural
Formaldehyde
Acetaldehyde

According GSE's contractor, Environmental Resource Group, there were a number of problems associated with the dryer stack compliance tests conducted on March 31, 2001. For one, there were interference problems during the gas chromatography analysis of lactic acid, acetic acid, methanol, and ethanol (7). The sample was subsequently re-analyzed with a non standard stack testing method (ion chromatograph) resulting in more questionable data (7). Furthermore, the Test Run 3 lactic acid mass

rate of 190.6 lbs/hr varied by 1200 % when compared with Test Runs 1 and 2 (7). In Test Runs 1 and 2, the lactic acid emission rates were 19 and 16 lbs/hr respectively. The average emission rate for lactic acid during the March 2001 sample round, not including Test Run 3, was 17.5 lbs/hr. For comparison, in the Gopher State Ethanol Screening Risk Assessment (October 2000), the average emission rate for lactic acid was 4.72 lb/hr. Problems with the aldehyde sample collection were also reported. See Table 4 for March 2001 DDGS Dryer Stack Performance Testing Results.

When comparing the October 2000 mass emission rates to the March 2001 results, ethanol decreased, formaldehyde increased, and acetaldehyde increased. The other test compounds emission rates were similar in the two performance tests. It is not clear which results are more accurate. In short, the results from the March Performance testing did not help establish the emission rates of lactic acid and acetic acid. These two chemical constituents account for a significant portion of the DDGS Dryer Stack effluent.

Thermal-Oxidizer

A Thermal-Oxidizer (TO) began operation in June 2001 for the purposes of controlling the dryer emissions. In essence, the TO consists of a combustion chamber where the DDGS Dryer gasses are "burned" for 0.7 seconds at approximately 1400 ^{O}F before discharging to a new 75 ft. TO stack. The TO generates steam for production, thus permitting one of the plant's boilers to be turned off. Before the TO was installed, all the DDGS Dryer untreated exhaust discharged out the 206-foot brick stack. In August 2001, compliance testing was conducted on the inlet and outlet of the TO by Interpol Laboratories. The following VOCs were collected:

Acetic Acid	Lactic Acid	Ethanol
Acrolein	2-furaldehyde	Formaldehyde
Methanol	Glycerol	Acetaldehyde

The VOC emission rates (lb/hr) were determined and reported as THC. The methanol and ethanol emission rates were also determined. Table 1 lists the TO testing requirements and emission limits before the Consent Decree took effect.

The nominal glycerol emissions in the August 2001 test represented approximately 4.67 lb/hr of the total VOC emissions from the TO of less than 5.74 lb/hr due to an elevated detection limit (see Table 5). GSE's contractor, Environmental Resource Group (ERG), asserts that glycerol results were below detection limits and inclusion of the glycerol detection limit skews the test results significantly (8). Total VOC emissions are at most 1.07 lb/hr without glycerol, and this emission rate represents approximately 14% of the 7.7 lb/hr permit limit. Table 5 contains the individual compound emission rates and THC data for the TO inlet and outlet. Every sampling attempt to chemically characterize the DDGS Dryer emissions has been problematic, especially for glycerol emissions. However, comparison of total hydrocarbons at the inlet and outlet suggest about 99.5 % destruction. Note that the currently rerouted cooling cyclone, and carbon-bed steam regenerator were not connected to the TO when it was tested August 2001 for compliance. Although cooling cyclone, and carbon-bed steam regenerator emissions were treated in the original TO, this was short-lived because the TO failed completely and needed to be replaced after approximately one and a half years of intermittent service. The new TO was installed in January 2003. The first engineering tests were scheduled for completion in March 2003 and compliance testing in June 2003 (see Appendix B for proposed emissions testing schedule). The current TO configuration does not treat any other waste streams except the DDGS dryer gases. The TO has a fresh air intake that supplies additional combustion air when the dryer is not able to supply sufficient air. MDH is concerned that untreated dryer gases are released from the fresh air intake during upset

conditions. GSE added an additional 6 ft of piping to the TO air intake to help prevent the release of untreated DDGS Dryer gasses. MDH believes that the TO should be tested every 2 years ensure that it will perform after sustained use. Typically, the PCA requires monitoring once every 5 years after passing a compliance test.

MDH was not able to confirm how long the TO had been inoperable, but complaints of odors and health effects starting escalating in July 2002. Even though the TO was not functioning, the facility continued to operate by shipping out the mash without drying (wet process). VOC monitoring data for the wet process have not been collected; therefore, it is not certain whether GSE is in compliance with its permit or what additional emissions are being generated.

MDH reviewed all of the identified compounds found in emissions of the DDGS dry stack, distillation and fermentation scrubbers for flash point temperatures to determine if they are combustible in the original TO at a 3-hour rolling average operating temperature of 716.11° C (1321°F) (See Table 6). It is not uncommon for the TO to operate at 737.89 Celsius (1425 Fahrenheit). Most of the compounds being sent to the TO are straight chain compounds, which makes them more combustible. The auto-ignition temperature for each compound needs to be considered along with the desired percent destruction. Higher temperatures and longer resident times are needed for increasing percent destruction. For example, ethanol has an auto-ignition temperature of 799 degrees Fahrenheit. If 95% destruction is desired, an additional 300 degrees with 0.5 sec residence time is needed (25). To achieve 99% destruction, 475 degrees above the auto-ignition temperature and a 0.75 second residence time is required (25). But complete combustion is a function of several factors including but not limited to turbulence, waste stream composition, and water content. It is also important to note that a >90% reduction in emissions do not equate to a 90% reduction in odor. This information may be useful should GSE again route these waste streams to the new TO. GSE applied for a permit renewal on April 15, 2003. The new permit will contain the following TO operating conditions and requirements as stipulated in the Amended Consent Decree (see Consent Decree section).

DDGS Dryer/Thermal Oxidizer	
Pollutants:	VOC, HAPs, CO, PM/PM10, NOx, Ethanol, Acetic Acid, Methanol, Formaldehyde, Acetaldehyde, Acrolein, 2-Furaldehyde, and Lactic Acid.
Sampling location:	Thermal Oxidizer inlet/outlet
Test Methods:	Methods 1, 2, 3A or 3B, 4, 7E, 10, 25A (inlet and outlet) 18 NCASI CI/WP-98.01, 5/202 (outlet only)
Operating Range:	>1321°F or as determined by the most recent performance test
Monitoring Frequency:	Continuous monitor with a recording frequency no greater than once every 3 minutes

The VOC permit limit was 7.7 lb/hr, but the Amended Consent Decree now mandates a facility cap of 95 tons per year that considers emissions from other sources including the cooling cyclone, ethanol fermentation, and ethanol loading rack (See Table 14). An additional smaller TO maybe required to treat emissions from the Ethanol Loading Rack if the VOC emissions are too high and they cannot be treated in the existing TO. The TO is still required to have a 95% VOC destruction efficiency.

Distillation Scrubber and Fermentation Scrubber (CO_2 Scrubber)

Emission Compliance testing was conducted on the distillation and fermentation scrubbers on November 7-8, 2000. Testing consisted of the following measurements at the outlets:

- Three independent one-hour samplings for methanol/ethanol.
- Integrated gas sampling for VOCs, and total reduced sulfur.
- Three independent one-hour continuous monitoring periods for total hydrocarbons as carbon concurrent with the above.
- Three independent one-hour samplings for aldehydes.

The objective was to quantify emission constituents and compare them to applicable air emissions regulations stipulated by Minnesota Rules and the facility permit.

The distillation scrubber has a VOC emission limit of 1.8 lbs/hr. The VOC emission rate is determined by measuring THC. The VOC emission rate for the distillation scrubber was determined to be 0.002 lb/hr. The methanol/ethanol combined emission rate from the distillation scrubber was 0.0037 lb/hr. The following aldehydes were identified in the distillation scrubber stack:

Formaldehyde Acetaldehyde m, p-Tolualdehyde Methyl Ethyl Ketone

Their combined emission rates equal 0.0000073 lb/hr. Although this is very small emission rate, it is another source of chemical irritants being emitted to the air at GSE. Table 7 is a summary of the test results.

Emissions from the Distillation Scrubber stack were analyzed for 38 VOCs. The only positively identified distillation scrubber stack emission was tetrachloroethene at 140 parts per billion by volume (ppbv). This compound was only identified in one of the 3 test runs (Test Run 3), and its emission rate in pounds/hour was not provided. There were also18 different tentatively identified compounds (TICs) found in the distillation scrubber emissions (See Table 8) along with some undetermined hydrocarbons. The TICs estimated emission rates were not calculated because no analytical standards were run. The distillation scrubber stack emissions were not included in the air dispersion model for the site. The distillation scrubber is scheduled for additional odor testing in the winter of 2002. In an effort to get better dispersion from the distillation scrubber stack, GSE has moved the stack from the horizontal position (out the side of the building) to a vertical position (out the roof top).

Fermentation Scrubber Outlet

The objective of the testing in November 2,000 was to quantify emission constituents and compare them to applicable air emissions regulations stipulated by Minnesota Rules and the facility permit. The fermentation scrubber stack had a VOC emission limit of 6.82 lb/hr. The mean THC emission rate was found to be 1.2 lb/hr. The methanol/ethanol emission rate mean was found to be 3.15 lb/hr. Note that 4 Test Runs were collected, but Test Run 1 was not used in calculations due to technical difficulties during data collection. Data from Test Run 2 through Test Run 4 were used for emissions calculations (See Table 9). Testing was also done to chemically characterize 38 VOCs. Due to elevated detection limits, some VOCs for which the method was designed were not detected, even though they might have been present. The fermentation scrubber samples were diluted for the VOC analysis because of high levels of non-target analytes in the samples, resulting in elevated detection limits (9). It was not apparent from the

report what the non-target analytes were. The analysis detected the presence of 16 different tentatively identified compounds (TICs). Table 10 list the TICs for each sample run. No estimated emission rates were provided for the TICs. The fermentation stack emissions were not included in the air dispersion model for the site.

Emission rates for several aldehyde species were determined. The two positively identified aldehydes were formaldehyde and acetaldehyde with emission rates of 0.0005 and 0.10 lb/hr respectively (see Table 9). Both compounds are known irritants. Acetone was also found in all sample runs but was believed to be a laboratory contaminant.

The results of the total reduced sulfur analysis show the presence of hydrogen sulfide, carbonyl sulfide, and carbon disulfide. The total reduced sulfur (sum total of all detected sulfur compounds) emission rate for the fermentation scrubber was 0.025 lb/hr (see Table 9). These compounds are likely to be the most objectionable odor causing compounds coming from the fermentation scrubber stack. Additional testing was conducted at this stack for chemical and odor characterization in March 2003. The results of the testing will be compared to the data presented here to determine the effectiveness of the new post-scrubber. The post-scrubber is an additional water scrubber that will collect water soluble VOCs from the fermentation scrubber. Currently, some of the emissions sent to MG-CO_2 plant are not being processed by the fermentation scrubber and are being vented to the atmosphere because the MG-CO_2 plant does not operate continuously. GSE has installed a pressure relieve valve that will allow emissions to be vented to the atmosphere. However, the water scrubbers are ineffective for non-condensable sulfur compounds, and these will be vented to the atmosphere.

The new testing requirements for the Fermentation Scrubber as stipulated in the Amended Consent Decree are as follows:

Fermentation Scrubber	
Pollutants:	VOC, HAPs
Sampling location:	Fermentation Scrubber inlet and Post-Scrubber outlet
Test Methods:	Methods 1, 2, 3A, 4, 25A (inlet and outlet) 18 NCASI CI/WP-98.01 (outlet only)

The Amended Consent Decree stipulates that fermentation scrubber emissions be included in the facility cap of 95 tons per year.

Consent Decrees

The EPA compared the emissions data presented in this report with emission data from other ethanol plants in Illinois, and Indiana and determined that all ethanol plants who dry their mash are “major sources” (produce greater than 100 tons per year of air pollution), and operated in violation of the Clean Air Act. The EPA, U.S. Department of Justice, and the MPCA lodged Consent Decrees against 12 ethanol plants (including GSE) in Minnesota. EPA and the Department of Justice, initiated their enforcement actions in Minnesota (Region 5) because the first evidence of violations came from GSE studies presented in this document. Additional enforcements actions are pending in other EPA Regions that have ethanol plants. The Consent Decrees outlines compliance programs, civil penalties, stipulated penalties, and other general provisions for each of the ethanol plants. The 12 Minnesota ethanol plant Consent Degrees were posted on the Federal Registry on October 24, 2002. A public comment period

for the Consent Decrees was extended to January 24, 2003. An Amended Consent Decree was posted on the Federal Registry on June 5, 2003. The Amended Consent Decree requires a compliance program that consists of the following (26):

- Control and minimize fugitive particulate matter emissions.
- Demonstrate compliance with the required emission levels on a unit- by-unit basis by the use of performance testing, and parametric monitoring.
- Maintain records to demonstrate compliance with New Source Performance Standards.
- Accept source-wide allowable emission caps equivalent to 95 tons per year for each pollutant, including VOCs, Particulate Matter, Sulfur Dioxide, NOx and CO based on 12 month rolling average.
- No individual Hazardous Air Pollutant (HAP) is to exceed 9 tons per year.
- Implement a Leak Detection, Monitoring and Repair program for fugitive VOCs
- Quantify emissions from wet cake operations, and limit the wet cake operations during breakdown or malfunction of the grain dryer if wet cake emissions are not quantified.

See Appendix F for the Amended Consent Decree's monitoring requirements, and emission limits for each pollution control device.

Fugitive Emissions And Accidents

Reported fugitive emissions at Minnesota Brewing Company (MBC, is adjacent to GSE and under the same ownership) include anhydrous ammonia (4817 lbs), cyclohexane (26 lbs), and n-hexane (78 lbs), as reported in the 2000 Toxic Release Inventory (TRI). The only other TRI data recorded was an annual loss of approximately 1000 pounds of ammonia in 1990. There were two ammonia releases at MBC in 2001 that caused the St Paul Fire Department to evacuate employees. On September 2, 2001 at 6:30 pm, the Hazmat team responded to a call alleging a bad odor was coming from the ethanol plant. The Hazmat team determined there was a leak coming from the 1,000 gallon tank in the back of the property. Meters showed a reading of 4.7 ppm ammonia at the base of the tank and 87ppm on the top of the tank. It was determined that 4 bolts connected to a gauge on top of the tank were loose. After the bolts were tightened, the meters were not able to detect any ammonia gases (10).

On August 7, 2001, at 10:30 pm, St Paul Fire Department sent two fire engines and the Hazmat team to GSE to respond to a report of strong odors in the area. The odor was identified as anhydrous ammonia and monitoring equipment registered 40 ppm 300 feet down wind. Readings inside the building were 40-50 ppm (10). An estimated 8000 lbs of anhydrous ammonia were released in approximately 1 hour. The MDH ammonia Acute Health Risk Value (HRV) is 3.2 ppm and the ammonia chronic HRV is 0.08 ppm. The HRV is a value promulgated in rule by MDH that specifies a safe exposure level for the general public, including sensitive sub-populations. The building was evacuated and several city blocks were closed to traffic on the north side of the plant. The ammonia leak resulted after two large refrigeration compressors overheated. Two firefighters entered the building in full protective gear and were unable to shut down the compressors. With the help of GSE personnel, the ammonia was shut off, but they were unable to shut down the compressors (10). After the building was ventilated, an electrician was able to enter the building and shut down the compressors. It was not clear from the report how many of the 18 civilians taken to hospitals for exposure to ammonia were staff or residents. Fortunately, the wind was out of the northwest; therefore, the gas plume did not migrate into the more densely populated areas across the street to the north. Because the release occurred in the middle of the night, there were few potential receptors outside at the time.

GSE has begun to address some of its more obvious fugitive emissions like the centrifuges, yeast tanks, ethanol load out system, and others identified in the *Knutson Ventilation Review* report dated March 2002 (See Figure 2). However, there are many smaller unidentified fugitive emissions of irritant and odorous gases throughout the facility in the form of leaking pumps, valves, pipefittings, and leaking tanks. The MBC/GSE/MG-CO_2 facility contains extensive plumbing lines including a lot of very old and some new lines. Some of the lines are no longer in use, and it is not clear where all the lines lead or vent. Appendix D contains pictures of some of the many stacks and vents at the facility. The 2 centrifuge vents are examples of fugitives emitting irritant gases at street level (see Figure 3). MDH observed that the condensates from the gases were corroding the metal and concrete where they collected. GSE has plans to conduct odor and chemical characterization on the centrifuge fugitives and install a scrubber for the centrifuge system (see Appendix B). Fugitive emissions inside the facility vent through building windows or roof top vents. These vapors can drift across the street into the neighborhood leading to resident complaints of odors and health effects. The Gopher State Amended Consent Decree requires implementation of a Leak Detection and Repair (LDAR) program for fugitive VOCs.

The fire department responded to a fire on the GSE roof near the thermal-oxidizer on September 17, 2001 (10). The St. Paul Fire Department responded to another fire at the plant on June 25, 2003 (27). The cause of the blaze was reported to be dislodged fire brick insulation inside the thermal oxidizer resulting in enough conductive heat to accumulate and ignite the building roof insulation two feet away. The fire investigator reported that this was the 2nd fire for the same cause within a year (27). GSE has recently submitted an Emergency Response Plan to the St. Paul Fire Department and the City of St. Paul, but the plan did not list the types or quantities of hazardous materials stored on site.

Particulates

Particulate testing was conducted on the Grain Cooler Stack and the Baghouse Stack during the week of October 13, 2000. The objective was to quantify emission particulates and compare them to applicable air emissions regulations in Minnesota Rules and the facility permit. Particulate measurements were conducted at maximum through-put (11). Table 11 lists the measured emission rates and old permit emission limits for the Grain Cooler/Cooling Cyclone, and Baghouse Stacks.

Although test results suggest that these particulate sources are in compliance under “normal” operating conditions, residents around the plant have complained that they often find small yellow particulates on their windowsills and cars in the mornings. MDH and MPCA staffs have observed these emissions and believe that the Cooling Cyclone is the main source, but others sources may exist. There have been several eruptions from the cooling cyclone because it clogs and eventually blows distiller dried grain all over the rooftop, and wind then blows it across the street. MDH and the MPCA also noted that there was a mat of this material on the roof centered around the cooling cyclone. Figures 4 and 4a illustrate two pronounced eruptions. Figure 5 shows particulate on a car across the street from the plant.

Studies have shown that airborne dust particles can concentrate odorants such as organic acids and ammonia on their surfaces (12). In other words, particulates and odorants can act synergistically to cause increased irritancy (12). For a short time, the cooling cyclone exhaust was being sent to the TO but this is no longer the case. Exhaust and particulates from the cooling cyclone are reportedly being sent to a DDGS Baghouse (new and additional equipment). GSE is planning to perform odor and chemical characterization tests on the exhaust from the DDGS Baghouse in 2003.

The Amended Consent Decree stipulates that the following requirements on the DDGS Cooling Cyclone, and DDGS Baghouse:

Cooling Cyclone/DDGS Baghouse	
Pollutants:	VOCs & HAPs, PM/PM10, Ethanol, Acetic Acid, Methanol, Formaldehyde, Acetaldehyde, Acrolein, 2-Furaldehyde, and Lactic Acid.
Sampling location:	DDGS Cooling & Storage Baghouse outlet
Test Methods:	Methods 1, 2, 3A or 3B, 4, 5/202 18 NCASI CI/WP-98.01, 25

Per the Amended Consent Decree, the MPCA will establish a VOC limit for the Cooling Cyclone and evaluate the technical feasibility and cost effectiveness of reducing VOCs in the Cooling Cyclone emissions (26).

The hammer mill baghouse stack is currently in compliance. However, in July 2000, the Minnesota Pollution Control Agency cited MBC for not maintaining daily emission readings on the Hammer mill baghouse, and failed to keep records of quarterly inspections of the baghouse filters as required by permit (13). These records are used by the MPCA to determine if these emission controls are maintained and in working order.

Screening Risk Assessment

Environmental Resources Group and STS Consultants submitted three drafts of a screening risk assessment for the DDGS Dyer stack dated October 2000, February 2001, and November 2001. The first two drafts addressed the emissions from the DDGS dryer stack without the Thermal Oxidizer (TO). The November 2001 draft addresses DDGS dryer emissions after passing through the TO. All three drafts use an EPA air dispersion model (Industrial Source Complex Short-Term 3) to calculate estimated exposure point concentrations to DDGS/TO stack chemicals at 82- feet intervals along the property boundary and extending out to an area of 2,966,803 square feet surrounding the Facility. The model uses MBC/GSE building and DDGS Dryer/TO stack dimensions and measured emission rates for 11 target compounds (Contaminants of Potential Concern (COPC)) investigated in the performance tests. Five years (1987-1991) of wind speed and direction data from the Minneapolis/St. Paul Airport were used in the model to calculate the highest estimated one-hour and annual COPC concentrations. These exposure point concentrations were compared to the irritancy potential of each COPC. Inhalation is the most significant exposure pathways for COPC impacts on the surrounding population. The modeled air concentrations from the DDGS stack did not exceed any chronic or acute Health Risk Values (HRVs). MDH believes that respiratory irritancy is the most probable health effect to result from inhalation of MBC/GSE/MG-CO_2 emissions. A literature search was performed for each of the COPCs to determine what exposure concentrations resulted in health effects in either animals or humans. Both short-term (acute) and long-term (chronic) exposure studies were considered with an emphasis on inhalation or ingestion studies. MDH believes that COPCs found in the DDGS Dyer emissions are being emitted from other emission sources at the MBC/GSE facility. Table 6 lists all the COPCs found in the DDGS dryer, fermentation scrubber, and distillation scrubber. Note that several of the compounds listed are known lacrimators (tearing agent), respiratory irritants, or odorants. Many of the compounds in Table 6 have not been studied for irritancy as single compound, and it is less likely that any mixture studies have been conducted with these compounds.

MDH believes that because ethanol fuel production and beer making are similar, it is likely that other emission sources at the facility will contain very similar chemical constituents including lacrimators, and respiratory irritants. In other words, when evaluating a single emission point like the DDGS Dryer/TO for potential irritancy effects, it is possible that other MBC/GSE/$MGCO_2$ emissions including fugitives contribute to the same health effect but are not considered. MDH believes there many unidentified fugitive emissions sources at the MBC/GSE/$MGCO_2$ facility. These should be identified and controlled. Also, it is important to note that health effects from odorous chemical irritants can occur below acute and chronic health criteria (see Odor Health Effects Paradigms section below).

While there are inadequate toxicological criteria suitable for exposures to the general public for most of the chemicals detected, taken together with the presence of fugitive emissions and emissions from the $MGCO_2$, citizen complaints of health effects (Appendix A) are plausible. The TO has undoubtedly reduced emissions levels from the DDGS. However, as noted above, particulate emissions may contain allergens and may concentrate effects of VOCs that bind to particulates. Furthermore, citizen complaints from the immediate neighborhood have continued even after the installation of the TO (Appendix A). MDH staff who live on the bluff to the northwest of the site confirm that the plant continues to emit odors. These odors are expected to be more bothersome in the immediate vicinity of the plant (see below).

Olfactometry

An assessment of odor was conducted for several emission points at GSE. This assessment was conducted due to the numerous community complaints in an attempt to gauge the apparent offensiveness of these odors. The study evaluated gasses collected from the following locations:

- DDGS dryer stack, cooling cyclone, distillation scrubber, fermentation scrubber, cooker room cupola, and brew kettle No. 2 (April 5, 2001 sample event).
- Thermal Oxidizer, DDGS Handling Baghouse, Distillation Scrubber (February 5, 2002 sample event).

The gas samples were collected in a tedlar bag and presented to an assessor (human) for establishing odor detection thresholds, recognition thresholds, intensity, and hedonic tone (pleasant odor) values. Five trained odor assessors were used by St. Croix Sensory conduct the odor studies at GSE.

The Detection Threshold (DT) is the concentration at which an odor from an air sample is just detectable. An odor at the detection limit is defined to be 1.0 odor unit/m^3. Odor units are used to describe the concentration of an odor. For example, the Carbon Bed Steam Regenerator odor sample is 7000 odor units concentrated which means that the odor would need approximately 7000 dilutions for it to be at the odor threshold. The two other highest DT measurements were from the distillation scrubber (13000-15000 units) and cooling cyclone (4600 units) (see Table 12). The distillation scrubber odor measurements increased between the two sampling events because a fan was installed on the scrubber that increased the air flow rate and increased odorous emissions collected in the sample.

The Recognition Threshold (RT) is the dilution ratio at which one can first detect the odor's character (floral, fishy, etc.). At the RT, an odor can be distinguished from other odors. The higher the RT the greater the distance from its source an odor can be identified. The highest RT for the sample points tested, was the distillation scrubber with a value ranging from 1900 -10,000. The second highest RT measurement was the carbon bed steam regenerator with a value of 4600 (see Table 12).

Hedonic Tone (HT) is a measure of the pleasantness or unpleasantness of an odor sample. HT is often rated on a 21 point scale of +10 (pleasant) to -10 (unpleasant). HT is a subjective value based on the assessor's personal likes and dislikes. HT is independent of the odor character. The three most unpleasant emission points tested thus far are the distillation scrubber, cooling cyclone, and carbon bed steam regenerator, with HT values of -5.6, -4.2, and -3.4 respectively (see Table 12).

An odor's character is an assessor's opinion of what a sample smells like. Odors are characterized using a reference vocabulary for taste, sensation, and descriptors. The taste descriptors are sweet, bitter, sour and salty. Sensation descriptors are itching, tingling, warm, burning, pungent, sharp, cool, and metallic. For all sample locations, the odor descriptor that rated the highest was "offensive." For the responses to the other descriptors see Appendix E. Figure 6 shows what emission sources tested in April 2001 produced the most odor. Note that the cooling cyclone and the carbon bed steam regenerator produce significant odor but have much smaller emissions by volume compared to the DDGS dryer. The cooling cyclone is no longer routed to the TO. An updated emissions inventory (pie chart) was not available for this draft.

Odor Health Effects Paradigms

Offensive odors can have a negative effect on an individual's health. Schiffman et al (12) describe three paradigms by which odor emissions from agricultural operations and municipal wastewater treatment facilities may produce health effects in receptors. Although developed for different purposes, these paradigms are applicable to GSE's emissions because ethanol production also emits odorous irritant compounds.

In the first paradigm, health effects are caused by irritant compounds found in an odorous emission. In this case, exposure to chemical irritants rather than odor is causing health effects. Health complaints expressed by citizens at the October 2000 City Council meeting include increased asthma attacks, shortness of breath, difficulty breathing, skin rashes, and nausea. This anecdotal evidence along with identified chemical constituents of DDGS dryer, fermentation scrubber, distillation scrubber, and fugitive gases suggest that irritation is a possible cause for past complaints. In this paradigm irritancy will likely to occur at concentrations 3-10 times higher than the odor threshold (12). Emissions from GSE are a complex chemical mixture that varies over time depending on the phase of production and what emission points are active.

Another paradigm suggests that health effects occur at odorant concentrations below irritation thresholds. An example is exposure to sulfur-containing compounds and organic amines at concentrations at the odor thresholds but below the irritant threshold (12). Variables including physical and emotional factors play a role in this paradigm. The mechanism that induces health effects in this paradigm is not well understood. Beliefs that malodorous exposures are a safety issue can lead to stress induced changes in one's sleeping and eating patterns. Other reported health effects include stinging sensation, nausea, vomiting, and headaches (12). A number of irritants and odorant compounds have been identified in GSE stack emissions (see Table 6).

The third paradigm applicable to the site involves a conditioned response to a co-pollutant in the odorant mixture that is initially responsible for the reported somatic health effects (12). In other words, odorous emissions from the facility could include an allergen like respirable particulate resulting in increased asthma attacks in susceptible individuals. In this case, the odor is a marker or signal for exposure, and the health effects can become a conditioned response to the odor. Thus, it is possible for an individual to associate a health effect with an odor exposure. Over time these individuals may continue to have a

health effect, like an asthma attack, when exposed to an odor without the causative agent (particulate). For example, people who live near GSE could be having an allergic reaction to particulates coming from the facility, and the odorous compounds are the marker for exposure. Individuals may develop a conditioned response (allergic reaction) to the odor even though the causative agent (particulate) is no longer present.

Schiffman, et. al., defined 8 levels of odor exposure in an effort to delineate the intensities associated with potential health impacts associated with the three paradigms. However, the range of odor intensities and odorant concentrations that correspond to these 8 levels varies across individuals. Table 13 lists the odor levels in order of increasing intensity.

Noise

GSE has been sited by the MPCA and the City of St. Paul numerous times for operating above the permissible daytime and nighttime noise levels. In October 2000, both the MPCA and the City of St. Paul sent GSE a letter stating that the facility has exceeded noise standards. Additional noise monitoring on December 1, 2000 conducted by a City of St. Paul inspector, found the facility to be out of compliance again. On December 21, 2000, GSE submitted a Noise Reduction Plan to the MPCA. These efforts to mitigate noise levels did not bring the facility into compliance. Injunctive relief from noise was sought by the City of St. Paul and the motion was denied in court. The City of St. Paul and the facility entered a settlement agreement to better define the noise sources and mitigate noise levels to meet the nighttime noise standard. Nighttime noise levels are not to exceed a mean measurement of 50 decibels, and noises louder than 55 decibels must be limited to 10% of the night time starting on March 1, 2002. Based on the City of St. Paul's records, GSE has made progress at lowering its decibel levels but is not consistently meeting its compliance requirements at all monitoring locations. Monitoring location M-1 is nearest the cooling towers and the MG-CO_2 plant. GSE was out of compliance at this location during the most recent monitoring event (3/14/03). The M-3C location is the monitoring site closest to the TO and it has been in compliance since 7/12/02, but during this most of this time the TO has not been operational. GSE has built a noise barrier along the roof line on one of its buildings to help damper noise.

ATSDR Child Health Considerations

ATSDR recognizes that the unique vulnerabilities of infants and children make them of special concern to communities faced with contamination of their water, soil, air, or food. Children are at greater risk than adults from certain kinds of exposures to hazardous substances. Often health risk calculations do not include values for children. Children tend to be more physically active than adults, and therefore can breathe a larger air volume per day than adults. Furthermore, children are also lighter, resulting in higher doses of chemical exposure per body weight. The developing organ systems of children can sustain permanent damage if toxic exposures occur during critical growth stages. Most importantly, children depend completely on adults for risk identification and management decisions, housing decisions, and access to medical care.

MDH believes the health-based values, including the HRVs are protective of all age groups. MDH will continue to monitor research in the area of children's health and incorporate any additional information that becomes available into the HRV process. At the present time, child exposure to levels of VOCs in excess of HRVs from MBC/GSE stack emissions has not been documented.

Conclusions

- The GSE/MG-CO_2 facility is an indeterminate health hazard because chemical data are lacking for many emission sources at the GSE facility. There is a completed air exposure pathway to citizens in the surrounding community, but air emissions and their toxicity are not sufficiently characterized. MDH concludes that the November 2001 modeled air concentrations resulting from operation of the Thermal Oxidizer do not exceed any MDH Health Risk Values; however, the air modeled concentrations did not include other emission points or fugitive emissions. Such fugitive emissions will likely increase exposure point concentrations. In addition, many chemical emissions lack health based air criteria; however, lack of exceedances of MDH Health Risk Values (HRVs) may not indicate that the facility is safe.

Recommendations

- GSE/MG-CO_2 should conduct a new Screening Risk Assessment that includes all stack and fugitive emissions unless these are controlled or eliminated.

- MDH recommends that GSE/MG-CO_2 conduct a comprehensive fugitive emissions study to identify and eliminated all fugitive sources of chemical irritants, odorous compounds, and particulates at the ethanol/ MG-CO_2 facility. GSE should certify that all emissions sources, and fugitives have been identified, eliminated or controlled.

- MDH recommends that the TO be tested at least twice every five years after the effective period of the Consent Decree ceases. More frequent compliance testing is warranted given the analytical problems encountered during testing and the complete mechanical failure of the first TO. The additional performance testing will help ensure that the TO will perform as intended during extended periods of maximum production and help track performance if any changes are made to the gasses sent to the TO.

- MDH recommends that known sources of irritant or odorous gases, and particulates be routed to the TO or otherwise be controlled. If this is impractical, these emissions should be characterized for odors and chemical irritants.

- MDH recommends that the chemical and odorous emissions from the wet process be characterized for VOCs, chemical irritants, and odors. MDH recommends that chemical and odor studies be conducted on all emissions generated by potential beer (beverage) making operations that may resume at the facility.

- As a matter of prudent public health practice, MDH recommends that noise violations be corrected. MDH also recommends that a copy of any GSE/MG-CO_2 plant reports provided to EPA, MPCA or MDH be provided to the West 7^{th} Street Federation. In addition, MDH recommends that GSE list the types and quantities of hazardous materials stored on site in its Emergency Response Plan.

Public Health Action Plan

- MDH will continue to review environmental reports regarding the GSE/MG-CO_2 facility. MDH will continue to respond to citizen calls concerning the GSE/MG-CO_2 facility. MDH will share this document with the EPA, MPCA, City of St. Paul officials, GSE/MG-CO_2 representatives, and concerned citizens. Currently, evaluation and permitting of a new TO, installed January 2003, has been ongoing during the spring and summer of 2003. MDH will continue to collaborate with the EPA, MPCA, City of St. Paul, and GSE/MG-CO_2 representatives to address complaints of odors, health effects and noise.

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CERTIFICATION

This Gopher State Ethanol Health Consultation was prepared by the Minnesota Department of Health under a cooperative agreement with the Agency for Toxic Substances and Disease Registry (ATSDR).

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

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Tables

Table 1

Pre-Consent Decree DDGS Dyer/Thermal Oxidizer Testing Requirements and Emission Limits		
Applicable Rule or Regulation	Pollutant Tested and Applicable Emission	Test Method and Length of Run
40 CRF 52.21	VOC Ò7.7 lbs/hr, Methanol, Ethanol,NOx	Method 1,2,3B,4,5,and 202, three one hour runs
Minnesota Rules 7011.1005 (3) (d)	PM Ò10.62 lbs/hr, PM10 Ò10.62 lbs/hr, Opacity,	Method 308, three one hour runs Method 7E, three one hour runs

Adapted From Reference 5

Table 2

Dryer Stack Data Collected October 12-13, 2000					
Compound	Run 1 Mass Rate (LB/HR)	Run 2 Mass Rate (LB/HR)	Run 3 Mass Rate (LB/HR)	Average (LB/HR)	Emission Standard
NOx	1.87	1.64	1.4	1.64	Not Applicable
Total Sulfur	0.022	0.023	0.024	0.02	
Particulate	9	7.9	7.7	8.20	PM 10 less than or equal to 10.62 lbs/hr
Total Hydrocarbons as Propane	19.2	25.1	34.9	26.40	Not Applicable
Total Hydrocarbons as Methane	20.9	27.4	38	28.77	Not Applicable
Total Hydrocarbons as Carbon	15.7	20.5	28.5	21.57	
Methanol	<0.74	<0.75	<0.75	<0.75	
Ethanol	3.96	2.04	3.74	3.25	
Toluene	0.024	0.023	0.023	0.023	
Ethylbenzene	0.005	0.004	<0.005	0.005	VOC less than or equal to 7.7 lbs/hr
Acetone	0.04	0.1	Not Detected	0.07	
Formaldehyde	0.07	0.11	0.02	0.07	
Acetaldehyde	0.79	0.99	0.92	0.90	
Acrolein	0.047	0.06	0.07	0.06	
Benzene	0.091	0.088	0.098	0.092	
Styrene	0.061	0.081	0.033	0.058	

Adapted from Reference 5

Table 3

Dryer Stack Tentatively Identified Compound (TIC) Data Collected October 2000		
Compound	**Estimated** Concentration ppb	Chemical Abstract Number
1,3-butadiene	38	1575-41-0
1,3-butadiene, 2-methyl-	38	78-79-5
1,3-pentadiene	38	504-60-9
1-2-propadiene	60.8	463-49-0
1-4-pentadiene	53.1	591-93-5
1-decene	41.8	872-05-9
1-dodecene	38.2	112-41-4
1-heptene	115	592-76-7
1-hexene	198	592-41-6
1-methy-2-cyclopropene	33.9	41977-37-1
1-nonene	33.8	124-11-8
1-octene	57.8	111-66-0
1-undecene	31.2	821-95-4
2-butanone	480	78-93-3
2-butenal	45.9	4170-30-3
2-furancarboxaldehyde	657	98-01-1
2-heptenal	42.2	18829-55-5
2-methyl-1-pentene	200	763-29-1
2-methyl-2-propenal	46.3	78-85-3
2-methyl-butanal	63.6	96-17-3
2-methyl-furan	29	534-22-5
2-methypropenal	184	78-84-2
2-pentyl-furan	38.1	3777-69-3
2-propen-1-ol	36.7	107-18-6
2-propenal	353	107-02-8
3-methyl-butanal	232	590-86-3
6-heptenoic acid	50.2	25118-23-4
acetaldehyde	6180	75-07-0
benzaldehyde	205	100-52-7
ethanol	2340	64-17-5
furan	54.6	592-41-6
hexanal	161	66-25-1
Nitro-methane	127	75-52-5
nonanal	41.3	124-19-6
propene	427	115-07-1
unknown hydrocarbons	1088.9	Not available

Adapted from Reference 5

Table 4

Dryer Stack Performance Testing March 31, 2001 Results Summary				
Compound	Run 1 Mass Rate (LB/Hour)	Run 2 Mass Rate (LB/Hour)	Run 3 Mass Rate (LB/Hour)	Mean (LB/HR)
Lactic Acid	19.2	15.7	190.6*	17.45
Acetic Acid	20.6	19.4	15.3	18.43
Furfuraldehyde	0.17	0.28	0.3	0.25
Methanol	<0.45	<0.46	<0.45	<0.45
Ethanol	1.91	1.92	1.71	1.85
Formaldehyde	1.35	1.6	1.7	1.55
Acetaldehyde	1.65	3.59	3.37	2.87
Acrolein	0.13	0.08	0.07	0.09
Benzene	0.026	0.03	0.029	0.03
Styrene	<0.019	<0.020	<0.019	<0.019

Adapted from Reference 18; * = flagged data because value is not consistent with other data points

Table 5

Thermal Oxidizer VOC Emission Rates				
Compound	Run 2 (LB/HR)	Run 3 (LB/HR)	Run 4 (LB/HR)	Mean Emission Rate (LB/HR)
Ethanol	0.02	0.02	0.02	0.02
Acetic Acid	0.53	0.66	0.49	0.56
Formaldehyde	0.03	0.02	0.02	0.02
Methanol	0.02	0.02	0.02	0.02
Acetaldehyde	0.19	0.11	0.09	0.13
Acrolein	< 0.02*	< 0.07*	< 0.02*	< 0.04*
2-Furfuraldehyde	0.02	0.03	0.02	0.02
Lactic Acid	< 0.24*	< 0.26*	< 0.24*	< 0.25*
Glycerol	< 4.56*	< 4.92*	< 4.53*	< 4.67*
Total (lb/hr)	5.64	6.12	5.46	5.74
Total (lb/hr) without Glycerol	1.07	1.19	0.88	1.05
Total Hydrocarbon as Carbon lb/hr (Inlet)	35.35	35.07	31.75	34.057
Total Hydrocarbon as Carbon lb/hr (Outlet)	0.261	0.182	0.052	0.165

Adapted from Reference 19
(lb/hr) = Pounds per Hour
*= below detection limit.

Table 6 Identfied Compounds From Ethanol Production

Compound	CAS #	flash point (Celsius)	Comments	Odor Threshold ppm
propanoic acid	105-37-3	12	fruity odor	0.05
butane	106-97-8	-138		
1,3-butadiene	106-99-0			0.5
2-propenal/acrolein	107-02-8		a piercing, disagreeable odor, Lachrymator.	0.1-2.0
2-propen-1-ol/ally alcohol	107-18-6	21	odor like mustard. Lachrymator.	1.5
pentane, 2 methyl	107-83-5	-23		
pentane	109-66-0	-49	gasoline-like odor	
formic acid	109-94-4	-20	a fruity odor	5
hexane	110-54-3	-22	mild gasoline-like odor detectable at 65 to 248 ppm	100
1-octene	111-66-0	13		100
6-heptenoic acid	1119-60-4			
1-dodecene	112-41-4	77		
1 butanol 3-methyl, aceta/ isoamyl alcohol	123-51-3	43	causes coughing	0.05
1 butanol 3-methyl, aceta	123-92-2	25		
1-nonene	124-11-8	25		
1 butanol 2-methyl	137-32-6	43		
ethyl acetate	141-78-6	-4	pleasant, fruity odor detectable at 7 to 50 ppm	10.0-20.0
heptane	142-82-5	-4	gasoline-like odor	100
1 butanol 2-methyl (s)	1565-80-6	43		
1-butanol, 2-methyl- (S)	1565-80-6	43		
2-pentyl-furan	3777-69-3			
2-butenal/ crontonaldehyde	4170-30-3	13	lachrymator	
1-2-propadiene	463-49-0			
1,3-pentadiene	504-60-9	-28 fp	lachrymator	
1-undecene	821-95-4			
1-decene	872-05-9	47		
2-methyl-butanal/ 2-Methylbutyraldehyde	96-17-3	-5		
cyclopentane, methyl-	96-37-7	-10		
Ammonia	7664-7	11	respiratory irritation	0.05
Benzene	71-43-2	-11	reproductive/ developmental	10.0-60.0
Ethylbenzene	100-41-4	15		0.1-0.5
Hydrogen sulfide	1183-06-4	-82.4	strong odor of rotton eggs	0.001-0.005
Formaldehyde	50-00-0	60	lachrymator	0.3

Table 6 Continued Identfied Compounds From Ethanol Production

Compound	CAS #	Flash Point (Celsius)	Comments	Odor Threshold ppm
2-methyl-furan	534-22-5	-26		
glycerol	56-81-5	160		
sucrose/DP3, DP4	57-50-1			
hexane, 3-methyl	589-34-4	-3		
3-methyl-butanal/ isovaleraldehyde	590-86-3	-5	stench	
hexane 2-methyl	591-76-4	-3		
1-4-pentadiene	591-93-5	4		
1-hexene	592-41-6	-26		
1-heptene	592-76-7			
1 butanol 3-methyl, aceta	624-41-9			
ethanol	64-17-5	12	Pleasant alcoholic odor detectable at 49 to 716 ppm	50.0-100.0
1-propanol	71-23-8	15		
acetaldehyde	75-07-0	-27	lachrymator	
dimethyl sulfide	75-18-3	-37	stench	
Nitro-methane	75-52-5	35	fruity odor	
butane, 2, 2-dimethyl	75-83-2	-48		
2-methyl-1-pentene	763-29-1	-26		
butane, 2-methyl	78-78-4	-51		
2-methyl-1,3-butadiene/ isoprene	78-79-5	-48		
1-propanol, 2-methyl	78-83-1	28		
2-methylpropanal/ isobutyraldehyde	78-84-2	-24	nonviscous liquid. Stench	
2-methyl-2-propenal/ methacrylaldehyde	78-85-3	-15	lachrymator	
2-butanone/ MEK	78-93-3	-7	odor det. 2-85ppm	
butane, 2, 3-dimethyl	79-29-8	-28		
2-furancarboxaldehyde/ Furfuraldehyde	98-01-1	60		
styrene	100-42-5	32		
lactic acid	50-21-5		irritant	
unknown hydrocarbons				
Tetracholoroethylene	127-18-4	CNS- mild eye and respiratory irritation	Human data	20000
Toluene	37000	eye and respiratory irritation	human data	37000
Sodium hydroxide	8	skin eye, and respiratory irritation	human data	8
Styrene	21000	eye and respiratory irritation	human data	21000
Xylenes	22000	skin eye, and respiratory irritation	human data	22000

Table 7

Distillation Scrubber Stack Emission Data Collected November 8, 2000				
Test Compound	Test Run 1 lbs/hr	Test Run 2 lbs/hr	Test Run 3 lbs/hr	Average (lb/hr)
Methanol	<0.012	<0.0009	<0.0003	< 0.0008
Ethanol	0.0056	0.0028	0.0004	0.0029
Total Hydrocarbons as Carbon	0.002	0.0043	0.0003	0.0022
Total Hydrocarbons as Propane	0.0024	0.0053	0.0003	0.0027
Total Hydrocarbons as Methane	0.0026	0.0058	0.0003	0.0029
Total Sulfur	0.00002	0.000015	0.000004	0.000013
Carbonyl Sulfide	0.00002	0.000015	0.000004	0.000013
Formaldehyde	0.0000021	0.0000015	0.000005	0.0000014
Acetaldehyde	0.0000074	0.0000039	0.0000006	0.000004
MEK/Butyraldehydes	0.0000006	<0.0000004	<0.0000001	0.0000004
m,p-Tolualdehyde	0.0000025	0.0000018	0.0000003	0.0000015
Adapted from Reference 9				

Table 8

Distillation Scrubber Tentatively Identified Compound (TIC) Data Collected November 2000		
Compound	Estimated Concentration ppbv	Chemical Abstract Number
1 butanol 3-methyl	366	79-29-8
1 butanol 3-methyl, aceta	517	123-51-3
1-butanol, 3methyl- (S)	27	1565-80-6
1-butanol, 3methyl- aceta	105	123-92-2
butane	175	106-97-8
butane, 2, 2-dimethyl	28.9	75-83-2
butane, 2, 3-dimethyl	37.8	79-29-8
butane, 2-methyl	953	78-78-4
cyclopentane, methyl-	123	96-37-7
ethanol	2180	64-17-5
ethyl acetate	322	140-78-6
heptane	35.2	142-82-5
hexane	561	110-54-3
hexane 2-methyl	41.3	592-76-4
hexane, 3-methyl	32.4	589-34-4
Nitro-methane	96	75-52-5
pentane	887	109-66-0
pentane, 2 methyl	357	107-83-5
unknown hydrocarbons	55.4	Not available

Adapted From Reference 9

Table 9

Fermentation Scrubber Outlet Emission Data Collected Nov 7, 2000					
Test Compound	Run 1 lb/hr	Run 2 lb/hr	Run 3 lb/hr	Run 4 lb/hr	Mean* lb/hr
Methanol	<0.06	<0.06	<0.04	<0.04	<0.04
Ethanol	8.98	3.6	3.01	2.64	3.083
Total Hydrocarbons as Carbon	1.9	1.2	1	1.3	1.167
Total Hydrocarbons as Propane	2.3	1.5	1.2	1.7	1.467
Total Hydrocarbons as Methane	2.5	1.6	1.3	1.8	1.567
Total Sulfur	0.029	0.02	0.029	0.026	0.025
Hydrogen Sulfide	<0.004	<0.004	0.008	0.005	0.0065
Carbonyl Sulfide	0.001	0.001	0.001	0.001	0.001
Dimethyl Sulfide	0.028	0.019	0.014	0.02	0.018
Formaldehyde	0.0007	<0.0006	<0.0003	0.0005	0.0005
Acetaldehyde	0.038	0.138	0.081	0.086	0.102

Adapted from Reference 9

*= Mean does not include Test Run 1 due to technical difficulties

Table 10

Fermetation Scrubber Tentatively Identified Compound (TIC) Data Collected November 2000		
Compound	Estimated Concentration ppbv	Chemical Abstract Number
1 butanol 2-methyl	1060	137-32-6
1 butanol 2-methyl (s)	772	1565-80-6
1 butanol 3-methyl, aceta	2660	123-92-2
1 butanol 3-methyl, aceta	273	624-41-9
1 butanol 3-methyl, aceta	5410	123-92-2
1,3-pentadiene	1390	504-60-9
1-butanol, 3-methyl	4310	123-51-3
1-propanol	282	71-23-8
1-propanol, 2-methyl	1000	78-83-1
acetaldehyde	5860	75-07-0
dimethyl sulfide	1700	75-18-3
ethanol	65200	64-17-5
ethyl acetate	10200	141-78-6
formic acid	254	109-94-4
pentane	551	109-66-0
propanoic acid	614	105-37-3

Adapted from Reference 9

Table 11

Particulate Emissions Compliance Testing October 13-23, 2000				
Equipment	Test Run 1 Particulate Emission Rate (lbs/hr)	Test Run 2 Particulate Emission Rate (lbs/hr)	Test Run 3 Particulate Emission Rate (lbs/hr)	Applicable Particulate Emission Limit
Grain Cooler Stack/Cooling Cyclone	0.3	0.3	0.2	PM Ò1.0 lbs/hr, PM10 Ò1.0lbs/hr
Baghouse Stack	0.4	0.4	0.3	PM Ò2.0 lbs/hr, PM10 Ò0.7 lbs/hr

Adapted from Reference 11

Table 12

Odor Evaluation Report Results				
Sample Location	Detection Threshold (DT)	Recognition Threshold (RT)	Hedonic Tone (HT)	Evaluation Date
DDGS Exhaust	5000	2600 - 3400	-2.2 to -3.2	3/31/2001
DDGS Exhaust	5000-5800	2600-3400	-2.2 to -3.2	4/5/2001
Fermentation Scrubber/CO2 Scrubber	2300	1300	NA	
Distillation Scrubber	3200	2300	-4.6	
Carbon Bed Steam Regenerator	7000	4600	-3.4	
Cooling Cyclone	4600	2800	-4.2	
Cooker Room Cupola Exhaust	220	140	6	
Brew Kettle No. 2	620	340	1	
Thin Stillage Surge Tank	1600	94	NA	
Thermo Oxidizer	1300-2000	720-1200	-0.2 to -1.4	2/5/2002
DDGS Handling Baghouse	210-410	90-260	-2.2 to -3.0	
Distillation Scrubber	13000-15000	9100 - 10000	-4.6 to -5.6	

Adapted from Reference 4; NA= not available

Table 13

8 Levels Of Odor Exposure	
Level	Description
1) odor detection	The level of odor that can first be differentiated from ambient air.
2) odor recognition	The level of odor at which the odor quality can be characterized (identified)
3) odor annoyance	The level at which a person is annoyed by an odor but does not show or perceive a physical reaction. Note: health symptoms not expected at the first three levels unless the odor includes a co-pollutant like particulate as in paradigm 3 or the level of annoyance is intense or prolonged.
4) odor tolerance (causing somatic symptoms)	The level at which an individual may show or perceive physical (somatic) symptoms to an odor. This level corresponds to Paradigm 2 in which the odor induces symptoms even though the odorant concentration is lower than that known to cause irritation.
5) perceived irritant	The level at which a person reports irritation or physical symptoms as a result of stimulation of nerve endings in the respiratory tract.
6) somatic irritant	The level at which an odorant results in a negative physical reaction regardless of an individual's predisposition. This can occur when an odorous compound damages tissue.
7) chronic toxicity	The level at which an odorant can result in a long-term health impact.
8) acute toxicity	The level at which an immediate toxic impact is experienced.

Adapted from Reference 12

Table 14 AMENDED CONSENT DECREE EMISSION LIMITS FOR POLLUTION CONTROL EQUIPMENT

Process Description	Control Device	Control Device Description	Pollutant	Short Term Emission Rate	Long Term Emission Rate
DDGS Drying	CE 002 CE 010	Dryer Cyclones and Thermal Oxidizer	PM/PM10	To be determined pursuant to Paragraph 24 of the Consent Decree.	12-month rolling sum, source-wide PM/PM10 cap of 95 TPY
			VOC	95% reduction or emissions no higher than 10 ppm; lb/hr limits to be established based on performance testing under the process outlined in Paragraph 24 of the Consent Decree.	12-month rolling sum, source-wide VOC cap of 95 TPY.
			HAPs		12-month rolling sum, total facility emission cap of 9.0 TPY for any single HAP and 24.0 TPY for total HAPs.
			NOx	To be determined pursuant to Paragraph 23 of the Consent Decree.	12-month rolling sum, source-wide NOx cap of 95 TPY and 12-month rolling sum for Group NOx limit.
			CO	90% reduction or emissions no higher than 100 ppm	12-month rolling sum, source-wide CO cap of 95 TPY.
Cooling Cyclone	CE 006 CE (tbd)	Cyclone (existing) Baghouse	PM/PM10		12-month rolling sum, source-wide PM/PM10 cap of 95 TPY
			VOC	lb/hr limits to be established pursuant to Paragraph 22 of the Consent Decree.	12-month rolling sum, source-wide VOC cap of 95 TPY.
			HAPs		12-month rolling sum, total facility emission cap of 9.0 TPY for any single HAP and 24.0 TPY for total HAPs.
			HAPs		12-month rolling sum, total facility emission cap of 9.0 TPY for any single HAP and 24.0 TPY for total HAPs.
Ethanol Fermentation	CE 008 CE (tbd)	Packed Column Scrubber (existing) Packed Column Scrubber (Post-scrubber)	VOC	95% reduction or not to exceed 20 ppm if inlet concentration is less than 200 ppm; lb/hr limits to be established based on performance testing under the process outlined in Paragraph 24 of the Consent Decree.	12-month rolling sum, source-wide VOC cap of 95 TPY.
			HAPs		12-month rolling sum, total facility emission cap of 9.0 TPY for any single HAP and 24.0 TPY for total HAPs.
Cooling Cyclone	CE 006 CE (tbd)	Cyclone (existing) Baghouse	PM/PM10		12-month rolling sum, source-wide PM/PM10 cap of 95 TPY
			VOC	lb/hr limits to be established pursuant to Paragraph 22 of the Consent Decree.	12-month rolling sum, source-wide VOC cap of 95 TPY.
			HAPs		12-month rolling sum, total facility emission cap of 9.0 TPY for any single HAP and 24.0 TPY for total HAPs.
Wet Cake Alternate Operating Scenario			VOC	lb/hr limits to be established pursuant to Paragraph 15(k) of the Consent Decree.	12-month rolling sum, source-wide VOC cap of 95 TPY.
			HAPs		12-month rolling sum, total facility emission cap of 9.0 TPY for any single HAP and 24.0 TPY for total HAPs.
Ethanol Loading Rack	CE (tbd)	Thermal Oxidizer	VOC	Truck Loadout: 95% reduction of VOCs or no greater than 10 ppm.	12-month rolling sum, source-wide VOC cap of 95 TPY.
			HAPs		12-month rolling sum, total facility emission cap of 9.0 TPY for any single HAP and 24.0 TPY for total HAPs.
Boiler #1	EU001		NOx		12-month rolling sum, source-wide NOx cap of 95 TPY and 12-month rolling sum for Group NOx limit.
Boiler #2	EU002		NOx		12-month rolling sum, source-wide NOx cap of 95 TPY and 12-month rolling sum for Group NOx limit.

Adapted from Reference 26

Figures


Large Stack
West 7th Ave.
Minnesota Brewing Company
and
Gopher State Ethanol Facility
N

Figure 1

Figure 2

Pre-Thermal Oxidizer

DDGS Dryer Stack Fugitive Emissions

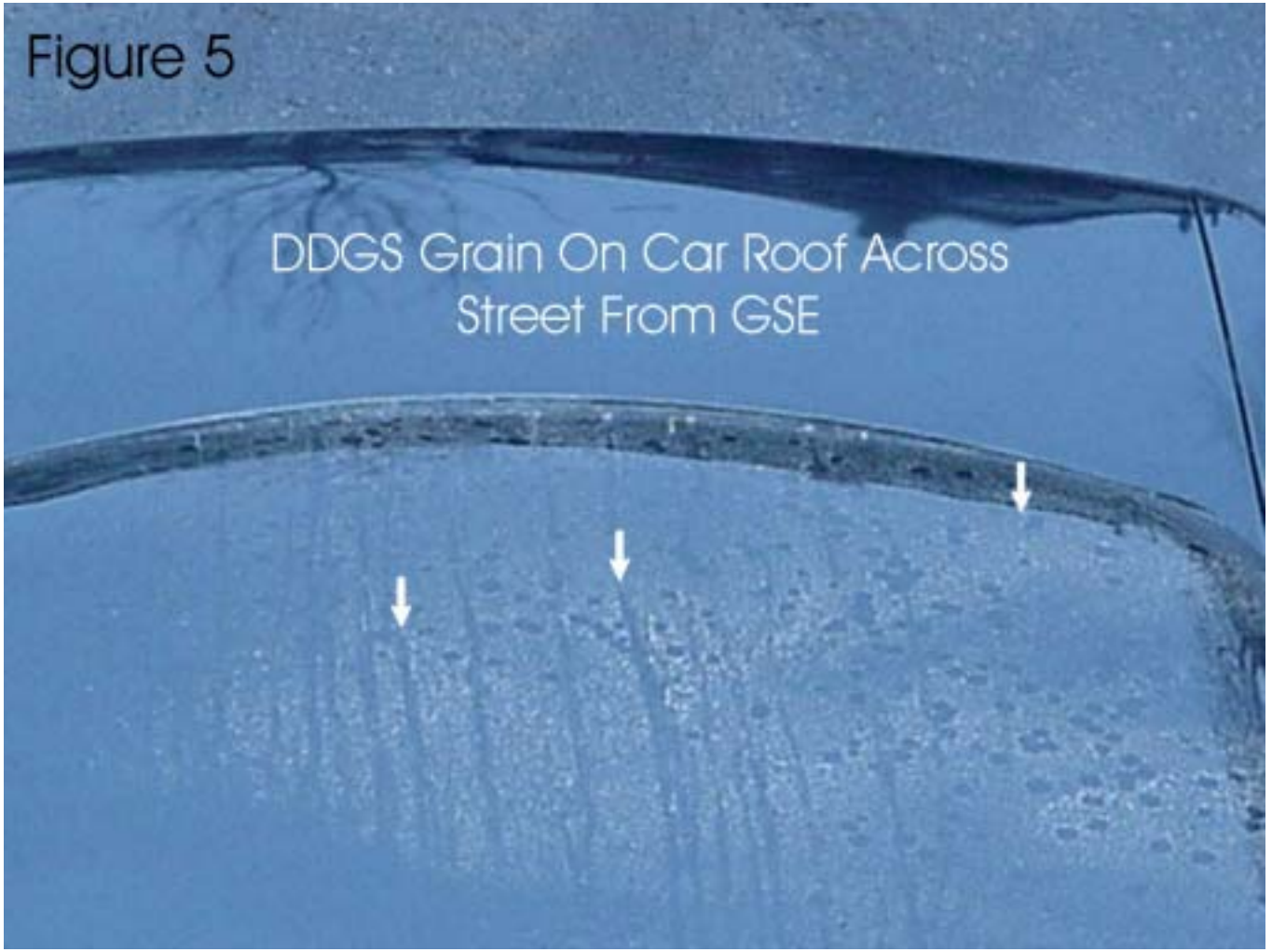
(This stack has been removed)

Figure 3
Corrosive Gasses Released Inside Building

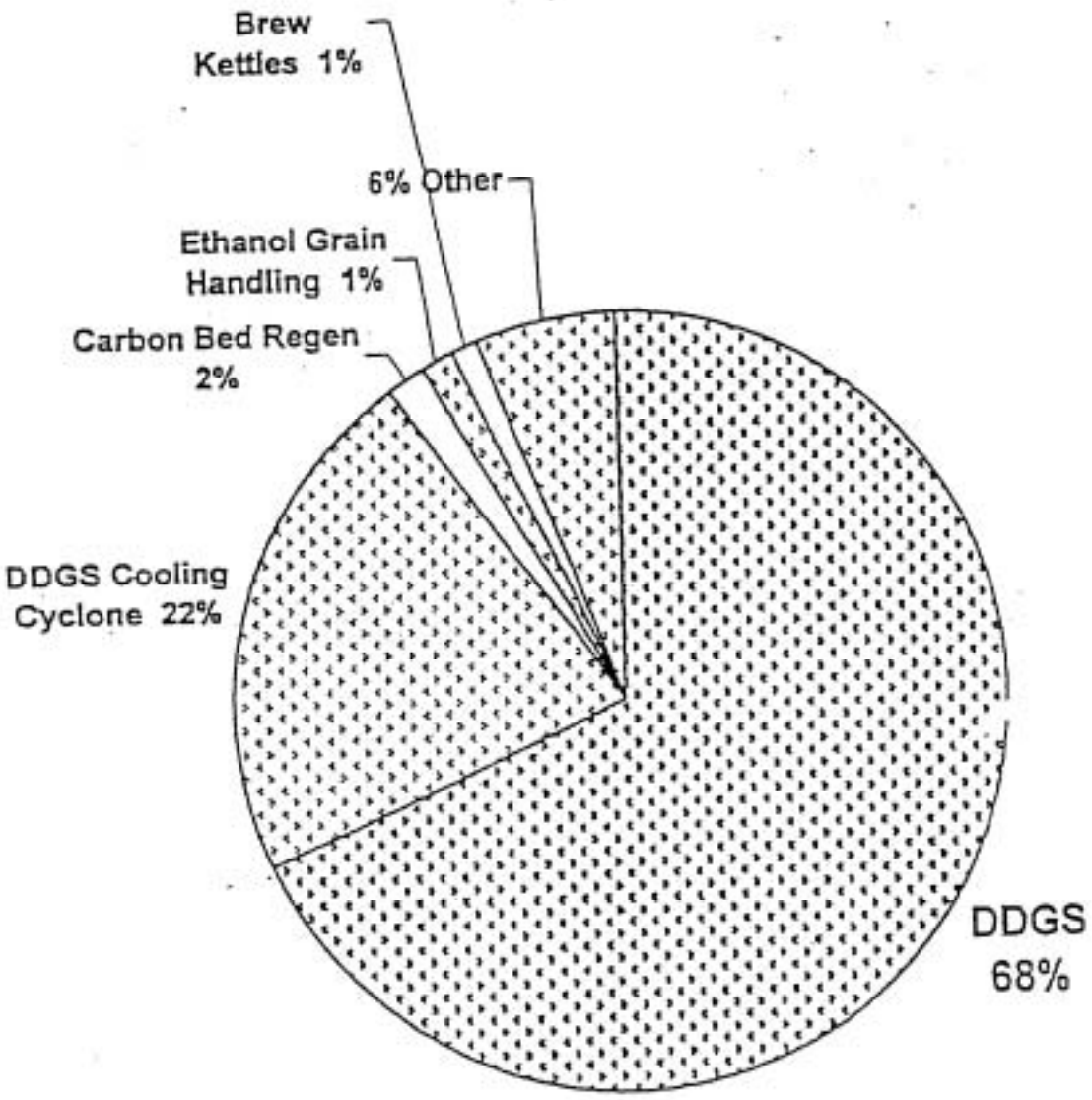
Figure 4 DDGS Release

Figure 4a

Figure 5



MBC Odor Emission Inventory



April 2001

Figure 6

Appendix A

Three Citizen Journals
And
Complaints of Odors, Health Effects and Noise

When GSE first started operating in Spring 2000 there were many of complaints of odors and noise. Many of the complaints were not logged because citizens did not know what agency should receive the complaints. However, approximately 400 citizens filled a City Council Public Hearing meeting at Monroe Elementary in October 18, 2000 to complain to Council Members.
From September 2000 to December 2001, **36** Minnesota Duty Officer complaints of odors and health effects were received. GSE odor, alleged health effects, and noise complaints from June 2002 (approximate month the TO stopped working) to August 4, 2003 (**408 total**) reported to the Minnesota Duty Officer :

Month year / complaint numbers
June 02 / 6
July 02 / 55
Aug 02 / 31
Sep 02/ 30
Oct 02 / 19
Nov 02 /19
Dec 02 / 18
Jan 03 / 21
Feb 03 / 32
March 03 / 49
April 03 / 44
May 03 / 25
June 03 / 8
July 03 / 46
August 1- 4, 2003 / 5

Complaints sent to the City of St. Paul for June 20, 2002 - August 9, 2002 totaled **125**.

Appendix B

Proposed Emissions Testing and Mechanical Improvements at GSE

Appendix C

Public Comments to the Draft Gopher State Ethanol PHA

Appendix D

Photos of Uncharacterized Stack Emissions At the MBC/GSE Facility

Appendix E

St. Croix Sensory Odor Descriptor Histograms

Appendix F

GSE Amended Consent Decree Summary Tables for Control Equipment Monitoring Requirements and Emission Limits