Air quality impacts from manure stored at animal feeding operations feeding distiller's grains: hydrogen sulfide

OVERVIEW:

Major gases that result from manure storage include methane, ammonia, carbon dioxide and hydrogen sulfide. Methane is produced from the decomposition of manure and is non-toxic at low amounts (Donham et al., 2006). At concentrations of 5 to 15 percent, methane is highly flammable or explosive and can cause asphyxiation. Ammonia is the primary gas released during manure storage. Its characteristic odor is detectable at 5 parts per million (ppm). Ammonia is generally more an irritant than a safety concern. Hydrogen sulfide (H_2S) is the most dangerous gas associated with manure. It is produced by anaerobic bacterial decomposition of protein or other sulfur-containing organic matter (Hooser et al., 2000). High concentrations of hydrogen sulfide can be fatal for both humans and animals (Donham et al., 2006), and there are several documented cases of deaths resulting from acute overexposure to hydrogen sulfide produced by manure pits (Hooser et al., 2000; Beaver and Field, 2007).

At low concentrations (less than 1 ppm), hydrogen sulfide is an irritant with the odor of rotten eggs. At higher concentrations, however, it deadens the sense of smell, often immediately, making detection difficult (Donham et al., 2006; Doss, Person and McLeod, 2002; Hooser et al., 2000). Abrupt exposure to amounts of greater than 500 ppm of hydrogen sulfide has killed humans; exposure to 200 ppm of hydrogen sulfide has killed swine. Extended exposure to lower amounts of hydrogen sulfide has also resulted in a range of symptoms from eye irritation to respiratory illness to unconsciousness (Donham et al., 2006; Hays et al., 1972).

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Anaerobic Digestion

Distiller's grain and manure -- sulfur

Some livestock producers are including significant amounts of distiller's grains in rations because it is an economical source for protein and energy and an available co-product from the ethanol industry. Distiller's grains can come in various forms and be classified as wet or dry, depending on the moisture content. Wet distiller's grain is typically 50 to 70 percent moisture, whereas dry distiller's grain (with or without solubles) is usually around 10 percent moisture. Beef cattle diets may contain 40 percent or more distiller's grains. Inclusion amounts for dairy and swine diets are generally less -- about 20 percent -- and poultry diets can include distiller's dried grains with solubles (DDGS) up to 10 percent. The concentration of sulfur in distiller's grains (0.4 percent to 0.9 percent) is higher than in corn (0.07 percent to 0.15 percent). Most of the additional sulfur found in distiller's grains is from the sulfuric acid used during production of ethanol and the greater proportion of sulfur-containing amino acids in distiller's grains than in corn (NRC, 1998). Including too much sulfur in the diet has the potential to cause health-related problems such as polioencephalomalacia in cattle, a neurological disease that most often results in death.

Animals fed distiller's grains excrete increased amounts of sulfur in their manure, so extra caution should be practiced if distiller's grains are being utilized in the diet of animals contributing manure to the storage pit. Shurson, Whitney and Nicolai (1998) showed that nursery pigs housed in confinement and fed a diet with increased sulfur excreted higher amounts of sulfur, and their manure had higher hydrogen sulfide emissions than pigs fed a diet with less sulfur. Cattle fed wet distiller's grain had higher fecal and urinary sulfur excretions than control cattle not fed distiller's grains (Spiehs and Varel, 2009). Although these authors did not measure hydrogen sulfide in their study, they conclude that it is likely that increased hydrogen sulfide would result from cattle being fed wet distiller's grain.

One research study from Michigan State University observed that feeding swine diets containing 20 percent DDGS increased the hydrogen sulfide emissions from animal rooms by 30 percent (Li, Powers and Hill, 2011). Another study found no differences in hydrogen sulfide, ammonia and odor concentrations in swine diets containing DDGS rather than corn and soybean meal (Spiehs, Whitney, Shurson and Nicolai, 2000).

A study conducted at South Dakota State University reported that cattle fed 35 percent DDGS had increased amounts of hydrogen sulfide at the floor level of clay dirt cattle pens compared with cattle fed 0 percent, 15 percent and 25 percent DDGS (Benson, Wright, McCarthick and Pritchard, 2006). These researchers did

not find any hydrogen sulfide concentrations above 13 parts per billion (ppb) at the floor level of the pen, indicating no safety concern related to hydrogen sulfide in this type of housing system. It is possible that feeding high amounts of distiller's grains to cattle in indoor confinement operations, especially those with manure pits underneath the animals that store manure for long periods of time, may result in hydrogen sulfide production that could create a hazardous situation.

Important to practice safety – humans and livestock

Proper safety precautions are necessary when removing manure from storage pits. When removing manure from pits, it is best to remove livestock from the pens and/or barn where manure is being agitated and pumped. If removal of animals is not possible, provide adequate ventilation through exchange of air (outside, down through slats, exhaust through ventilation fans). Weather is a consideration when pumping manure from pits. On rainy days, hot days or days when the wind is not blowing, air may be more stagnant and stay in place longer than on a day when the sun is shining and wind is blowing. Time your pumping for optimal ventilation conditions or provide adequate pit and animal space ventilation. For information on proper ventilation of confined manure storage areas, consult the fact sheet by Manbeck, Murphy and Steel (2011).

Workers should never enter the pen or barn when problems with animals are seen during pumping of manure pits. They should observe animals from a distance and discontinue agitation immediately if signs of trouble exist. Many animals show signs of difficulty with breathing or act lethargic. Cattle exposed to high concentrations of hydrogen sulfide can collapse and exhibit paddling prior to rapid death (Hooser et al., 2000).

Gas concentrations in and around manure pits can vary widely during agitation and pumping, even under similar operational conditions (Patni and Clarke, 1991). It has been reported that hydrogen sulfide production is mainly associated with liquid manure and becomes trapped in bubbles of manure in pits under confinement facilities (Pickrell, 1991). Upon agitation of manure pits, hydrogen sulfide concentrations can rapidly increase from 200 to 1,500 ppm or more in a matter of seconds (Donham et al., 2006; Patni and Clarke, 1991). Because

Table 1. Effects of exposure to hydrogen sulfide on humans at various exposure limits (adapted from Doss et al., 2002, and OSHA, 2005, 2007).

Exposure level	Effect or symptom
5 ppm	**RECOMMENDED MAXIMUM FOR HUMAN HEALTH**
10 ppm	Eye irritation
20 ppm for more than 20 minutes	Irritation to the eyes, nose and throat
20 ppm for 8 hours	OSHA permissible exposure limit
50 to 100 ppm	Vomiting, nausea, diarrhea
100 ppm or above	**IMMEDIATELY DANGEROUS TO LIFE AND HEALTH**
200 ppm	Dizziness, nervous system depression, increased susceptibility to pneumonia, fluid in lungs with prolonged exposure
500 ppm for 30 minutes	Nausea, excitement, unconsciousness
600 ppm and above	Rapid death

of this rapid increase in concentration of hydrogen sulfide during agitation and pumping of manure pits, time-weighted average concentrations are of little value in monitoring for immediate safety effects in these situations (Patni and Clarke, 1991). These authors advise agitating pits using submerged recirculation because another critical time for potential elevated amounts of hydrogen sulfide is when the pit is near empty and the recirculation pump is above the level of manure. Long-term signs that gases have reached toxic amounts include blackening of copper pipes, wiring or lead-based paint, as well as white deposits of zinc sulfate on galvanized steel (Donham et al., 2006).

Most human deaths associated with manure removal happen when a person enters a barn or pit that has high amounts of hydrogen sulfide present. High amounts of hydrogen sulfide can build up quickly in confined spaces, and one must use caution when working around such areas. Doss et al. (2002) caution that hydrogen sulfide can build up above the layer of liquid manure in a pit because it is heavier than air. Additionally, because of its weight, hydrogen sulfide can also accumulate near the bottom of a manure pit (NIOSH, 1990). Most reported deaths of humans due to hydrogen sulfide happen within seconds. The person is overcome so quickly that there are no additional warning signs. Doss et al. (2002) have summarized effects or symptoms to various levels of exposure to hydrogen sulfide (Table 1). These symptoms can be related to severe illness as a result of exposure to hydrogen sulfide at lower levels. Even in situations where good ventilation is supplied or the pit has been recently emptied, workers should never enter a pit without a self-contained air supply.

Commercial gas monitors can be used to determine amounts of hydrogen sulfide or other gases present. Many of these devices are hand-held, and operators should consider wearing them when removing manure from storage pits. Monitoring devices are available from welding supply stores or companies that handle compressed gases. Portable gas monitors are available from the following companies/websites, among others: airgas.com, canarysense.com, allgasdetectors.com, draeger.com, gastec.co.jp, mathesongas.com/. On-site sampling techniques listed by OSHA (2007) include detector tube devices from three of the above manufacturers. Manufacturer recommendations should be used for establishing device settings.

Laboratory experiments have shown that hydrogen sulfide levels in manure can be reduced. Adding sodium nitrite or sodium molybdate to swine manure reduced hydrogen sulfide concentration to an almost undetectable amount that poses much little or no safety risk (Predicala, Nemati, Stade and Laguë, 2008). These authors found that lower amounts of nitrite needed to be added to aged manure (stored five to six weeks in a manure pit) than to fresh manure to reduce hydrogen sulfide emissions. Predicala et al. (2008) noted that adding nitrite or molybdate reduced hydrogen sulfide levels but not odors. Hydrogen peroxide and potassium permanganate added to swine manure resulted in at least 91 percent reduction in hydrogen sulfide concentrations (Smith and Nicolai, 2005). In one of their experiments, these authors found the dramatic reduction from 50 ppm to 0.38 ppm in hydrogen sulfide concentration 3 inches above the manure layer in the pit within six minutes of adding hydrogen peroxide. More research needs to be conducted on commercial application of reducing hydrogen sulfide concentration in manure through the use of additives. This work needs to include evaluating the effects of methods to manipulate the hydrogen sulfide emissions from manure on changes it would make to the manure for field applications, including effects on water quality.

Conclusion

Remember to keep safety practices in mind when handling manure and be aware of the potential dangers that confined anaerobic spaces pose. Workers should wear monitoring equipment such as portable gas detectors when working in confined areas that may contain hydrogen sulfide. It is important for human and animal health to provide proper ventilation to maintain indoor air quality. Never enter an area where an animal or human appears to be having difficulty due to hydrogen sulfide exposure without an approved self-contained breathing apparatus. Call for emergency help immediately.

Distiller's grains are an important feed source, but increased hydrogen sulfide emissions from manure may pose challenges. When feeding co-products containing high amounts of sulfur, such as distiller's grains or DDGS, it is advised to remove additional sources of sulfur from mineral supplements. When water sources also contain high amounts of sulfur, have your water analyzed and consider sulfur consumption via water intake when formulating rations.

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