

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

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AIR QUALITY EDUCATION IN ANIMAL AGRICULTURE

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This publication discusses hydrogen sulfide emissions from concentrated animal feeding operations and their potential effects on the environment and human health.

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Hydrogen sulfide (H₂S) is a naturally occurring, colorless gas with a foul smell like rotten eggs. It is often produced when sulfurous compounds in organic matter, such as manure, are decomposed by bacteria in anaerobic (without oxygen) conditions. It also occurs in natural gas, groundwater, and volcanic gases. Common anthropogenic sources of hydrogen sulfide include sour crude oil refineries, pulp and paper mills, oil and gas operations, sewage treatment plants, and animal agriculture.

Hydrogen Sulfide Sources on Beef Feedyards

In general, hydrogen sulfide emissions from concentrated animal feeding operations (CAFOs) come from two sources. The first source is treatment lagoons or runoff retention structures. Anaerobic decomposition of manure in these structures produces hydrogen sulfide gas.

The second source is surfaces where manure accumulates, such as in pens, alleys, or manure storage areas. Extended anaerobic conditions on these surfaces, which are normally associated with standing water or wet manure, can generate this gas over large areas.

“Purple sulfur bacteria,” which use carbon dioxide, hydrogen sulfide, and ammonia for cell growth, thrive in such conditions and may be easily detected by their distinctive color (Figure 1). Although purple lagoons are less likely to be considered an odor nuisance than



Figure 1. Aerial photograph of a concentrated animal feeding operations runoff retention structure with a distinct purple color indicating the presence of purple sulfur bacteria. (Photo: S. Sakirkin)

Hydrogen sulfide emissions on concentrated animal feeding operations can occur when extended anaerobic conditions develop in standing wastewater or wet manure.

lagoons of other colors, data have shown little difference in sulfide concentrations (Koelsch et al., 1997).¹

Cattle consume sulfur in their feed and drinking water, and absorb it into their bodies primarily as sulfide. It is an essential nutrient for ruminants, but when sulfur is consumed in excess of dietary requirements, it is excreted. According to the National Research Council (NRC), cattle require at least 0.15 percent of sulfur on a dry matter basis (dm), and can tolerate up to 0.40 percent. Water in some areas may contain sulfur levels as high as 2,000 mg/L. Feed rations containing wet distillers grains plus solubles (WDGS) balanced for energy exceed the NRC requirements for sulfur, because sulfuric acid is added to grain during the ethanol production process, making WDGS higher in sulfur content than the feedstocks it substitutes. It has been estimated that every 1,000 head of beef cattle consume about 25 to 42 kg of sulfur daily in the Texas Panhandle. Cattle retain 10 to 20 percent of the sulfur they consume — that means 80 to 90 percent of ingested sulfur is excreted.

Hydrogen Sulfide and Human Health

Hydrogen sulfide is highly toxic at elevated concentrations. Exposure can occur by inhalation of contaminated air or ingestion of contaminated water. Breathing air with high levels of hydrogen sulfide may cause immediate death, and exposure to low levels over a long period can cause headaches, fatigue, and eye irritation. Hydrogen sulfide is heavier than air and may accumulate in enclosed or low-lying areas.

According to TOXNET, a federal database of information on hazardous substances, more than 80 percent of humans can smell hydrogen sulfide at concentrations between 0.5 to 30 ppbv (parts per billion by volume). The irritant threshold (the concentration at which classic irritation symptoms begin to appear in 83 percent of the population) begins at 25 ppmv (parts per million by volume) and is well above human detection levels (the concentration at which 83 percent of humans can detect the gas by smelling it).

Humans cannot detect hydrogen sulfide at levels above 150 ppmv because it paralyzes the olfactory nerve, disabling the sense of smell. Some health effects from exposure to hydrogen sulfide, such as damage to the olfactory nerve, are potentially reversible. However, anosmia (inability to perceive odors) and respiratory damage may be chronic, and damage to the eyes or brain is often permanent.

Human exposure to high levels (around 100 ppmv) will instantly cause lung damage, respiratory failure, and unconsciousness. Complete nervous-system failure and sudden death result at very high levels (around 800+ ppmv).

Short-term exposure to moderate concentrations of hydrogen sulfide (between 1 to 10 ppmv) will cause eye, nose, and throat irritation, nausea, dizziness, breathing problems, headaches, loss of appetite, and problems sleeping. Extended exposure will irritate breathing passages and may lead to pulmonary edema (fluid buildup in the lungs). People living near hydrogen sulfide sources such as paper mills, refineries, geothermal features, or meat-packing plants have an increased risk of eye irritation, cough, headache, nasal blockage, and impaired neurological function.

Chronic exposure to even very low levels of hydrogen sulfide may cause health effects (Von Essen and Auvermann, 2005). Exposure over a period of time to levels below the irritant threshold can result in physiological symptoms such as eye or respiratory irritation, and neuropsychological symptoms such as depression, memory loss, anxiety, sleep disruption, numbness, loss of balance, and fatigue (Legator et al., 2001).

Some officials are concerned that hydrogen sulfide concentrations downwind of feedyards may exceed regulatory or public-health limits. However, a recent literature review (Auvermann and Rogers, 2000) and field monitoring near and within cattle feedyards (Koelsch et al., 2004) concluded that concentrations measured downwind of concentrated animal feeding operations are usually very low. Hydrogen sulfide can be emitted at very low rates by open-lot beef cattle feeding facilities (feedyards) in gaseous form from pen surfaces and runoff retention structures. The main threat of hydrogen sulfide arises in enclosed housing structures or below-grade, enclosed manure-storage pits, features not generally found on beef feedyards.

Footnote 1

¹“Lagoon” refers to a pond that is designed and operated for treatment of organic wastes, by which we mean biochemical stabilization via digestion of volatile solids (VS) and reduction of biochemical oxygen demand (BOD). In contrast, “runoff retention structures” are designed only for detention (short-term) storage, not treatment. Consequently, the emergence of a dominant population of purple sulfur bacteria in lagoons is a management objective, but for runoff retention structures such an event may indicate the pond is under designed.

Environmental Concerns

Because it oxidizes rapidly to sulfuric acid in the presence of water, hydrogen sulfide may corrode structural steel or concrete, causing it to fracture or fail altogether. Severe damage in municipal wastewater systems across the United States prompted the Environmental Protection Agency to produce a technical handbook aimed at detecting and controlling hydrogen sulfide corrosion. It is well known for causing corrosion of equipment, pipes, and fittings in water, oil, and gas production wells.

Hydrogen sulfide, which is found throughout pulp and paper mills, also may result in extensive damage to electronics in control systems. Biogenic sulfide corrosion of concrete is an increasingly pervasive problem in wastewater systems, including manure storages. Corrosion due to hydrogen sulfide is not generally a problem in 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 have closed structures where the gas can accumulate.

Regulatory Issues

Due to its toxicity, hydrogen sulfide is 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). In December 2008, feedyards were exempted from reporting hydrogen sulfide releases under CERCLA, but EPCRA [40 CFR §355 App A] requires feedyards to report hydrogen sulfide releases in excess of 45 kilograms (100 pounds) per day.

Cattle headcounts in excess of approximately 11,750 trigger EPCRA reporting requirements. Producer organizations, such as Beef USA and the National Cattlemen's Beef Association, have provided research-based guidelines to feedyards for estimating and reporting hydrogen sulfide releases.

Federal regulatory values for hydrogen sulfide are health-based standards pertaining to occupational exposure. A ceiling limit is a maximum permissible concentration limit that must never be exceeded. The Occupational Health and Safety Act (OSHA) has established an acceptable 10-minute ceiling limit for hydrogen sulfide of 20 ppmv, and the National Institute for Occupational Safety and Health (NIOSH) recommends a 10-minute ceiling limit of 10 ppmv. Feedyards are not exempt from OSHA and NIOSH ceiling limits unless they meet employment-based criteria² (29 CFR §1904.2(b)(2)).

The Texas Administrative Code (30 TAC §112.31-32) sets two thresholds for locations downwind of a hydrogen sulfide source. The first threshold is an urban standard of a net, ground-level concentration³ of 0.08 ppmv (parts per million by volume) averaged over any 30-minute period at any residential, business, or commercial property. The second threshold is a rural standard of a net, ground-level concentration 0.12 ppmv averaged over any 30-minute period, which applies to any other type of property. Accordingly, the Texas Commission on Environmental Quality (TCEQ), which enforces the thresholds specified in the TAC, 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 hydrogen sulfide, but only five of those clearly require compliance by CAFOs: Iowa, Minnesota, Nebraska, Rhode Island, and Texas. *Table 1* presents the criteria for each of those five states. CAFOs are clearly exempt from hydrogen sulfide ambient air concentration regulations in 15 states because they are specifically exempted, 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.

Human health, welfare, or property protection are common rationales for establishing specific hydrogen sulfide ambient air concentrations. Some states derive their

Footnotes 2 and 3

²Feedyards that employ 10 or less non-family workers are exempt from OSHA record-keeping requirements, but remain subject to reporting requirements.

³"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.

Hydrogen sulfide is highly toxic at elevated concentrations. Exposure can occur by inhalation of contaminated air or ingestion of contaminated water.

regulatory values from the EPA's No Observable Adverse Effect Level (NOAEL) of 10 ppmv, and Lowest Observable Adverse Effect Level (LOAEL) of 30 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 EPA also derived a chronic inhalation reference value (RfC) of 0.001 ppmv for hydrogen sulfide, to which some states applied uncertainty factors and then based their regulations on the more stringent value. 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 hydrogen sulfide. Others, such as New York and California, base their levels on odor thresholds. Property damage from the corrosive effect of hydrogen sulfide on buildings and structures is the rationale for levels set by Nebraska and Pennsylvania.

Due to its strong, distinctive smell, hydrogen sulfide is sometimes chosen as a surrogate for regulation of odor. Minnesota, New York, Hawaii, and Texas base their regulations in part on nuisance odor abatement. For example, the Minnesota Pollution Control Agency (MPCA) currently regulates feedlot nuisance odor by limiting hydrogen sulfide emissions as measured at the property line of the feedyard (Ambient Air Quality Standards, MR7009.0080, 18 April 2000). *Table 1* presents hydrogen sulfide ambient air concentration standards currently regulated by five different states.

Monitoring Methods

Compliance monitoring of hydrogen sulfide concentrations requires continuous monitoring according to established protocols with approved instrumentation (*Figures 2, 3, and 4*). Instruments must be regularly inspected and calibrated by knowledgeable personnel to ensure accurate measurements. Many scientific instruments are capable of measuring hydrogen sulfide, including Dräger Tubes®, Jerome Hydrogen Sulfide Analyzers, and pulsed fluorescence analyzers.

One of the more common, portable instruments is the Jerome Meter 631-X® (Arizona Instrument LLC, Chandler, AZ). It can detect hydrogen sulfide from 2 ppbv to 50 ppmv. In a Jerome meter, sulfur compounds adsorb to a gold film sensor, whose resistivity varies with adsorbed sulfur molecules. The change in resistivity corresponds to a total reduced sulfur (TRS) value, which includes trace amounts of other sulfur compounds such as dimethyl sulfide, dimethyl disulfide, diethyl disulfide, and methyl

Table 1. Five states clearly requiring CAFO compliance with hydrogen sulfide 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 consec. 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

mercaptan. Because some of those trace compounds are also present at feedyards, actual hydrogen sulfide concentrations reported by a Jerome meter are biased slightly upward. The degree of the bias depends on the concentration of other sulfurous compounds in the air.

Another instrument used to measure hydrogen sulfide is a pulsed fluorescence analyzer.⁴ The electronic hydrogen sulfide analyzer is capable of detecting the gas between 3 ppbv and 100 ppmv. This instrument is designed for use in a laboratory or other protected environment (such as a mobile instrument shelter), but with a protective housing and adequate power supply it also can be used in the field. This instrument catalytically converts hydrogen sulfide to sulfur dioxide and then measures the sulfur dioxide concentration with a pulsed fluorescence analyzer. If background sulfur dioxide is present, these analyzers must be operated in differential mode by bypassing the catalytic converter with a second sampling tube. Other gases present at feedyards, such as ammonia, may interfere with hydrogen sulfide measurements.

Dräger Safety Inc. (Telford, PA) makes the Dräger Tube, which detects hydrogen sulfide gas by drawing an air sample through a glass vial filled with a reagent. The reagent changes color to indicate the presence of hydrogen sulfide gas, and the length of the color change along the tube indicates the concentration. Different models of Dräger Tubes use various reagents to detect hydrogen sulfide 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 concen-



Figure 2. Several gas analyzers operating inside a trailer deployed at a concentrated animal feeding operation including two hydrogen sulfide analyzers (Model 450i, left rack, second from top; Model 45C, left rack, third from top) by Fisher Scientific (Waltham, MA). (Photo: K. Casey)

Compliance monitoring of hydrogen sulfide concentrations requires continuous monitoring according to established protocols with approved instrumentation.

Footnote 4

⁴One of the more commonly used pulsed fluorescence analyzers is the Model 450iC (Fisher Scientific, Waltham, MA).

Thirty-five states have regulations pertaining to ambient air concentrations of hydrogen sulfide, but only five of those clearly require compliance by CAFOs: Iowa, Minnesota, Nebraska, Rhode Island, and Texas.

trations between 2 and 200 ppmv. Other gases may interfere with hydrogen sulfide readings, depending on the model of the instrument and the reagent used.

Other hydrogen sulfide monitoring equipment includes microprocessor-based electrochemical sensors, which can be used for personal protection in areas where hydrogen sulfide gas may exist. These instruments are smaller, portable, and can be mounted near equipment, clipped to a belt, or carried in hand. Primarily used as an early warning device to alert users when they should vacate an area, 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 Dräger Pac III®.

What We Know

Data concerning hydrogen sulfide emissions from feedyards and runoff retention structures are scarce, especially prior to 2003. Koelsch et al. (2004) used Jerome meters to monitor three feedyards in Nebraska for one week in the spring, summer, and fall. The weekly average hydrogen sulfide point concentrations downwind of the pens ranged from 0.0006 to 0.013 ppmv among the three feedyards. The data revealed a diurnal pattern (daily cycle), with higher concentrations occurring during warmer afternoons.

Another researcher, See (2003), also reported evidence of a diurnal pattern of hydrogen sulfide emissions in a study measuring hydrogen sulfide concentrations downwind of a Texas feedyard in June 2000. In this study, the 15-minute average hydrogen sulfide concentrations downwind of both the pens and the runoff retention structures were on the order of 0.005 ppmv.

Rhoades et al. (2003) measured hydrogen sulfide concentrations upwind and immediately downwind of feedyard pens and runoff retention structures at three different Texas feedyards during one year. Averaging times were approximately 10 minutes. Average concentrations downwind of pens ranged from 0.004 to 0.104 ppmv, and downwind of the runoff retention structures ranged from 0.003 to 1.075 ppmv. Because all of the readings were taken during the day and diurnal emission patterns are suspected, the concentrations reported by Rhoades et al. (2003) may not be representative of daily averages.



Figure 3. An intake port mounted on the roof of a trailer deployed at a concentrated animal feeding operation provides air samples to hydrogen sulfide analyzers inside the trailer. The pen surfaces and runoff retention structure visible in the background are potential sources of hydrogen sulfide. (Photo: K. Casey)



Figure 4. A wind tunnel floating on the surface of a runoff retention structure collects air samples, which are sent to a hydrogen sulfide analyzer. (Photo: K. Casey)

A fourth study (Koziel et al., 2004) measured ambient hydrogen sulfide concentrations using an electronic 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. Koziel et al. reported mean hydrogen sulfide concentrations of 0.030, 0.003, and 0.035 ppmv for fall, winter, and spring, respectively. None of the above studies reported ambient 30-minute average hydrogen sulfide concentrations in excess of the state of Texas regulatory value (0.08 ppmv).

Data on hydrogen sulfide emission rates from feedyards are limited. No published data are available on direct measurements of the emissions from runoff retention structures. Attempts have been made to measure hydrogen sulfide fluxes from feedyard surfaces using a Jerome meter, but the concentrations were below the detection limit of the instrument (Duyson et al., 2003).

One study in Minnesota (Wood et al., 2001) reported a mean hydrogen sulfide emission rate of 103 $\mu\text{g}/\text{m}^2/\text{min}$ from a feedyard surface. Two other studies (Baek et al., 2003; Koziel et al., 2005) used a flux chamber and electronic hydrogen sulfide analyzer to measure emission rates from pen surfaces at different feedyards. Baek et al. (2003) reported an emission rate of 1.88 $\mu\text{g}/\text{m}^2/\text{min}$, and Koziel et al. (2005) reported 1.39 $\mu\text{g}/\text{m}^2/\text{min}$.

Equilibrium flux chambers have been shown to underestimate hydrogen sulfide concentrations in comparison with other methods such as backward calculating dispersion models. These computer models begin with observed concentrations and weather data, and then calculate backward to estimate hydrogen sulfide emission rates. Ambient downwind hydrogen sulfide concentration data collected by Rhoades et al. (2003) and Galvin and Parker (2005, unpublished data) were entered into two backward calculating dispersion models. The WindTrax[®] model (Thunder Beach Scientific, Edmonton, AB) uses a backward Lagrangian stochastic (bLS) algorithm, while Ausplume[®] (Environmental Protection Agency, Victoria, Australia) uses a Gaussian algorithm.

There was a significant discrepancy between the predictions two models generated and what was experimentally observed using flux chambers by Baek et al. (2003) and Koziel et al. (2005). The models predicted emission rates from feedyard pens ranging from 3.6 to 3.7 kilograms per day per 1,000 head, which was approximately 100 times greater than the flux-chambers measurements. Using overall mass-balance calculations as the reference point, the dispersion models yielded more plausible flux estimates than the flux-chamber studies.

Data on hydrogen sulfide emission rates from feedyards are limited.

It now appears that hydrogen sulfide emissions from cattle feedyards are a matter of intermittent bursts rather than a continuous flux.

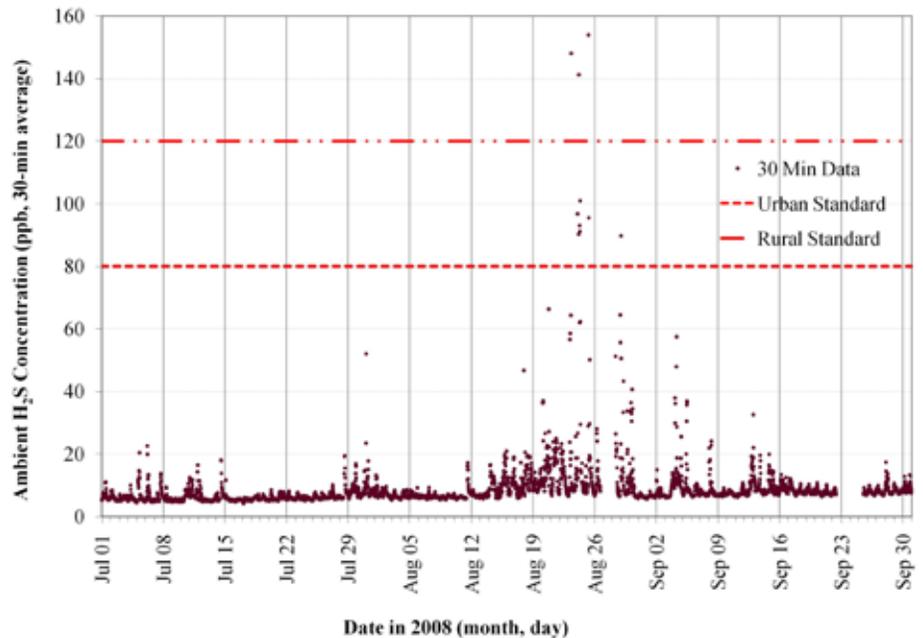


Figure 5. Ambient hydrogen sulfide concentration (30-minute average) observations from July through September, 2008, juxtaposed with Texas regulatory values.

What We Are Learning

Most of the available data on hydrogen sulfide emissions from feedyards has been collected from intermittent spot measurements with Jerome meters. These data do not provide information about diurnal or seasonal variations in hydrogen sulfide emissions. Recent continuous monitoring by Casey et al. (unpublished data) of ambient hydrogen sulfide levels at a feedyard in the Texas Panhandle provided insight into the diurnal and seasonal emission rates and shed light on the uncertainty of hydrogen sulfide measurement methods. Air samples were collected every minute from 3.3 meters above a feedyard pen surface and measured using a TEI H₂S analyzer. Ambient hydrogen sulfide 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 hydrogen sulfide emissions were observed after one rainfall event, but no peaks were observed after subsequent rainfall events. While flux per unit area was often higher from runoff retention structure surfaces, cumulative mass emissions from the pen surfaces were much greater due to their larger surface area. *Figure 5* presents ambient hydrogen sulfide concentrations (30-minute average) from a feedyard located in the Texas Panhandle through July and September 2008 (Casey et al., unpublished data).

Results from the pen area indicated that ambient hydrogen sulfide 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 diurnal trend was evident as hydrogen sulfide emissions tended to increase with warmer air temperatures.

New research is attempting to explain these peaks and learn more about the factors that affect hydrogen sulfide emission rates. Some factors being investigated include ambient temperature, precipitation events, changes in barometric pressure, cattle activity, the amount of hydrogen sulfide held in the manure matrix, and differences in ration formulation. It now appears that hydrogen sulfide emissions from cattle feedyards are a matter of intermittent bursts rather than the more continuous fluxes associated with ammonia gas (NH₃), for example.

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