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Hydrogen Sulfide Emissions from Open/Dry-Lot Cattle-Feeding Operations

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Introduction

Hydrogen sulfide (H_2S) is a naturally occurring, colorless gas with a foul smell like rotten eggs. Toxic to humans at certain concentrations, it is regulated by federal and state governments. Hydrogen sulfide has been detected downwind of beef cattle feedlots, but usually at very low concentrations.

Hydrogen sulfide sources on beef feedyards

Hydrogen sulfide is often produced when bacteria decompose organic matter containing sulfur, such as manure, in anaerobic (without oxygen) conditions. In general, H_2S emissions from feedyards come from surfaces such as pens or manure piles where manure accumulates and from the surface of treatment lagoons or runoff holding ponds.[1] Extended anaerobic conditions on surfaces normally associated with standing water or wet manure can generate H_2S gas over large areas.

Sulfur is found in livestock feed and drinking water and is an essential nutrient for cattle. It has been estimated that every 1,000 head of beef cattle in the Texas Panhandle consume about 25 to 42 kilograms of sulfur daily. Cattle retain only 10 to 20 percent of the sulfur they ingest, and excrete the remaining 80 to 90 percent.

Hydrogen sulfide and human health

Hydrogen sulfide is toxic to humans and causes negative health effects even at low concentrations (Table 1). Some are reversible, but others are often permanent, such as damage to the lungs, eyes, or brain. At elevated concentrations, H_2S is highly toxic and can cause instant death.

Humans can be exposed to H_2S by breathing contaminated air or drinking contaminated water. Natural sources of H_2S contamination include groundwater, natural gas, and volcanic gases. Anthropogenic sources (those caused by human activity) include sour crude oil refineries, pulp and paper mills, oil and gas operations, sewage treatment plants, and animal agriculture.

[1] A "lagoon" is a pond designed to treat organic wastes. A "runoff holding pond" is a pond designed to store runoff water for a short term.

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Table 1: Health effects of exposure to H_2S

Hydrogen sulfide concentration	Human health effects
0.5–30 ppbv*	Odor detectable by most (83%) people
1–10 ppmv** (short-term exposure)	Appetite loss, breathing problems, dizziness, eye/nose/throat irritation, headache, nausea, and sleeping problems
1–10 ppmv (chronic exposure)	Anxiety, depression, eye and respiratory irritation, pulmonary edema, fatigue, impaired neurological function, loss of balance, memory loss, numbness, and sleep disruption
~ 25 ppmv	Irritation symptoms begin in most people
~ 100 ppmv	Instant lung damage, respiratory failure, unconsciousness
> 150 ppmv	Odor undetectable because the olfactory nerve is paralyzed, disabling the sense of smell
> 800+ ppmv	Complete nervous system failure and sudden death

*parts per billion by volume
**parts per million by volume

Some officials are concerned that H_2S concentrations downwind of feedyards may exceed regulatory or public-health limits. However, a recent literature review and field monitoring near and within cattle feedyards concluded that concentrations measured downwind of feedlots are usually very low. Hydrogen sulfide can be emitted at very low rates from pen surfaces and runoff holding ponds, but the health threat is low due to the open-air environment of beef feedlots. More serious threats arise in enclosed buildings or pits which are not generally found on beef feedlots.

Environmental concerns

Hydrogen sulfide oxidizes rapidly to sulfuric acid (H_2SO_4) in the presence of water. Sulfuric acid is very corrosive and well-known for damaging structural steel and concrete to the point of failure. It has destroyed electronic controls in pulp and paper mills and components in water, oil, and gas production wells, municipal wastewater plants, and manure storage systems. Severe damage across the US prompted the US Environmental Protection Agency (EPA) to produce a technical handbook aimed at detecting and controlling H_2S corrosion. Corrosion due to H_2S is not generally a problem on feedyards in the semi-arid High Plains because the gas is present at very low levels, relative humidity is low, and most feedyards do not feature closed structures where H_2S gas can accumulate.

Regulatory issues

The toxic nature of H_2S makes it subject to state and federal regulations. Reporting requirements fall under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Emergency Planning and Community Right-to-Know Act (EPCRA). Health-based exposure standards are established by the Occupational Health and Safety Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH). Feedyards are subject to these reporting and exposure regulations.

Under EPCRA, feedyards with more than 11,750 head of cattle must report releases in excess of 45 kilograms (100 pounds) per day. All feedyards are currently exempt from reporting

Table 2: Five states clearly require CAFO compliance with H_2S ambient air quality standards

State	Regulation	
Iowa	0.03 ppmv 1-hr daily maximum	
Minnesota	0.05 ppmv 30-min average, not to exceed 2x/yr	0.03 ppmv 30-min average, not to exceed 2x in 5 consecutive days
Nebraska	0.01 ppmv 30-day average	
Rhode Island	0.03 ppmv 1-hr average	
Texas	0.08 ppmv 30-min average, residential, business, commercial property	0.12 ppmv 30-min average, other property

H_2S releases under CERCLA. Producer organizations, such as Beef USA and the National Cattlemen's Beef Association, have provided research-based guidelines to feedyards for estimating and reporting H_2S releases.

A ceiling limit is a maximum permissible concentration limit that must never be exceeded. The OSHA-acceptable 10-minute ceiling limit for H_2S is 20 ppmv, and NIOSH recommends a 10-minute ceiling limit of 10 ppmv. Feedyards must keep records and file annual reports with OSHA regarding H_2S, but are exempt from the record-keeping requirements if they employ 10 or fewer non-family workers.

The Texas Administrative Code (TAC) sets two thresholds—urban and rural—for locations downwind of a H_2S source:

- The urban threshold is a net, ground-level concentration[2] of 0.08 ppmv (parts per million by volume) averaged over any 30-minute period at any residential, business, or commercial property.
- The rural threshold is a net, ground-level concentration of 0.12 ppmv averaged over any 30-minute period and applies to any property that is not residential, business, or commercial.

The Texas Commission on Environmental Quality (TCEQ) enforces the thresholds specified in the TAC and has established regulatory values for a 30-minute average ambient concentration of 0.08 ppmv downwind of sources, including feedyards.

Thirty-five states have regulations pertaining to ambient air concentrations of H_2S, but only five of those clearly require compliance by concentrated animal feeding operations (CAFOs): Iowa, Minnesota, Nebraska, Rhode Island, and Texas (Table 2). CAFOs are clearly exempt from H_2S ambient air concentration regulations in 15 states because they are specifically exempted, are not defined, or not included as an industry. These states include Alabama, Arizona, Colorado, Delaware, Hawaii, Illinois, Louisiana, Maryland, Michigan, Missouri, Montana, New Hampshire, New Mexico, North Dakota, North Carolina, Pennsylvania, South Carolina, Tennessee, Vermont, Wisconsin, and Wyoming. The applicability of existing regulations to CAFOs is unclear in the remaining 15 states.

States establish limits on H_2S concentrations in ambient air to protect human health, welfare, and property, but use different methods to set

[2] "Net concentration" refers to the numerical increase in concentration between a measurement upwind of a source and a corresponding measurement downwind of that source. "Ambient concentration" refers to an absolute measurement, usually at a location that does not isolate a single source but represents the broader area around the monitoring site.

those limits. Some states derive their regulatory values from EPA estimates of human health effects.[3] Other states, such as Iowa, use data from local monitoring studies and health data to establish regulatory levels. North Dakota established its levels from a literature review on H_2S. Others, such as California and New York, base their levels on odor thresholds. Property damage from the corrosive effect of H_2S on buildings and structures is the rationale for levels set by Nebraska and Pennsylvania.

Due to its strong, distinctive smell, states sometimes regulate H_2S as a nuisance odor. Hawaii, Minnesota, New York, and Texas base their regulations, in part, on nuisance odor abatement. Similarly, Minnesota currently regulates feedlot nuisance odor by limiting H_2S emissions.

Monitoring methods

Compliance with environmental regulations requires continuous monitoring of H_2S according to established protocols with approved instrumentation. Instruments must be regularly inspected and calibrated by knowledgeable personnel to ensure accurate measurements.

There are many scientific instruments capable of measuring H_2S, including Dräger tubes, Jerome hydrogen sulfide analyzers, and pulsed fluorescence analyzers.

Dräger tube

A Dräger tube detects H_2S gas by drawing an air sample through a glass vial filled with a reagent. The reagent changes color to indicate the presence of H_2S gas, and the length of the color change along the tube indicates the concentration.

Different models of Dräger tubes use various reagents to detect H_2S gas at specific ranges. For example, model 0.2/b uses mercuric chloride ($HgCl_2$) to detect concentrations between 0.1 and 6 ppmv, while model 2/a uses a mercuric ion (Hg^{2+}) to detect concentrations between 2 and 200 ppmv. Other gases may interfere with H_2S readings, depending on the model of the instrument and the reagent used.

Jerome meter

The Jerome Meter 631-X is a common, portable instrument that can detect H_2S from 2 ppbv to 50 ppmv. In a Jerome meter, sulfur compounds adsorb to a gold film sensor causing changes in its resistivity. Trace amounts of other sulfur compounds can also affect the sensor resistivity, so the H_2S concentrations reported by a Jerome meter may be biased slightly upward. The degree of the bias depends on the concentration of other sulfurous compounds in the air.

Pulsed fluorescence analyzer

An electronic pulsed fluorescence analyzer can detect H_2S between 3 ppbv and 100 ppmv. Designed for use in a laboratory or other protected environment such as a mobile instrument shelter, it can also be used in the field if equipped with a protective housing and power supply. This instrument catalytically converts H_2S to sulfur dioxide (SO_2) and then measures the SO_2 concentration with a pulsed fluorescence analyzer. Other gases present at feedyards, such as ammonia (NH_3), may interfere with the H_2S measurements.

Other equipment

Microprocessor-based electrochemical sensors can be used for personal protection in areas where H_2S gas may exist. These smaller,

[3] The EPA's No Observable Adverse Effect Level (NOAEL) for H_2S is 10 ppmv, and Lowest Observable Adverse Effect Level (LOAEL) is 30 ppmv, and the Reference Concentration for Chronic Inhalation (RfC) is 0.0001 ppmv. The NOAEL and LOAEL values are inhalation reference concentrations and are extrapolated using uncertainty factors from effect levels observed in rats to predicted effect levels for humans. The RfC is an estimate of a continuous inhalation exposure concentration to humans, including sensitive subgroups, that is not likely to risk harmful health effects during a lifetime.

Several gas analyzers operating inside a trailer deployed at a CAFO including two hydrogen sulfide analyzers (Model 450i, left rack, 2nd from top; Model 45C, left rack, 3rd from top) by Thermo Scientific (Waltham, MA). (Photo courtesy of K. Casey)

portable instruments can be mounted near equipment, clipped to a belt, or carried in hand. They are used primarily as an early warning device to alert users when they should vacate an area. However, they are not designed for precise concentration measurements or regulatory compliance monitoring. When gas concentrations exceed a predetermined threshold, the instrument emits a visual and/or audible alarm. Examples of this type of instrument include the MSA Altair Pro and the Drager Pac III.

What we know

Data concerning H_2S concentrations near feedyards are scarce, especially prior to 2003. Among the four studies described below, none reported ambient 30-minute average H_2S concentrations in excess of the State of Texas regulatory value (0.08 ppmv).

- Jerome meters were used to monitor three feedyards in Nebraska for 1 week in the spring, summer, and fall of 2000. The weekly average H_2S point concentrations downwind of the pens ranged from 0.0006 to 0.013 ppmv among the three feedyards. The data revealed a daily cycle, with higher concentrations occurring during warmer afternoons.
- A Texas study reported evidence of a daily pattern of H_2S concentrations downwind of a feedyard in June 2000. In this study, the 15-minute average H_2S concentrations downwind of both the pens and the pond were on the order of 0.005 ppmv.
- Another Texas study measured H_2S concentrations upwind and immediately downwind of feedyard pens

An intake port mounted on the roof of a trailer deployed at a CAFO provides air samples to hydrogen sulfide analyzers inside the trailer. The pen surfaces and runoff holding pond visible in the background are potential sources of hydrogen sulfide. (Photo courtesy of K. Casey) and runoff holding ponds at three different Texas feedyards over a period of 1 year from May 2002 through April 2003. Averaging times were approximately 10 minutes. Average concentrations downwind of pens ranged from 0.004 to 0.104 ppmv, and downwind of the ponds ranged from 0.003 to 1.075 ppmv. Because all of the readings were taken during the day and daily emission patterns are suspected, the concentrations reported may not be representative of daily averages.

- A fourth study measured ambient H_2S concentrations using an electronic H_2S analyzer stationed on the west side of a Texas feedyard. The data are not considered representative of downwind ambient concentrations because the wind was variable and the position of the analyzer was not always downwind. The mean H_2S concentrations were 0.030 ppmv in the fall of 2002, 0.003 ppmv in the winter of 2003, and 0.035 ppmv in the spring of 2003.

Data on H_2S fluxes from feedyards are also limited and their accuracy is uncertain. There are no published data available on direct measurements of H_2S flux from runoff holding ponds. Attempts have been made to measure H_2S fluxes from feedyard surfaces using a Jerome meter, but the levels were below the detection limit of the instrument. One study in Minnesota reported a mean H_2S emission rate of 103 $\mu g/m^2/min$ (micrograms per square meter per minute) from a feedyard surface. Two other studies used a flux chamber and electronic H_2S analyzer to measure flux from pen surfaces at different feedyards and reported emission rates of 1.88 $\mu g/m^2/min$ and 1.39 $\mu g/m^2/min$.

Equilibrium flux chambers can underestimate H_2S concentrations in comparison with other methods such as backward calculating dispersion models. These models begin with observed concentrations and weather data and then calculate backwards to estimate H_2S emission rates.

WindTrax and Ausplume are two computer models that use different methods to calculate backwards and estimate H_2S emission rates. When ambient downwind H_2S concentration data from two different studies were entered into WindTrax and Ausplume, there was a significant discrepancy between the results of the two modeling programs. Further, the results from the computer models were 100 times greater than the emission rates actually measured using flux chambers. When compared to mass-balance calculations, the computer model results were more reasonable than the flux-chamber studies.

A wind tunnel floating on the surface of a treatment lagoon collects air samples that are sent to a hydrogen sulfide analyzer. (Photo courtesy of K. Casey)

What we are learning

Most of the available data on H_2S emissions from feedyards has been collected from intermittent spot measurements with Jerome meters. These data do not provide information about daily or seasonal variations in H_2S emissions. Recent continuous monitoring of ambient H_2S levels at a feedyard in the Texas Panhandle provided insight into cyclical emission rates and shed light on the uncertainty of H_2S measurement methods (Fig. 1).

- Air samples were collected every minute from 3.3 meters above a feedyard pen surface and measured using a Thermo Scientific H_2S analyzer.
- Ambient H_2S concentrations in the pen area were recorded continuously from March 2007 to July 2010.
- Almost all of the 30-minute average concentrations were below the TCEQ level of concern (0.08 ppmv).
- The long-term average concentration in the center of the feedyard was 0.005 ppmv, which is close to the detection limit of the instrument.
- Significant peaks in H_2S emissions were observed after one rainfall event, but no peaks were observed after subsequent rainfall events.
- Despite having low to very low H_2S concentrations, cumulative emission fluxes from the pen surfaces were much greater than those from the runoff holding ponds.
- Results from the pen area indicated that ambient H_2S concentrations were generally low, with an average of 4.2 ppbv between March and June of 2008.
- Occasionally the levels spiked for short periods of time.
- A daily trend was evident as H_2S emissions tended to increase with warmer air temperatures.

It now appears that H_2S emissions from cattle feedyards are a matter of intermittent bursts rather than the more continuous fluxes associated with ammonia gas (NH_3). New research is attempting to explain these peaks and learn more about the factors that affect H_2S emission rates. Some factors under investigation include ambient temperature, the amount of H_2S held in the manure matrix, cattle activity, changes in barometric pressure, differences in ration formulation, and precipitation events.

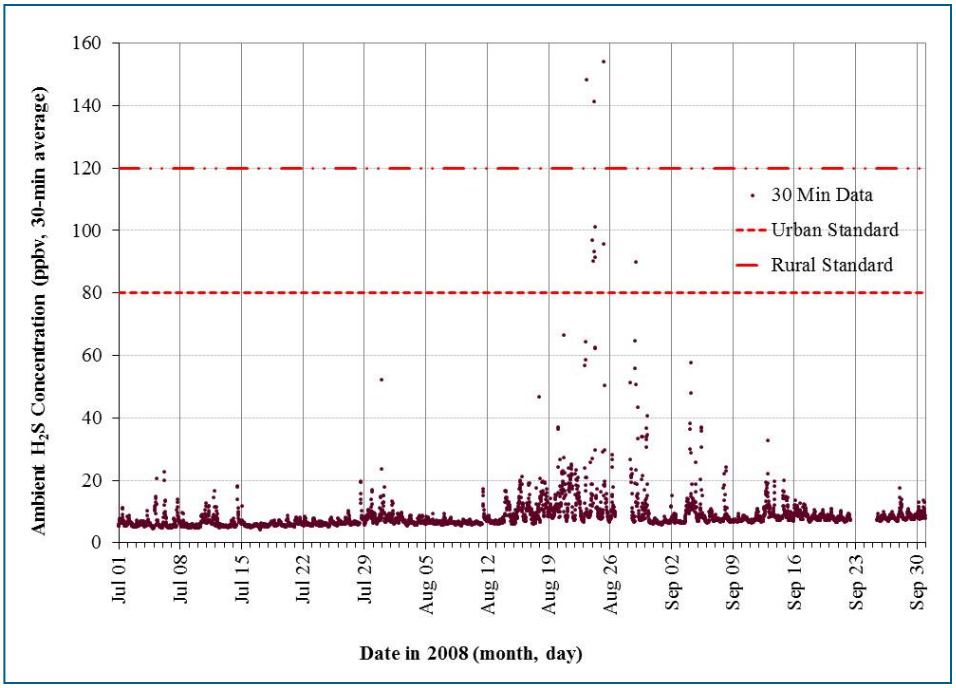

Figure 1. Ambient hydrogen sulfide concentration (30-minute average) observations from July through September 2008 juxtaposed with Texas regulatory values. (Source: K. Casey, 2008)

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