Spring 2017

Evaluation of low-cost hydrogen sulfide monitors for use in agriculture

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EVALUATION OF LOW-COST HYDROGEN SULFIDE MONITORS FOR USE IN AGRICULTURE

by

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A thesis submitted in partial fulfillment
of the requirements for the Master of Science
degree in Occupational and Environmental Health in the
Graduate College of
The University of Iowa

May 2017

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Graduate College
The University of Iowa
Iowa City, Iowa

CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's thesis of

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has been approved by the Examining Committee for
the thesis requirement for the Master of Science degree
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To Mom

ACKNOWLEDGEMENTS

This culmination of this work has been a long time in the making, and is complete thanks to the support I've had from many people in my life. Thank you, first and foremost, to Dr. Renée Anthony for her support and guidance through this project and throughout this degree program. I am incredibly lucky to have found such an amazing mentor and friend. Thank you to Dr. Tom Peters and Dr. Matt Nonnenmann for their participation in my research committee and for the training they provided during my time in the graduate program. I would also like to thank the rest of the faculty and staff of the Department of Occupational and Environmental Health, who supported and assisted me in countless ways through my time here. Thank you to Deirdre, Elanie, Russ, Joel, Jae, Laura, Levi, Anthony, Rich, Changjie, Craig, Aimee Liz, Sarah, Kate, Taryn, Abby, Emily, Jessica, Christie, Austin, and all of the other students I worked with in this program. I am so grateful to have been part of such a positive and supportive group of students.

My completion of the graduate program would never have happened without the support of my VA friends and co-workers, who allowed me a level of patience and flexibility far greater than I could have hoped for during this process, and for which I will be forever grateful.

Finally, I would like to thank my family: my amazing husband for his unwavering support even when the nights ran late; Janelle, my best friend and sister, for always being there for me no matter what; and for my mom, for always encouraging me to pursue my education and supporting me all along the way.

ABSTRACT

Toxic exposure to hydrogen sulfide (H_2S) is a well-recognized hazard in agriculture, particularly in livestock operations that manage large amounts of manure. Numerous fatalities have been observed, often multiple fatalities in a single incident, due to toxic exposure to H_2S from manure pits at concentrations higher than 500 ppm. Direct-reading instruments that alarm workers in the areas when H_2S concentrations are high may prevent these fatalities. However, monitors that are commonly found in industries with robust safety programs are impractical for agricultural use as they are often prohibitively expensive and require regular maintenance and calibration that may be above the expertise level of agricultural workers.

In more recent years, manufacturers marketed simpler models of direct-reading H_2S monitors as “low-maintenance” or “maintenance-free” at a much lower cost than traditional monitors, which may cost $500 for basic models or more than $1000 for more complex models. The objective of this study was to test several models of low-cost, low-maintenance monitors in order to examine the features of each for comparison, as well as to test the performance of these monitors with no maintenance over time while under constant exposure to low levels of H_2S.

Two types of monitors were examined: qualitative monitors that were lowest-cost (around $100) and provided only alarm settings with no concentration displayed (Honeywell BW Clip and MSA Altair), and quantitative monitors that cost slightly more (around $200) but displayed concentration readings (Dräger Pac 3500 and Industrial Scientific T40 Rattler). All models were exposed to H_2S for a test period of 4 months, at concentrations slightly higher than typical background concentrations to simulate expected monitor exposure for a year in a barn.

The performance of qualitative (‘alarm-only’) monitors declined faster than over the course of the simulated barn year than the quantitative monitors, with both models of qualitative

meters failing to alarm at the high setting before the test period was complete. The quantitative ('concentration-display') models showed fewer effects from long-term exposure over the duration of testing, but both models exhibited inaccuracies in the concentration readings when compared to calibration gas concentrations. The T40 Rattler provided consistently higher readings (+2.3 ppm) than the calibration gas concentration, while the Pac 3500 showed consistently lower readings (-3.4 ppm) than the calibration gas concentration. Serious acute health effects for H_2S are not typically observed until exposure to concentrations above 500 ppm, so inaccuracies of this small magnitude are relatively insignificant.

Though each of the test monitors is advertised to be maintenance-free for two years, this study found that failures occurred within one simulated year in a barn. Bump checks should be performed regularly to ensure the monitor reacts to the presence of H_2S appropriately, even when the manufacturer's literature may say otherwise. Most importantly, agricultural workers should always inspect and bump check these monitors prior to any potentially high-risk activity such as manure agitation or pumping to ensure that the monitor is still providing the protection needed from a potentially toxic release of H_2S.

This study tested each of these models within a clean chamber at room temperature to isolate the effects of long-term exposure to H_2S. In an actual barn, these monitors may be exposed to variations in temperature and humidity, as well as other barn contaminants such as ammonia, dust, and chemicals. Each of these other exposures could also affect the performance of these monitors over time, and should be considered when storing and using these monitors. Furthermore, the potential interactions from other exposures is an opportunity for future study to better understand how these interactions may affect sensor performance in an agricultural environment.

PUBLIC ABSTRACT

Workers may be exposed to harmful gases in many industries, and gas monitors are often used to alert workers when gas concentrations approach dangerous levels. Agricultural workers are similarly at risk for exposure to toxic gases, particularly hydrogen sulfide exposure in livestock work. However, gas monitors that are used in traditional industries are typically impractical for agricultural operations because they require high levels of maintenance and are prohibitively expensive. Simpler, low-cost monitors for hydrogen sulfide have become available that are advertised to require little- or no-maintenance for up to two years. This study selected four models of low-cost monitors to compare features and to test performance when exposed to low levels of hydrogen sulfide over an extended period of time, as would be expected in an agricultural environment. Two types of models were selected: monitors that display the concentration of hydrogen sulfide and monitors that respond only to pre-set low and high alarm levels.

A year of hydrogen sulfide exposure was simulated at levels typically expected within a barn by enclosing the monitors inside a chamber of gas and observing performance. Monitors were tested at concentrations up to 10 ppm, while fatalities typically occur at greater than 500 ppm. Concentration-display models were consistently inaccurate when compared to known gas concentrations by ±3 ppm, but showed fewer performance issues related to duration of gas exposure. The performance of the alarm-only models degraded more noticeably over time, with both models failing to respond to high alarms before the end of the simulated barn year.

For worker safety, monitors must be checked for performance regularly to ensure proper operation in a hazardous environment.

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CHAPTER I

LITERATURE REVIEW

Hydrogen Sulfide in the Workplace

Hydrogen sulfide (H_2S) is a chemical compound with natural and industrial sources. As sulfur cycles through the natural environment, H_2S is formed and released from sulfur springs, natural gas wells, volcanoes, and anaerobic decay of organic matter. Industrial sources of H_2S include municipal landfills, asphalt production, sewage treatment plants, oil and gas extraction operations, oil refineries, Portland cement kilns, and confined animal feeding operations (CAFOs) (OSHA, 2016).

Regardless of the source, exposure to H_2S can be deadly, and exposure to H_2S has long been a recognized workplace hazard. As early as 1713, Bernardino Ramazzini wrote about irritation of the eyes and inflammation that occurred among workers in Parisian sewers, theorizing that an unknown volatile acid was produced when the waste was disturbed that was to blame for the disease (Smith 2016). The British used H_2S briefly as a chemical weapon during World War I (Foulkes, 1934). Alice Hamilton described the effects of H_2S exposure on sulfide factory workers in 1925 (Hamilton, 1925). In 1975, nine people of Denver City, Texas died after being overwhelmed by a cloud of toxic H_2S gas leaked from an injection well in a nearby oil field (Swindle, 1975).

Since then, work-related injuries and fatalities due to H_2S have been numerous and well-documented by several studies. From 1984 to 1994, there were 80 fatalities from occupational exposure to H_2S, an average of nearly eight per year (Danielsson et. al, 2009). Between 1993 and 1999, there were 52 worker fatalities due to H_2S exposure in the U.S., with the highest numbers occurring in the waste management and oil and gas industries (Hendrickson, et. al, 2004). Between 2001 and 2010, there were 60 occupational fatalities from H_2S exposure, and from 2011 thru 2014, there were 19 occupational fatalities incurred by contracted workers that were attributed to hydrogen sulfide (BLS, 2016). Many of these fatalities were multiple-casualty incidents, in which a rescue was attempted for a worker in distress, and the would-be rescuers also died.

Health Effects and Regulation of Hydrogen Sulfide Exposure

Hydrogen sulfide is a colorless gas that has the odor of rotten eggs at lower concentrations. Once concentrations rise to over 100 ppm, however, olfactory paralysis occurs and the odor is no longer detectable by most people. Thus, as concentrations of H_2S increase to more dangerous levels, workers become unable to detect the gas without instruments, greatly increasing the risk of fatal overexposures. In general, H_2S is known to cause irritation of the upper respiratory tract and impairment of the central nervous system. Typical health effects of H_2S exposure at differing concentrations are shown in Table 1.

Table 1. Typical health effects due to H_2S exposure.

Concentration (ppm)	**Health Effects**
0.00011-0.00033	Typical background concentration
0.01 – 1.5	Rotten egg odor first noticeable. Odor becomes more offensive at 3-5 ppm.
2-5	Prolonged exposure may cause nausea, headaches, loss of sleep, watery eyes.
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.
100	Coughing, eye irritation, inability to detect odor after 2-15 minutes. Altered breathing, drowsiness. After 1 hour, throat irritation. After 48 hours, possible death.
100-150	Loss of smell (olfactory fatigue or paralysis)
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure.
500-700	Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, “knockdown” or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death

Adapted from OSHA.

The Occupational Safety and Health Administration (OSHA) has developed requirements to safeguard workers that may be vulnerable to H_2S exposure. Most notably, 29 CFR 1910.146 requires industries to test the atmosphere for potential toxic gases prior to entry into any confined space. Industries such as mining, oil/gas refining, pulp and paper processing, sewer and wastewater treatment, textile manufacturing, food processing, and agriculture (silos and pits) are recognized by OSHA as the most likely to produce H_2S as a byproduct. With the exception of agriculture, these industries are required to maintain strict confined space policies that include direct-read monitoring and are subject to routine OSHA inspections to ensure compliance with safety requirements.

As a result of the well-documented health effects of H_2S exposure shown in Table 1, occupational exposure limits have also been established by OSHA and other health/safety agencies or organizations. These limit thresholds are shown in Table 2.

Table 2. Occupational exposure limits for H_2S.

Organization	**Worker Exposure Limits**
Occupational Safety and Health Administration (OSHA)*	8-hour TWA: 10 ppm General Industry Ceiling: 20 ppm General Industry Peak: 50 ppm for <10 minutes
National Institute for Occupational Safety and Health (NIOSH)**	10-minute ceiling: 10 ppm IDLH: 100 ppm
American Conference for Governmental Industrial Hygienists (ACGIH)**	8-hr TWA: 1 ppm STEL: 5 ppm
American Society of Agricultural Engineers (ASAE)**	8-hour TWA: 10 ppm 15-min ceiling: 15 ppm

* = required by law; ** = recommendations or guidelines

The agricultural industry is subject to less regulation and far less oversight by OSHA. Only portions of the general industry requirements that are outlined in 29 CFR 1910 apply to agricultural operations, and the confined space standard (1910.146) does not. Agricultural operations are regulated by 29 CFR 1928 which includes provisions for roll-over protective structures for tractors and guarding of farm field equipment, but this regulation does not include confined space entry or exposure to toxic gases. Agricultural operations are also required to abide by OSHA's general duty clause [5(a)(1)], which requires employers to furnish a workplace free of recognized hazards. Enforcement of this standard is typically only applied after a serious injury or fatality has already occurred.

There are two exemptions that reduce farm safety regulations even further. First, immediate family members of the farm owner are not considered employees and are, thus, not protected by OSHA. Second, agricultural operations with fewer than 10 employees are not subject to OSHA regulation by way of Congressional mandate. According to the US Department of Agriculture, only 2% of farms in 2012 employed 10 or more workers and those farms employed 53.8% of all hired farmworkers that year. Thus only 2% of farms, 54% of hired workers, and none of the immediate family members that worked on farms that year were subject to OSHA protection (USDA, 2014).

However, agriculture is a dangerous occupation in need of worker protections. According to the Bureau of Labor Statistics, the occupational fatality rate in 2014 was the highest for the agricultural sector at 22 per 100,000 workers, compared to 3.4 per 100,000 overall across all industries. The injury rate for animal production was 7.1 per 100 workers in 2014 (BLS, 2016). Agricultural workers are exposed to many of the same occupational hazards as industrial workers, and the potential exposure to hazardous confined spaces on the farm is high, particularly in grain bins, trenches, pipes, and manure pits.

Though the agricultural industry is not highly regulated, there are many organizations that provide guidelines or recommendations for agricultural safety, including confined space procedures. OSHA, NIOSH, the American Society of Agricultural and Biological Engineers (ASABE), and several academic research centers have published guidelines for farmers to help protect them from the dangers of confined spaces such as manure pits, a primary source of H_2S production on the farm. The University of Iowa Great Plains Center for Agricultural Health has published several fact sheets and technical guidance papers to educate workers about the dangers of working around manure pits (University of Iowa, 2015).

Manure Pit Management

CAFOs are typically designed with manure collection systems in the form of underfloor pits. A single finishing pig produces around 1.5 gallons of manure per day, while a mature dairy cow can generate up to 14 gallons per day (Tyson and Mukhtar, 2017; Purdue, 1994). Thus these pits are large, designed to hold tens of thousands of gallons of manure at a time. Livestock manure is collected and stored in these pits until pumped out once or twice a year to be applied to the field as fertilizer or stored elsewhere. Pit storage provides a more efficient means of managing a large amount of waste, but creates a dangerous potential hazard. Manure pit-related fatalities have occurred from drowning in the manure and asphyxiation from the toxic gases produced by the manure. Other forms of large-quantity manure storage, such as outdoor ponds and lagoons present the same hazards to agricultural workers. Even manure transport and spreading equipment, such as transport tanks, have served as deadly spaces for H_2S to collect at fatal concentrations (Donham et. al., 1982).

Over the course of several months that the manure is in storage, anaerobic conditions foster the production of H_2S and other toxic gases. Even without agitation, background concentrations of H_2S exist at low levels from the off-gassing of manure at around 1 ppm (Donham & Popendorf, 1985). This background concentration is dependent upon a number of factors such as size of the barn, number of animals, temperature/weather, level of manure accumulated in pit, and suitability of ventilation within the barn or storage structure. However, the gas concentration within the barn can rise to levels high enough to kill within seconds when the accumulated manure is disturbed for pumping or cleaning or other activities. Concentrations as high as 1500 ppm have been measured in manure pits beneath hog confinement buildings (Popendorf, 1991).

Fatalities occurring between 1975 and 2004 that were directly attributed to on-farm manure storage and handling facilities were examined by Beaver and Field (2007). Of the 77 fatalities that were identified, 34% of deaths occurred to persons conducting repair or maintenance on manure handling equipment and 22% were attempting to rescue another person. The most frequently identified cause of death among this group was asphyxiation with elevated levels of sulfide in the blood. Twenty-one percent of these fatalities were under the age of 16 (Beaver & Field, 2007).

Direct-Read Monitoring H_2S in Manure Operations

The regulatory framework that incentivizes other industries with high risks for worker exposure to H_2S to incorporate direct-reading monitors does not exist for the agricultural industry. Furthermore, high-risk industries such as oil/gas production and pulp/paper manufacturing typically employ occupational health and safety staff with the expertise and equipment to recognize and monitor H_2S hazards. Agricultural operations, despite also being recognized by OSHA as an industry with a high risk of H_2S exposure, seldom employ such staff, particularly at smaller operations. However, recommendations for monitoring H_2S exposure while working around manure pits or manure spreading equipment are found throughout the scientific literature.

In 1996, Aherin stated "the ability to identify, measure, and monitor potential danger from unsuspecting looking spaces is critical to a safe farm operation. Recognizing the potential hazard of confined spaces allows farmers to make provisions to minimize the need for entry and to use appropriate work practices and equipment when necessary." Aherin continued by describing essential factors to consider when selecting gas monitoring equipment for use in agriculture, such as: accuracy, specificity, response time, cost, durability, reliability, cost, and expertise required for the maintenance and operation of the equipment (Aherin et al., 1996).

Furthermore, the American Society of Agricultural and Biological Engineers (ASABE) have developed consensus standards for manure storage safety. First published in 1992 and updated in 2011, these standards identify measures to be taken by the farmer while working in or around manure storage facilities. These measures include storing safety and rescue equipment near the manure storage area (harnesses, respirators, ropes) and keeping gas detection equipment readily available. Limited information on selecting, maintaining, and using these monitors is provided in this or other ASABE standards (ASAE, 2011).

General recommendations for direct-reading instruments, however, are widely available. The NIOSH Manual of Analytical Methods provides a chapter on portable electrochemical sensors that discusses the principles of operation in general terms and provides recommendations for applications, environmental conditions, and limits of performance (NIOSH, 1998). Another NIOSH publication, Components for Evaluation of Direct-Reading Monitors for Gases and Vapors, also discusses important considerations to factor when choosing a direct-reading monitor, such as response time, calibration requirements, and chemical interferences (NIOSH, 2012).

Direct-reading monitors most commonly used to detect H_2S operate by facilitating a chemical reaction between H_2S gas and an electrolyte-coated sensor. The magnitude of the reaction generates an electric signal that corresponds proportionally to the concentration of H_2S. The accuracy of the monitor is dependent on the established relationship between electric current and concentration, which can deteriorate over the long-term performance of the monitor due to the continuous electrochemical reaction. To counter this deterioration, a reference electrode is built into the sensor that provides a stable level of potential to the electrode, improving the long-term performance of the sensor (Chou, 2000). Electrochemical direct-reading monitors are favorable for use in agriculture because the sensors have a high selectivity for the desired gas to be tested and respond quickly to the presence of gas. Generally speaking, the typical life of electrochemical sensors is one to three years but is heavily dependent on the environment to which they are exposed. Exposure to extremes in temperature, humidity, or dusty environments have shown to reduce the operational life of electrochemical sensors, making them potentially vulnerable to failure in agricultural environments (Aherin et al, 1996). Additionally, electrochemical sensors have an upper limit of measurement that is lower than other technologies, with good linearity of the electrochemical relationship established up to 100 ppm (Pandey, 2012). Though this limit is lower than the concentration at which fatalities occur (500 – 1000 ppm), these monitors can still benefit agricultural workers by providing a warning when H_2S concentrations rise to levels higher than background concentrations and prompting the workers to leave the environment before fatal concentrations occur.

Education efforts made by the University of Iowa, Iowa State Agricultural Extension, and other universities and non-profits have indicated that there remains a knowledge and training gap for agricultural workers with regard to the hazards of H_2S and the added safety provided by direct-reading monitors. In 2016, Iowa State Ag Extension found that 1-5% of commercial manure applicators owned or had access to H_2S monitors, but that 25 – 31% of applicators were interested in purchasing one in the future (ISU, 2016). Outreach efforts at several Iowa county fairs and trade shows were undertaken by the University of Iowa College of Public Health in the summer of 2016 to engage livestock producers about the use of direct-reading monitors to protect from toxic exposure to H_2S. In all, 90 livestock producers were surveyed regarding their knowledge, availability, and features preference of direct-reading monitors with a variety of responses. Survey responses ranged from those unaware of the risk of H_2S or the benefit that direct-read monitors could provide to those showing enthusiasm for monitors and their use in daily operations or during high risk activities. Many livestock producers considered monitors beneficial for the health of their livestock, even if they were still skeptical about the need for monitors to protect the health of themselves or their workers (Trenkamp, 2016). The use of low-cost, low-maintenance H_2S monitors may continue to grow in the agricultural industry as manufacturers identify and market to this industry and as educational outreach programs continue to raise awareness of the hazards of H_2S and worker protection that a monitor provides.

Objectives

This study aims to identify H_2S monitors that may be appropriate for agricultural use in order to support further outreach efforts. Low-cost, maintenance-free monitors have the ability to overcome the problem of lacking safety/health personnel and training in the agricultural industry, as long as they perform reliably and operate truly maintenance-free. If a monitor were present in a hazard situation but had failed without the workers' knowledge, those workers may be in even greater danger with a false sense of protection. Thus, this study is designed to test four models of monitors that meet the initial "low-cost, maintenance-free" requirements to determine their performance in a simulated agricultural setting. By observing each monitor's response to H_2S exposure over time, this study aims to identify qualitative strengths and weaknesses of each monitor, as well as determine the presence and/or magnitude of sensor drift or failure over exposure time.

CHAPTER II

GAS MONITOR EVALUATION

Introduction

Exposure to hydrogen sulfide (H_2S) gas is an occupational hazard in many industries, including oil and gas, pulp and paper, mining, wastewater treatment, and agriculture (OSHA, 2016). Workplace injuries and fatalities due to exposure to H_2S and other toxic gases have led to federal regulations and the implementation of policies in many of these industries requiring the use of direct-reading instruments for gas detection. In agriculture, however, the use of gas monitors is rarely used and workers in this industry are still very much at risk (Aherin et al, 1996).

Hydrogen sulfide is a colorless gas best known by its "rotten egg" smell. With acute exposures to low concentrations, exposure to H_2S can lead to headaches, nausea, and dizziness. At concentrations in the range of 100 – 500 parts per million (ppm), exposure can result in neurological symptoms and potentially death. When the concentration of H_2S reaches 700 – 1000 ppm, exposure can cause "knock-down", or rapid unconsciousness leading to death with just a few breaths. Furthermore, while the smell of H_2S is highly recognizable and easily detected at low concentrations (~1 ppm), exposure to a concentration of 100 to 150 ppm for 15 minutes can result in olfactory paralysis, or the inability to smell the gas. The Occupational Safety and Health Administration (OSHA) has set a general industry ceiling limit for H_2S at 20 ppm, or 50 ppm for no longer than 10 minutes during an 8-hour shift (OSHA, 2006). The National Institute for Occupational Safety and Health (NIOSH) has set a recommended exposure limit (REL) of 10 ppm (10-minute ceiling) and the immediately dangerous to life and health

(IDLH) level at 100 ppm, reduced in 1994 from 300 ppm. In 2009, the American Conference of Governmental Industrial Hygienists (ACGIH) reduced their recommended threshold limit value (TLV) from 10 ppm to 1 ppm (8-hr time-weighted average) and the 15-minute short-term exposure limit (STEL) to 5 ppm.

Occupational safety and health programs are required by OSHA under 29 CFR 1910. In most industries where workers are at risk of exposure to H_2S, safety professionals use direct-reading monitors to rapidly test the environment and warn workers if the concentration of H_2S is at an unsafe level. The most common type of direct-reading monitor for detection of H_2S is electrochemical sensors. These sensors detect H_2S through a reaction that occurs between the gas and an electrolyte layer within the sensor, creating an electrical signal that corresponds to a gas concentration in ppm. The monitor measures the electrical signal, translates it into concentration, and gives an audible alarm if concentration exceeds a preset alarm threshold.

The agricultural industry is exempt from most of the general industry rules outlined in 29 CFR 1910, including the confined space requirements. While OSHA's general duty clause does apply, the agricultural regulations do not adopt the general industry PELs. Agricultural operations have no requirement to employ or consult trained safety professionals with the expertise to calibrate and operate gas detection equipment. The American Society of Agricultural and Biological Engineers (ASABE) and NIOSH have published some guidance recommending the use of gas monitoring equipment in agriculture, but this guidance lacks specific instructions for how to obtain, maintain, and effectively operate these monitors in an agricultural environment (ASAE, 2011; NIOSH, 1990). As a result, traditional safeguards used by other industries to prevent H_2S exposure are not readily available to agricultural workers.

However, agricultural workers continue to die from H_2S concentrations because workers are unaware of this hazard (Adekoya & Myers, 1999; Beaver & Field, 2007).

In confined animal feeding operations (CAFOs), large numbers of swine and other livestock are contained in buildings with manure collection pits underneath the floor. These manure pits may hold many thousands of gallons of waste and are often emptied once or twice per year. Anaerobic bacteria present in the waste produce H_2S as the waste decomposes and, as such, manure pits are a significant source of H_2S in agricultural operations. Of all toxic gases present in manure, H_2S is thought to present the highest risk for illness or death to agricultural workers in these buildings (Donham et al, 1982). When the manure pit is left undisturbed, background concentrations in occupied spaces remain low, around 1 ppm H_2S (Guarrasi et al, 2015; Swestka, 2010). When the manure is agitated, such as during removal from the pit for maintenance or disposal, concentrations can rise within seconds to higher than 500 ppm (Donham et al, 1982) and have been observed well over 1000 ppm (Popendorf, 1991).

In the past 10 years, gas detection equipment manufacturers have developed gas monitors that are marketed as “low maintenance” or “maintenance-free” and cost a fraction of traditional gas monitors. The use of these monitors by agricultural workers would provide some protection against the potential for toxic exposure to H_2S without the requirement to have trained safety professionals available to calibrate and maintain the equipment, provided that these monitors remain effective for the duration of their warranty lifetime. Direct-reading monitors are favorable for agricultural use because they can detect gas quickly, usually within 10 – 60 seconds (Aherin, 1996). However, electrochemical sensors that are operated outside of their environmental limits for temperature, humidity, and potential cross-contaminants may experience a shorter lifespan, which raises concern for the applicability of such monitors in agricultural environments (Chou, 2000).

The purpose of this study was to identify several models of low- or no-maintenance monitors that are generally available to the public for purchase directly. These monitors were targeted with the assumption that educational outreach regarding direct-reading monitors to agricultural workers may prompt their purchase through more direct means, such as the internet. This study then evaluated the long-term reliability of selected models when exposed to typical background levels of H_2S found in agricultural locations, particularly livestock production, under the worst-case scenario in which the monitors would not be calibrated following activation.

Methods

Monitor Selection

Through internet searches, several H_2S monitors were identified that were marketed as "low-maintenance" or "maintenance-free." The cost and accessibility for online purchase by U.S. agricultural workers were obtained, and four monitors were identified as likely to be purchased and used by farmers. Table 3 provides specific features of each model selected: Dräger Pac 3500, Industrial Scientific T40 Rattler, MSA Altair, and Honeywell BW Clip. These are referenced as "test monitors" hereafter. Qualitative monitors were those that display a countdown of the warranty period in months, but does not provide a display of the concentration detected. Conversely, quantitative monitors displayed the H_2S concentration detected in ppm. As shown in Table 3, quantitative monitors cost approximately twice that of the qualitative monitors. These monitors are still significantly less than the multigas monitors traditionally used in larger industries for confined space entry, which cost \$600 to greater than \$1000 (PK Safety).

Table 3. Comparison of features of each test monitor.

Factor	Qualitative Monitors: MSA Altair	Qualitative Monitors: Honeywell BW Clip	Quantitative Monitors: Dräger Pac 3500	Quantitative Monitors: Industrial Scientific T40 Rattler
Cost, $	109	110	209	220
Battery	Lithium	Internal (2 yr)	Lithium	AA (1500 hr)
Replaceable?	No	No	Yes	Yes
Display:				
Concentration?	No	No	Yes	Yes
Default low alarm, ppm	10	10	10	10
Default high alarm, ppm	15	15	20	20
Warranty Period	2 yr/ 18 hr alarm	2 yr w/ 2 min alarm/day	2 yr	2 yr
Shelf-life	1-3 mo	10-11 mo	2 yr	10-11 mo
Concentration checks, per manufacturer:				
Bump?	Recommend	Possible	Recommend	Possible
Calibration?	Possible	Recommend if alarmed*	Possible*	Possible

* = requires additional proprietary hardware or software to perform (sold separately)

Experimental Setup

A chamber (0.047 m^3 internal volume, submersible enclosure, McMaster-Carr, PN 5376K312) was modified to support prolonged exposure of the test monitors to H_2S gas over time, Figure 1. Two of each brand of test monitors were placed inside the chamber: one was fully activated throughout the study (“primary” monitors) and the matched monitor was turned off or placed in a standby setting, if available, throughout the study (“secondary” monitors).

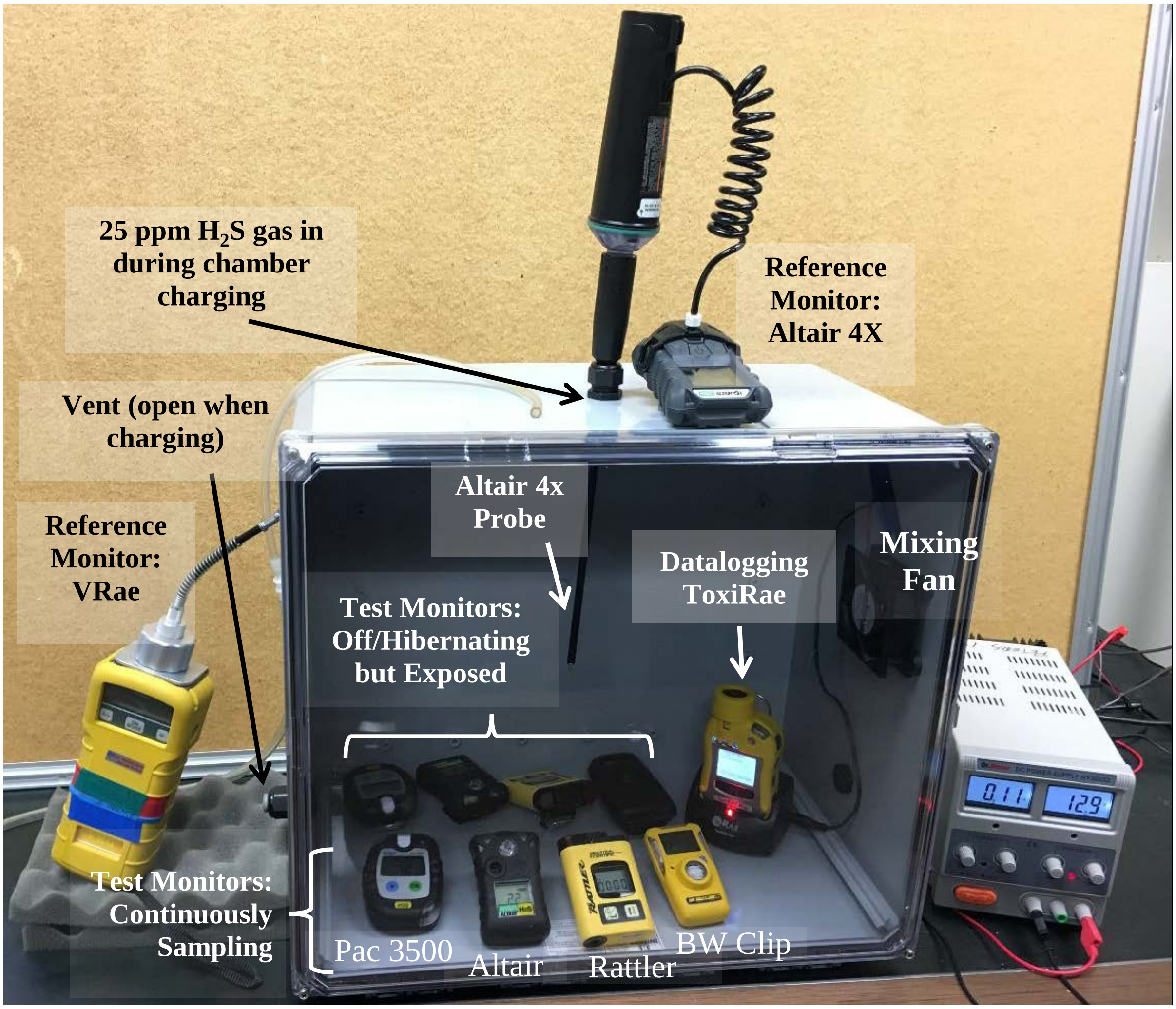


Figure 1. Experimental setup of test chamber, four paired sets of test monitors and ToxiRae inside; VRAE and Altair 4X (with probe pump) shown outside chamber with power supply for internal fan.

The reference concentration in the chamber was measured using three reference monitors. A ToxiRae Pro EC (H_2S, Rae Systems by Honeywell, San Jose, CA) provided continuous 1-minute logging throughout the testing. This was used to determine the cumulative concentration (ppm-time) that the test monitors were exposed to over the duration of the study. The ToxiRae was calibrated initially and between sequential test runs. Two additional reference monitors were used to measure concentrations at the start and end of each test run, with additional daily concentration checks: the Altair 4X (MSA, Cranberry Township, PA) and the VRae (Rae Systems by Honeywell). Each of these were probed to draw air out of the closed chamber, and each were zeroed and calibrated between sequential runs. These were used to validate the ToxiRae monitor readings.

Hydrogen sulfide gas (25 ppm H_2S, Praxair Technology, Danbury, CT) was delivered to the chamber through a side port, (top, left side in Figure 1). A fan was placed inside the chamber to ensure well-mixed air. Additional ports (right side) allowed power supply to the fan and ToxiRae; this was sealed with plumber's putty. A final "vent port" was installed (bottom, right side in Figure 1) to vent the chamber and prevent pressurization.

Test Protocol

Testing of the monitors was completed to simulate a one-year equivalent of H_2S exposure in an agricultural setting. This was completed in 18 actual weeks of testing by making an initial calculation to determine what the cumulative exposure in a barn would be under expected agricultural conditions over a year and then setting the target cumulative chamber concentration to that number (in ppm-day). The test period was shortened from a year by exposing the test monitors to slightly higher concentrations in the chamber than those assumed for agricultural conditions.

Assumptions for this calculation (Table 4) included low levels of background concentration in a livestock building (~1 ppm), occasional peak concentrations, and weekly calibration or bump checks. Chamber test concentrations (ppm-day) were converted to equivalent barn days of monitor exposure to estimate an equivalent continuous H_2S exposure in a livestock building. In one year, cumulative exposure to a monitor in the field was estimated at 366.76 ppm-day, which is equivalent to an average daily concentration of 1.005 ppm, indicating a minor increase in sensor exposure due to weekly bump testing and use in high concentration exposure tasks relative to continuous exposure of 1 ppm over a year. Thus, the cumulative concentration to which the test monitors were exposed in the chamber were divided by the cumulative daily concentration in a typical barn (1.005 ppm-day) to determine the number equivalent barn days of exposure. The study was terminated when the total equivalent barn days for the chamber tests exceeded 365, indicating the chamber tests simulated a full year of typical exposure likely within a livestock production operation.

Table 4. Assumption of typical exposure concentrations in livestock barn over one year.

Source of typical exposure	Concentration (ppm)	Frequency/Duration	Cumulative ppm-day
Background concentration (no pumping or agitation of manure)	1	Constant for 365 days	365
High concentrations during barn events (pumping, etc)	25	15 mins, 4/year	1.04
Weekly bump testing	20	1 min, 52/year	0.72
		Annual Total	366.76

A total of 24 sequential short-term test runs were conducted by charging the chamber with H_2S, measuring concentration, and then opening the test chamber to check test monitor performance. A test run was defined as the time between closing the chamber with test monitors inside and applying H_2S gas into the chamber until the time at which the chamber was opened to conduct performance tests. Individual test runs typically lasted between 3 – 7 calendar days, dependent on monitor behavior, researcher schedule, or other similar external factors. The study was broken into test runs in order to allow for download of ToxiRae data and for regular bump tests of the test monitors and recalibration of the ToxiRae.

Prior to the beginning of each sequential test run, all monitors were bump tested with calibration H_2S at 20 ppm (GASCO, 34L-428-20). Two of the test monitors (Rattler and Pac 3500) provided quantitative readings in concentration (ppm), and these bump concentrations were recorded. The other two monitors (BW Clip and Altair) are qualitative, alarming at pre-determined low (10 ppm) and high (15 ppm) thresholds with no quantitative display of concentration. For these bump tests, the response time to alarm at each threshold was measured in seconds via stopwatch.

Once the test monitors and the ToxiRae were placed inside the chamber, the airtight cover was screwed into place. The fan was turned on, and the vent port at the side of the chamber was opened. The regulator valve for the 25 ppm H_2S cylinder was opened to send gas into the chamber. Concentrations inside the chamber were recorded for each test monitor and for the ToxiRae at 2 minute intervals. Once the chamber concentration approached 10 ppm, the gas regulator valve was closed to prevent any more gas from entering the chamber. Every model of test monitor was programmed with a low alarm setting at 10 ppm, so the concentration in the chamber was kept below this level to prevent setting off alarms and reducing the battery life of the monitors. Once the H_2S valve was closed, the vent port was closed, and the initial chamber concentration of the ToxiRae was validated by measuring with the VRAE and Altair 4X.

Over several days, the H_2S concentration decreased within the sealed chamber. Re-charging of the chamber with H_2S followed one of two protocols, performed during two phases of testing. Initially, the chamber H_2S concentration was allowed to naturally decay to ~1 ppm, as indicated by the reference and test monitors, and the test run was ended. This occurred during the initial phase of the study and allowed for an assessment of the initial performance of these low-cost monitors. The initial phase of the study encompassed 21 runs spanning approximately 16 weeks actual time, or 273 equivalent barn days.

Once performance effects were observed in the monitors later in the study, the chamber concentration was allowed to decay naturally to ~3 ppm and then additional gas was added to increase the concentration back to ~10 ppm without opening the chamber. This allowed testing to be accelerated to efficiently simulate an equivalent one-year in-barn exposure. Changes in chamber re-charging methods to allow higher average concentrations within a test run were started only once the test monitors began to show effects of extended exposure to H_2S, such as alarm failures. The final three runs were performed in Phase 2, taking place over the last 2 weeks of the study but providing an additional 100 equivalent barn days of exposure to the monitors.

Following each test run, each primary test monitor was bump tested with concentration readings or alarm information recorded, as applicable to the monitor. The secondary test monitors were only bump tested at the end of the full testing period. ToxiRae data was downloaded with concentration data at 1-minute increments while inside the chamber. A flowchart of the procedure followed for each test run is shown in Appendix B.

Data Analysis

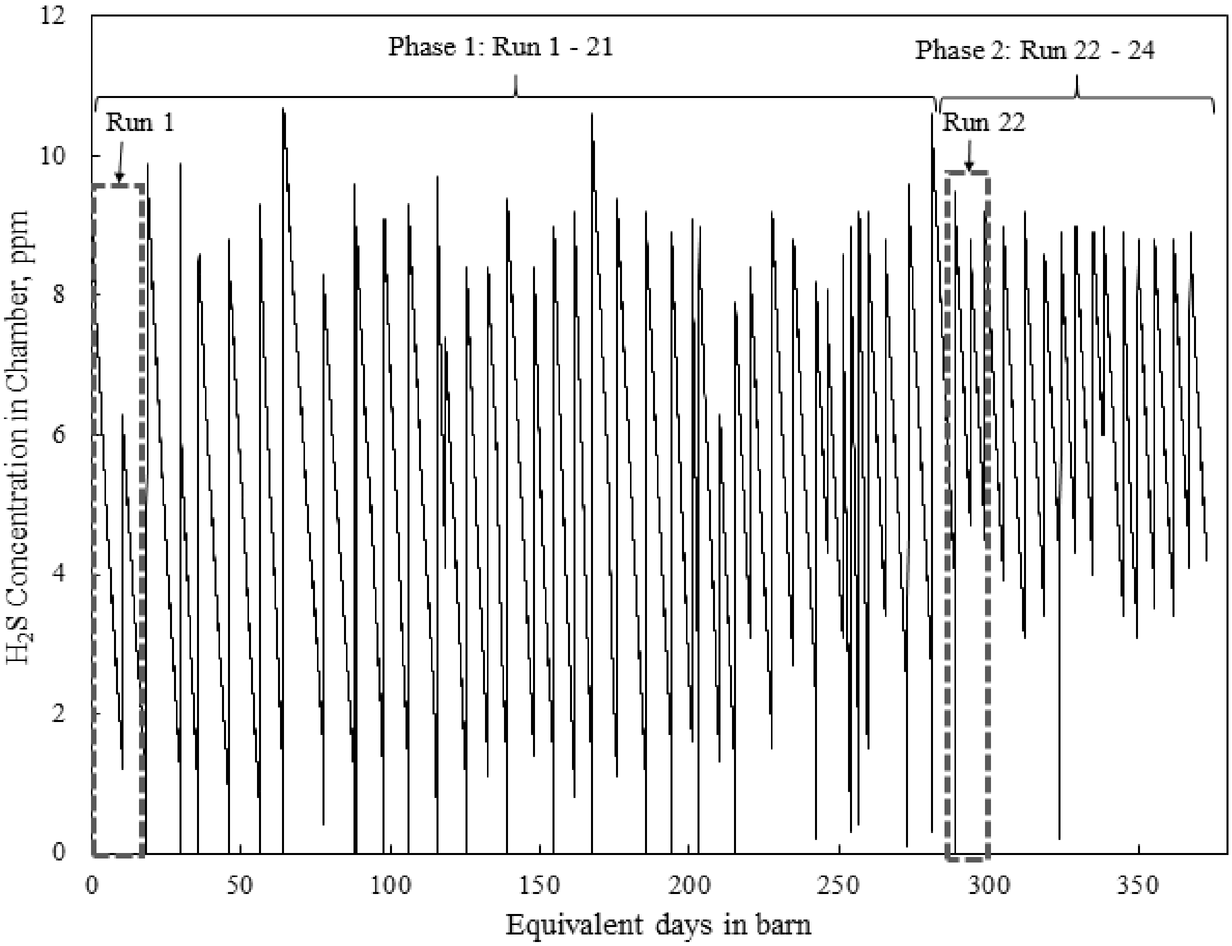
The cumulative H_2S exposure (ppm-day) of the test monitors was computed from the start of the test monitor use. The 1-min concentrations from the in-chamber ToxiRae served as the true indication of cumulative exposure during chamber tests. Since the chamber tests were operated at concentrations above those typically found in livestock buildings, these test concentrations (ppm-day) were converted to equivalent barn days of monitor exposure to estimate an equivalent continuous H_2S exposure in a livestock building.

The response to H_2S was evaluated for each test monitor. Performance parameters were the time at which the monitor failed to meet one of two criteria: (1) when did the monitor drift below calibration gas or reference monitors by 3 ppm (15% of the calibration gas concentration), and (2) when did the monitor fail to signal a high alarm within either a 60-second (manufacturer's criteria) or 15-second (field recommendation criteria) response time (Wanek, 2011). For test monitors that display gas concentration (Pac 3500, T40 Rattler), the difference in reported concentrations during both bump testing (compared to 20 ppm calibration gas) and test runs (compared to reference concentration measures) was computed. For monitors that only alarmed when high concentrations were detected (Altair, BW Clip), the reaction times to reach both high and low alarm was observed and trended over the chamber test period. Since manufacturers indicated these alarms should sound within one minute of gas detection, the monitor was considered to "fail" the bump test if the monitor failed to respond to the appropriate alarm level (low or high) within one minute of direct exposure to H_2S calibration gas. The time to fail was identified for each monitor, in both chamber total concentration-time and equivalent barn unit time.

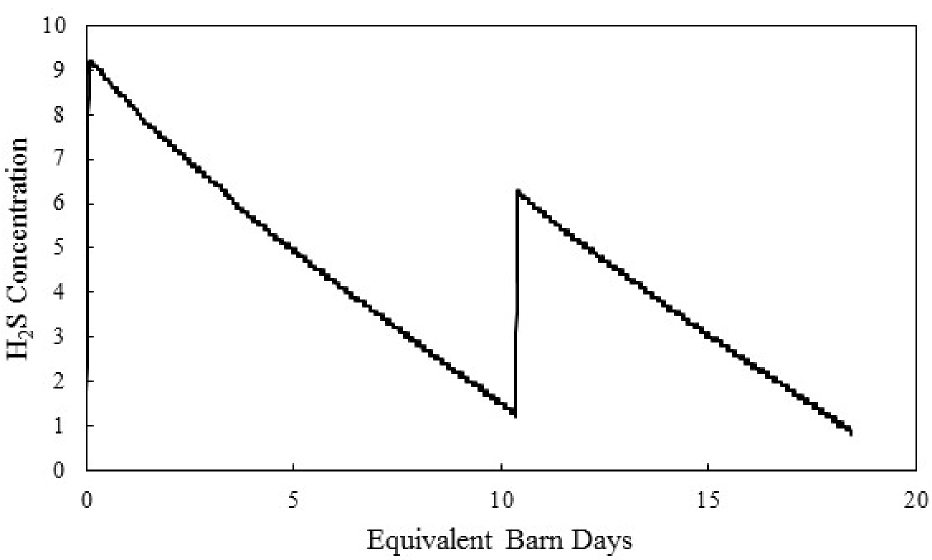
For the paired low-cost monitors that were in hibernation or "off" while in the chamber for the study duration, these same criteria were used at the end of the study only, examining if the concentration drifted by more than 3 ppm or if the alarm response failed. This information was obtained to examine whether leaving a monitor exposed to H_2S while turned off would reduce the performance, in order to provide guidance to where and how to store these monitors in the field.

Results

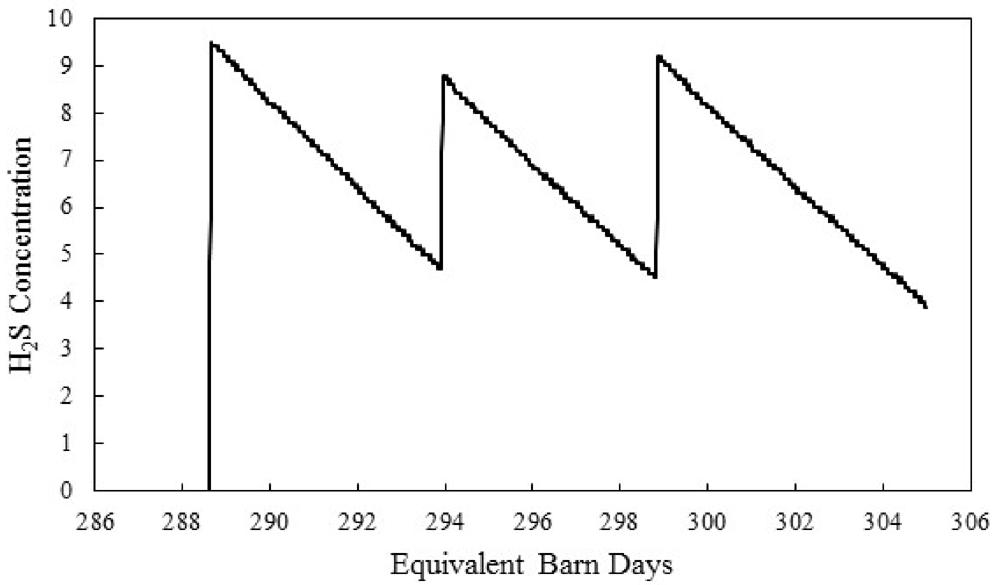
Test monitors were challenged in the chamber for a total of 373 equivalent barn days. Figure 2 illustrates the pattern of gas concentration within the chamber during test runs. Figure 2 shows the H_2S concentrations that the monitors were exposed to over the duration of testing. Figure 2(a) shows the entirety of testing, with Phase 1 and Phase 2 delineated; 2(b) shows a clearer view of Run 1 to illustrate the charging pattern during Phase 1 of testing, with a quick concentration increase to just under 10 ppm and then decay down to 1 ppm with a second charging at day 10 (equivalent barn day). Figure 2(c) shows a clearer view of Run 22 to illustrate how chamber concentrations were maintained higher in the later phase of the testing, where an initial charge to 9 ppm was followed by two additional chamber charges when concentrations decayed to 5 ppm on barn equivalent days 294 and 299.


Phase 1: Run 1 - 21
Phase 2: Run 22 - 24
Run 1
Run 22
H$_2$S Concentration in Chamber, ppm
Equivalent days in barn
0
50
100
150
200
250
300
350
0
2
4
6
8
10
12

(a)


H$_2$S Concentration
Equivalent Barn Days
0
5
10
15
20
0
1
2
3
4
5
6
7
8
9
10

(b)



(c)

Figure 2. Pattern of chamber gas concentration during (a) the entire duration of testing (24 test runs), with Run 1 and Run 22 emphasized for comparison; (b) over test Run 1 when concentrations were allowed to decay to 1 ppm; and (c) over test Run 22 when concentrations were maintained higher during the second phase of the study. All measures were taken with the ToxiRae reference device.

Figure 3 summarizes notable events that occurred with respect to each monitor during testing. Over the course of the study, the Rattler required battery changes four times. While not considered failures under the study's criteria, these events were noted to determine the higher maintenance requirements of the Rattler. The Altair exhibited failures of the high alarm nine times. The BW Clip experienced a high alarm failure once during testing, after 324 equivalent barn days. These events were considered critical failures, as the monitors failed to detect the gas at the high alarm setting within one minute of gas exposure. The Pac 3500 had 17 events in which the monitor reading was at least 3 ppm less than the concentration of the calibration gas. These events were worth noting because 3 ppm represents a 15% underestimation of the calibration concentration, which may not be critical at lower concentrations. However, if the underestimation scales up with increasing concentrations, a 15% underestimation could be fatal to a worker at high concentrations.

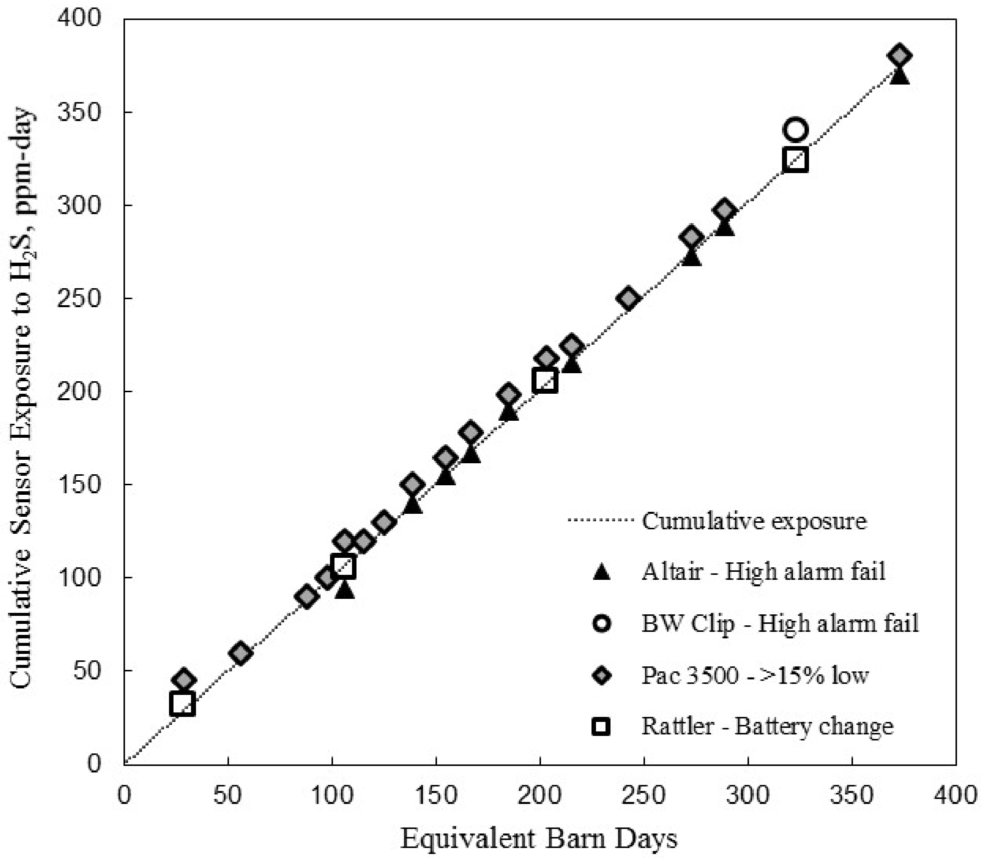


Figure 3. Test monitor notable events during bump testing, by equivalent barn days and cumulative concentration of monitor exposure (ppm-days).

Throughout the chamber tests, the Rattler read consistently higher than the calibration gas concentration by an average of 2.3 ppm (Figure 4). On equivalent barn day 203, the Rattler bump test read below the 20 ppm calibration gas, but the AA-battery was identified as low just after calibration. This indicates that battery management is critical to accurately measuring concentrations near the short-term exposure limit (STEL). The Pac 3500, on the other hand, displayed concentrations consistently lower than the calibration gas concentration by an average of 3.4 ppm. In fact, 17 of 22 bump checks on the Pac 3500 showed results of greater than or equal to 3 ppm less than the calibration gas concentration.

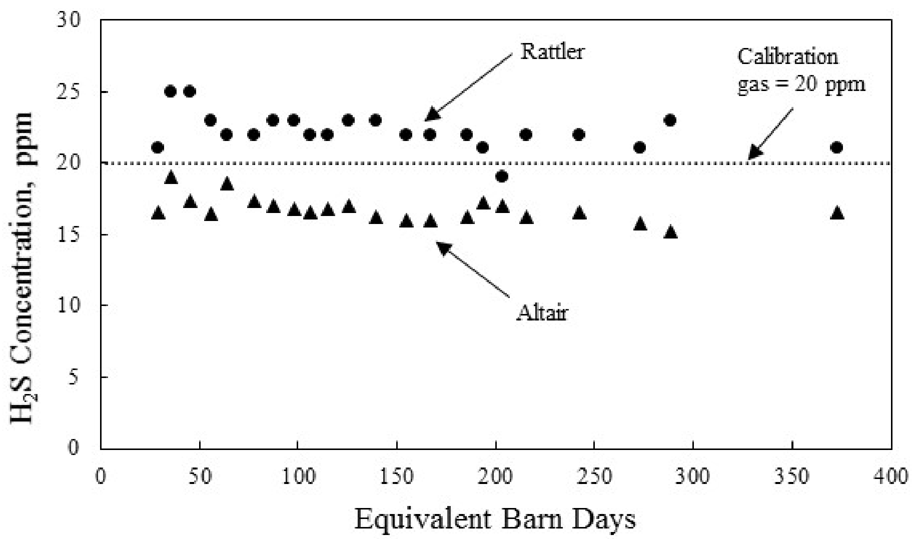


Figure 4. Result of bump checks over duration of testing for monitors with quantitative display of gas concentration using calibration gas concentration of 20 ppm.

Table 5 shows how long it took for the alarm-only monitors to alarm during bump-testing throughout the study. Both had the same default manufacturer-preset alarm levels: 10 ppm for the low alarm and 15 ppm for the high alarm. During the first phase of testing both monitors reached the low and high alarms quickly, but by equivalent barn day 98 the Altair took 31 seconds to signal the high alarm. By the end of the chamber tests, the Altair did not alarm when challenged with 20 ppm even though that threshold was set to 15 ppm. The BW Clip continued to activate the high alarm until day 289, although a noticeably longer response time was clearly developing.

Table 5. Alarm response for bump tests at 20 ppm.
Responses are pass or fail; numbers are time
taken to respond in seconds with pass defined as <60 sec.

Equivalent Barn Day	MSA Altair		BW Clip	
	10 ppm	15 ppm	10 ppm	15 ppm
0	pass	pass	pass	pass
30	pass	pass	pass	pass
36	pass	pass	pass	pass
46	pass	pass	pass	pass
56	pass	pass	pass	pass
64	pass	pass	pass	pass
78	pass	pass	pass	pass
88	pass	pass	pass	pass
98	pass	31	pass	pass
106	12	**fail**	pass	pass
115	11	49	pass	pass
125	12	40	pass	pass
139	12	**fail**	9	12
155	14	**fail**	10	13
167	12	**fail**	9	13
185	11	**fail**	10	18
194	13	49	10	19
203	11	42	10	18
215	10	**fail**	10	20
243	13	49	10	20
273	10	**fail**	10	23
289	12	**fail**	11	**fail**
373	16	**fail**	12	20

Finally, a secondary monitor of each model also resided in the chamber throughout the study period to examine whether these sensors degraded without the same handling as the primary monitors. The secondary monitor was either off (Pac 3500, Rattler), hibernating (BW Clip), or remained on (Altair) if it could not be shut off. These were bump checked prior to beginning the study and then only bump checked at both 273 and 372 equivalent barn days of chamber exposure. The secondary Rattler passed the alarm test and displayed 20 ppm to match the bump test gas. The secondary Pac 3500 reported 2.5 ppm below the calibration gas target, consistent with the paired primary Pac 3500. The secondary BW Clip was removed from its hibernation case at the end of the study: the countdown of months-remaining was noticeably paused, and the monitor responded adequately to the bump tests (alarm activations and speed). The secondary Altair, which cannot be shut off once activated, failed the high alarm test when it was challenged at equivalent barn day 273.

Discussion

Limited adoption of gas monitors has been identified in the agricultural industry. A 2016 survey of Iowa manure applicators identified that only 5% have used H_2S monitors, although 31% indicated they might purchase them in the future (ISU, 2016). Expertise in bump testing and calibration of direct-reading monitors is likely even more limited. Therefore, gas monitors that do not require extensive training, time, or financial investment would be attractive for recommending for adoption by farmers, provided that the monitors prove to maintain their effectiveness for the duration of their advertised warranty period.

Each of the four models of test monitors exhibited performance changes during the test period. The Altair and BW Clip experienced alarm failures during bump testing at equivalent barn days 106 and 289, respectively. The Pac 3500 showed a consistent underreporting of concentration throughout the duration of the testing by an average of 3.4 ppm. The Rattler required battery changes four times over the course of the simulated barn year, and tended to overestimate gas concentration by an average of 2.3 ppm. These effects demonstrated that long-term exposure to even low levels of H_2S, such as those found in agricultural livestock buildings, may jeopardize the reliability of direct-reading monitors without validation checks and at least a minimal amount of maintenance.

Monitor Recommendations

The observations and test results collected throughout the study were used to rank the monitors in terms of appropriateness for use in agriculture. Examining both performance of the monitors and qualitative observations, features, and manufacturer's instructions resulted in the following order of recommendation for use: Honeywell BW Clip, Industrial Scientific T40 Rattler, Dräger Pac 3500, and MSA Altair.

The Honeywell BW Clip monitors (primary and secondary) responded consistently to bump tests for most of the test barn year. Low alarms (10 ppm) occurred within 10 seconds for every bump test that was performed. For the high alarm, the time to respond grew longer as the testing went on, with the first (and only recorded) failure of the primary BW Clip occurring after 289 barn days. This monitor required the least amount of maintenance and showed the fewest failure events. This monitor also has a hibernation case, which allows the life of the monitor to be extended and seemed to protect the secondary sensor from exposure to H_2S while in storage. This monitor was also one of the least expensive monitors, due to its "alarm-only" functionality. After testing had begun, the manufacturer released a BW Clip with concentration display, known as the BW Clip RT. One of these monitors was introduced into the study much later than the others and was tested for 206 equivalent barn days, with no failure events noted in that time. Since undertaking this study, livestock producers were surveyed about preferences regarding H_2S monitors, and 89% indicated that concentration display was an important feature (Trenkamp, 2016). Thus, the availability of the BW Clip RT may be highly attractive to agricultural workers.

The Industrial Scientific T40 Rattler required more maintenance than the BW Clip due to the number of battery changes, but otherwise showed no failure events. Though the readings were not accurate with respect to the test gas, the higher concentration reading of the primary Rattler provides additional protection to the worker, as it would provide warning of toxic levels of H_2S earlier than the other monitors. It is of concern, however, that the secondary Rattler produced incorrect low concentrations during bump testing, though both Rattler monitors were corrected by calibration. The resulting range of readings produced by both Rattler monitors throughout testing indicate that this model may be vulnerable to battery charge affecting the concentration reading, and may be at greater risk of being out of calibration directly from the box.

The Dräger Pac 3500 provided concentration measurements that were lower than the calibration gas concentration by an average of 3.4 ppm during bump checks. This effect was observed immediately following monitor activation and was consistent throughout the duration of testing. Underreporting of the actual concentration of exposure is problematic, as that creates a false sense of safety in a situation that could actually be hazardous. For industries in which chronic low exposures are monitored and regulated, inaccurately low readings may be unacceptable. In agriculture, however, these monitors would be primarily used to alert workers of an acute hazard at high concentrations of H_2S of 100 ppm or greater. In this situation, a difference of 2 – 3 ppm would not likely make a difference in the decision to enter the space or not, as health effects are not readily observable within such a small window of concentrations. Thus, the performance of the Dräger Pac 3500 monitors in this study were certainly not ideal, but provided another factor of consideration when selecting a monitor for use in agricultural settings.

The MSA Altair monitors have no option to be turned off after initial activation. According to the manufacturer, the alarms should respond to bump testing within 60 seconds of gas application. The primary monitor failed this bump test at 106 equivalent barn days in the chamber. Including that initial failure, the primary Altair failed to activate the high alarm during 64% of bump tests performed after 100 barn days. Without bump tests to verify performance, the Altair provides no other indication of failure to successfully detect gas, which would put a worker in serious danger of exposure unknowingly. Due to the high failure rate of the Altair in this experiment, this monitor should not be used in an agricultural setting until further validation of its robustness can be tested.

Maintenance Requirements

The gas monitors tested in this experiment detect the presence of H_2S via electrochemical sensors. Chemicals within these sensors react with H_2S and a detector identifies a resulting electrical signal that is set to correspond with a given concentration of the gas. Over time, the sensor's performance may be reduced due to loss of electrolyte or contamination with environmental factors (i.e. water vapor or dust). This can cause the relationship between the electrical signal and concentration to drift, reducing the ability of the monitor to detect the gas accurately. For this reason, gas monitors using electrochemical sensor technology should be routinely calibrated to ensure that any changes in the electrical signal over time is still being translated into the correct gas concentration.

According to each of the manufacturers for these monitors, none need regular calibration. Two manufacturers (MSA and Dräger) recommend bump-testing their respective monitors, which consists of exposing the monitor to a known concentration of H_2S in order to verify that the monitor responds appropriately. This is typically performed using a canister of known concentration of H_2S with a regulator to normalize the flow of gas to the sensor. Additionally, each of these manufacturers recommends that bump-testing or other basic checks be performed “according to industry standards” or “according to local protocols”, but that guidance is not readily available for the agricultural industry.

It is unlikely that bump testing or calibration would be completed on a farm due to the additional equipment and technical experience required. However, results of this study show that even when designed to be low-maintenance, these monitors should indeed be checked for their ability to detect H_2S. Ideally, this check would happen upon first activation of the monitor, and then at least monthly thereafter to ensure the sensor hasn’t failed over time. Due to the high burden that this recommendation would be for agricultural workers, it may be more feasible for agricultural communities to set up a system in which a centralized location, such as a volunteer fire station or agricultural extension office, would maintain calibration/bump check equipment that farmers could visit to maintain their equipment.

A bump check is critically important to complete prior to completing any activity that may put the worker at risk of higher exposure to H_2S such as manure agitation, pumping, or application to the field or when entering any space where manure is stored or was stored recently, as H_2S can pool and remain in a space with poor ventilation for days or weeks following removal of the manure itself (Baker et al, 1999). Additionally, monitors should not be stored in exposure to even low levels of gas for prolonged periods, as this seemed to have an effect on the response times of the ‘alarm only’ monitors.

The Altair and the BW Clip have internal batteries not meant to be changed by the user. Thus, once the battery is dead the monitor must be replaced. If the alarm function is not activated, these monitors would theoretically last the duration of the 2-year warranty period. The Pac 3500 has a replaceable lithium battery, and the T40 Rattler operates using a single alkaline “AA” battery. At first glance, the AA battery seems to be a favorable feature because the battery is so common, and would likely be readily accessible and easily changed by agricultural workers. However, the number of battery changes that occurred with the Rattler during this study could indicate a vulnerability with the alkaline battery, however, and particular attention should be paid to the battery level to ensure that the monitor is still active and monitoring during practical use of this monitor.

Study Limitations

This study did not account for changes in humidity and temperature, which have been shown to affect the accuracy and useful life of electrochemical H_2S sensors. Temperatures above 25 degrees C have shown to increase sensor readings by approximately 0.5% to 1.0% per degree Celsius, dependent on type of sensor and manufacturer. Similarly, extremely high humidity can cause condensation to form on the electrode, interfering with the accuracy and operation of the sensor (Chou, 2000).

Additionally, this test did not measure how potential exposure to other barn contaminants might affect the sensors, such as ammonia, dust, or chemicals. Future testing should be completed to test the performance of these monitors in real-world agricultural environments, where temperature and humidity may vary considerably from summer to winter and where other contaminants are present. Environmental effects may be even more pronounced for the Rattler due to its use of alkaline batteries and should be studied accordingly.

Although these monitors were tested at higher concentrations than exist in typical barns, the study used equivalent barn exposure assumptions to simulate performance of each monitor over approximately one year in a livestock barn with a background concentration of 1 ppm. Under these conditions, both types of 'alarm-only' monitors showed signs of alarm failure at the high alarm setting and began to show effects at the low alarm levels. If background concentrations are higher than 1 ppm, typical in swine production buildings, these monitors may show signs of failure even earlier.

Finally, this study tested a very small sample of monitors. There were only four models tested, and only three monitors of each model. While the results of this study are informative regarding the general performance of monitors without maintenance over a long-term period, it is impossible to determine that one model is drastically better- or worse-suited for agricultural use without doing further study of each model, as even different lots of monitors may perform differently. Importantly, though, without doing an initial function test of the monitor and exposing it to gas at least upon initial activation, a worker has no way of knowing whether their monitor works straight out of the package.

Conclusion

Each of the four low-cost monitors that were studied exhibited performance characteristics that indicate that some maintenance should be performed if stored in an agricultural environment for the active life of the monitor. Monitors should be challenged with a test gas to ensure the sensor will detect H_2S, and this requirement becomes more important later in the life of the monitor as failures were shown to occur over time. If tested and maintained appropriately, however, these monitors have the potential to save the lives of agricultural workers. Future work is still needed to determine if environmental factors within a barn would contribute to sensor failures even earlier. The results of this study can be used in educational programs aimed at increasing awareness about H_2S exposure in agriculture and the use of direct-reading monitors, and to inform training on how to select and use the monitors on the farm and monitor limitations.

CHAPTER III

CONCLUSIONS

This study examined the reliability of low-cost monitors marketed as maintenance-free for potential use in agricultural operations at risk for hydrogen sulfide (H_2S) exposure, where sophisticated calibration equipment and trained safety professionals are not commonly found. The study first used internet searches to identify four models of H_2S monitors currently marketed as "low-maintenance" or "maintenance-free". Models that were selected were Dräger Pac 3500, Industrial Scientific T40 Rattler, Honeywell BW Clip, and MSA Altair. Qualitative data were collected prior to testing regarding the features, activation process, and manufacturer settings of each monitor. The MSA Altair and Honeywell BW Clip were basic models with internal, non-replaceable batteries. These models were designed such that once activated, they remained active until the end of battery life from alarm activity or after two years of constant monitoring, whichever came first. The BW Clip has an optional hibernation case that suspends operation of the monitor while inside the case, which extends the life of the monitor. The Altair and BW Clip alarm at preset low and high alarm thresholds, and the display screen shows a countdown of time left in the life of the monitor. The Dräger Pac 3500 and the Industrial Scientific T40 Rattler have replaceable batteries, lithium and alkaline respectively. These monitors display numerical gas concentration in ppm of H_2S.

Three monitors of each model were purchased and activated according to the manufacturer's guidelines, divided into three sets with one monitor from each model in a set. Each set of monitors was tested for sensor response to H_2S. The primary set was exposed to concentrations of H_2S between 0 and 10 ppm over time within an enclosed chamber. These monitors remained on and actively reading for the duration of the experiment. Each monitor was bump tested between each exposure cycle to determine the presence and extent of any sensor drift with respect to the H_2S readings. The second set of monitors was also placed within the chamber, exposed to the same H_2S cycles as the primary monitors. These monitors were turned off or in hibernation mode, if available, during each test cycle and were turned on only for bump testing. Monitors in the third set were kept outside of the chamber and protected from exposure to H_2S, except for bump testing at the beginning and end of the study.

A total of 24 test runs were performed, where the chamber was closed with monitors inside exposed to H_2S. Between test runs, each primary monitor was bump checked to test its response to gas. For the alarm-only monitors, a bump-test was considered a failure when the monitor did not react appropriately within 60 seconds of gas application, in accordance to manufacturer literature. The primary Altair failed bump testing at the high alarm level on 9 of 23 tests, with the first failure at 106 equivalent barn days. The BW Clip experienced a failure of the high alarm setting after 324 equivalent barn days. Neither of these monitors experienced low alarm failures, though slight response delays were observed between the start and completion of the study.

The concentration-reading monitors did not show noticeable difference in response over the duration of testing, but both showed consistent inaccuracy with respect to the exposed gas concentration. The Pac 3500 displayed concentrations 3 ppm or more lower than the calibration gas for 17 of 22 bump checks. Over all bump tests, the Pac 3500 underreported the calibration gas concentration by an average of 3.4 ppm. The Rattler, on the other hand, read consistently higher than calibration gas concentration by an average of 2.3 ppm. The Rattler also required higher maintenance than the others, as the alkaline battery required changing four times over the course of the study.

Based on the results of this study the monitors were ranked in terms of performance, with Honeywell BW Clip (best), Industrial Scientific T40 Rattler (2nd), Dräger Pac 3500 (3rd), MSA Altair (4th). Each monitor proved to have some vulnerability or limitation for use in an agricultural environment, and ultimately any monitor used should be given a basic amount of maintenance despite manufacturer guidance. At a minimum, monitors should be bump tested monthly with exposure to H_2S to ensure the monitor is responding appropriately. Additionally, it is critical that monitors are inspected and bump checked prior to completing any high-risk activity that may expose the worker to hazardous levels of H_2S, such as pumping the manure pit. This requirement may not be practical for most agricultural workers to complete individually, but perhaps implementing a program through local agricultural extension offices or fire departments can help meet this need. Bump checking provides confidence to the worker that the monitor will alert them to the presence of dangerous levels of gas.

Based solely on results of this study, the Honeywell BW Clip and the Industrial Scientific Rattler would be the most beneficial for use in agriculture, at least for the first year. The Drager Pac 3500 may also be used, particularly as an early alarm in cases where the accuracy of the concentration reading is not critical. At this point, it is impossible to recommend the MSA Altair for use in an environment where the monitor may not be bump checked regularly to ensure its performance. This study was small and there may be unforeseen circumstances that led to the frequent failure of this monitor, and further testing with this model may show better performance.

Future research should explore environmental factors that are often present in a barn that were not simulated in this chamber study, such as variations in temperature and humidity, as well as the presence of other substances that can affect the sensor such as ammonia and dust. In the meantime, the findings of this study can be a useful tool when educating farmers about the usefulness, operation, and limitations of H_2S monitors on the farm.

APPENDIX A: MONITOR STANDARD OPERATING PROCEDURES

The owner's manuals for each monitor were condensed into one-page instructions for ease of use on this study, and can also be used for educational purposes in training sessions for these monitors in the future.

Dräger Pac 3500 (H_2S – Hydrogen Sulfide) User Instructions

Activating new device:

1. Press (+) button for 3 seconds. The display will show a countdown (3-2-1). The device usable life has now started, and display will show "H2S". Verify correct gas is shown.
2. After 10 seconds, the display will shut off. Press (+) button to show remaining time in days of unit's useful life. After 10 seconds of no activity, display will turn off.
3. Upon initial activation, the sensor requires a 15-minute "warm-up" period before measurement can occur. The countdown will display (in seconds) for duration of this initial warm-up period. For all future uses, the sensors are ready for measurement immediately upon startup.

Daily Usage:

1. Press and hold (OK) button. Display will count down 3-2-1 to startup.
2. Device will perform self-test. Verify display and alarm settings are operating:
    a. LED lights will flash. Audible alarm and vibrator will activate.
3. Display will show software version and gas monitored.
4. The number of days of remaining operation will be shown.
5. Alarm thresholds will display.
    a. A "low" alarm threshold is set to 10 ppm, the "A1" setting.
    b. A "high" alarm threshold is set to 20 ppm, the "A2" setting.
6. A fresh air calibration can be performed by pressing (OK) while gas value is flashing immediately following alarm settings display. To perform fresh air calibration, ensure unit is removed to fresh air and from all possible sources of H2S.
7. If no key is pressed while display flashes, fresh air calibration is skipped and device automatically enters measurement mode. Measured gas concentration will be displayed.

Gas Detection:

1. If alarm thresholds are exceeded, unit will enter alarm mode. ***Upon alarm, evacuate area immediately.***
    a. LED lights will flash, audible alarm will sound, and vibration will activate.
    b. A1 threshold alarms flash and sound in a single repeating tone.
        i. A1 (low) alarm can be acknowledged by pressing (OK). This will silence the alarm.
    c. A2 threshold alarms flash and sound in a double repeating tone.
        i. A2 (high) alarms cannot be silenced. The alarm will stop once the concentration of H2S falls below the alarm set level of 20ppm, and the user then presses (OK).

Battery Change:

1. The battery for the monitor may require changing prior to the 2 year life of the unit.

a. A low battery icon will flash on the screen and audible alarm will sound when battery gets low. The battery will continue to power the unit for 1 – 7 days depending on external temperature. ***Change battery immediately.***
b. Turn device off and unscrew 4 screws from back of unit.
c. Remove battery and replace with similar Lithium 3V battery.
d. Replace cover and screws. Monitor will require a 15-minute warm up time for sensor once new batteries are installed.

End of Usable Life:

1. A warning period will begin prior to the end of the device's usable life. This will be shown by the remaining time flashing just after turning device on with a number and then "d" to indicate the number of days remaining. (For example, "30" and then "d" means 30 days remain.)
2. Once the usable life has expired, "0" "d" will flash and the monitor will no longer measure gas. ***At this time (or earlier), discontinue use of the monitor and replace the unit.***

MSA Altair Single Gas Detector (H_2S – Hydrogen Sulfide) User Instructions

Activating new device:

1. Remove unit from box and verify that "H2S" is printed on the unit.
2. Press and hold the "TEST" button for 3 seconds until "ON" and "?" are displayed. Release button.
3. Press "TEST" once again to complete activation.
4. Verify the following:
   a. Audible alarms sound
   b. Visible alarms (LED lights) light up
   c. Vibration alarm activates
5. Screen will cycle through following display information:
   a. Unit displays software edition.
   b. Unit displays correct gas type (H2S).
   c. Unit will display LO ALARM at 10 ppm. (Adjust?)
   d. Unit will display HI ALARM at 15 ppm. (Adjust?)
6. Unit will begin 99-second activation countdown. Once activated, instrument remains active until Low Battery error is shown.
7. Upon full activation, the Months Remaining counter will display 24 months and begin count down.

Daily Usage:

1. Check each day to verify time remains in operational life (up to 24 months).
   a. When less than 1 month remains, display will show number of days remaining.
   b. The unit will continue to run beyond 24 months. If this is allowed, display will show "+" followed by the number of days or months beyond guaranteed operational life.

2. During normal operation, the LED lights will flash briefly every 60 seconds to show unit is operating.

Gas Detection:

1. If gas concentration exceeds either of the LO or HI setpoints, the instrument will enter alarm state.
   a. Display will flash "ALARM" and "LO" or "HI", depending on which set point was exceeded.
   b. Audible horn alarms will sound.
   c. LED lights will flash and vibrator will activate.
2. ***Evacuate area IMMEDIATELY to fresh air.***
3. Alarms can be silenced for 5 seconds by pressing and holding "TEST" button. Alarms will clear automatically once gas concentration falls below alarm set points.

End of Unit Life:

3. If unit battery is nearing its end of life, a Low Battery warning indicator will show:
   a. Low battery indicator flashes
   b. Display will continue to show Months remaining
4. **User should discontinue use of the monitor at this time,** though monitor will continue to detect gas.
5. If unit battery has REACHED its end of life, a Low Battery alarm will activate:
   a. Audible horn will sound. Pressing "TEST" will silence this alarm.
   b. LEDs flash.
   c. Low battery indicator flashes.
   d. Display will show "ERR".
6. **User must discontinue use of monitor immediately. Unit is no longer detecting gas.**

Drager Pac 3500 (H_2S – Hydrogen Sulfide) User Instructions

Activating new device:

4. Press (+) button for 3 seconds. The display will show a countdown (3-2-1). The device usable life has now started, and display will show "H2S". Verify correct gas is shown.
5. After 10 seconds, the display will shut off. Press (+) button to show remaining time in days of unit's useful life. After 10 seconds of no activity, display will turn off.
6. Upon initial activation, the sensor requires a 15-minute "warm-up" period before measurement can occur. For all future uses, the sensors are ready for measurement immediately upon startup.

Daily Usage:

8. Press and hold (OK) button. Display will count down 3-2-1 to startup.
9. Device will perform self-test. Verify display and alarm settings are operating:
   a. LED lights will flash. Audible alarm and vibrator will activate.
10. Display will show software version and gas monitored.
11. The number of days of remaining operation will be shown.

12. Alarm thresholds will display.
    a. A “low” alarm threshold is set to 10 ppm, the “A1” setting.
    b. A “high” alarm threshold is set to 20 ppm, the “A2” setting.
13. A fresh air calibration can be performed by pressing (OK) while gas value is flashing immediately following alarm settings display. To perform fresh air calibration, ensure unit is removed to fresh air and from all possible sources of H2S.
14. If no key is pressed while display flashes, fresh air calibration is skipped and device automatically enters measurement mode. Measured gas concentration will be displayed.

Gas Detection:

2. If alarm thresholds are exceeded, unit will enter alarm mode. ***Upon alarm, evacuate area immediately.***
    a. LED lights will flash, audible alarm will sound, and vibration will activate.
    b. A1 threshold alarms flash and sound in a single repeating tone.
        i. A1 (low) alarm can be acknowledged by pressing (OK). This will silence the alarm.
    c. A2 threshold alarms flash and sound in a double repeating tone.
        i. A2 (high) alarms cannot be silenced. The alarm will stop once the concentration of H2S falls below the alarm set level of 20ppm, and the user then presses (OK).

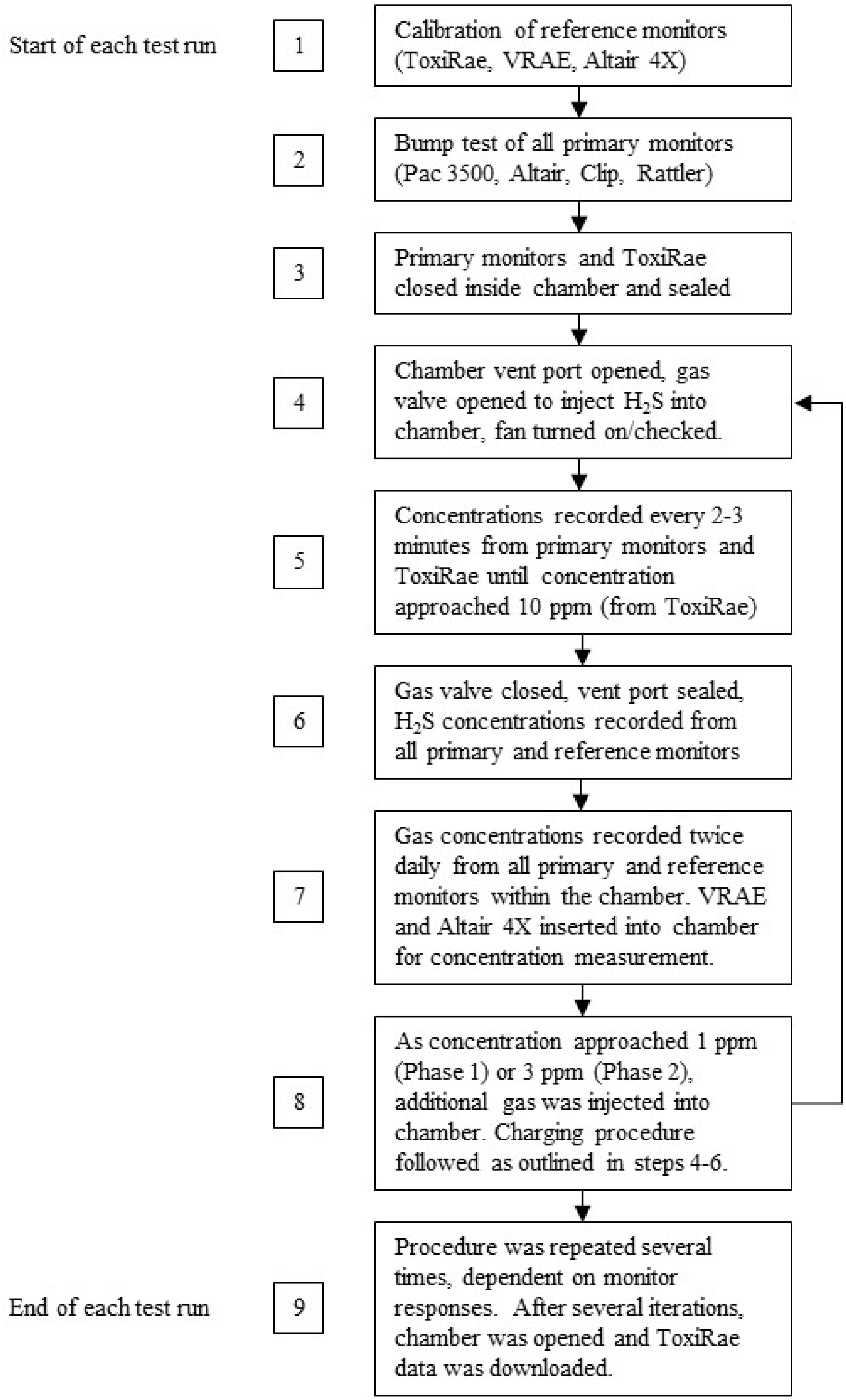
Battery Change:

2. The battery for the monitor may require changing prior to the 2 year life of the unit.
    a. A low battery icon will flash on the screen and audible alarm will sound when battery gets low. The battery will continue to power the unit for 1 – 7 days depending on external temperature. ***Change battery immediately.***
    b. Turn device off and unscrew 4 screws from back of unit.
    c. Remove battery and replace with similar Lithium 3V battery.
    d. Replace cover and screws. Monitor will require a 15-minute warm up time for sensor once new batteries are installed.

End of Usable Life:

3. A warning period will begin prior to the end of the device’s usable life. This will be shown by the remaining time flashing just after turning device on with a number and then “d” to indicate the number of days remaining. (For example, “30” and then “d” means 30 days remain.)
4. Once the usable life has expired, “0” “d” will flash and the monitor will no longer measure gas. ***At this time (or earlier), discontinue use of the monitor and replace the unit.***

APPENDIX B: EXPERIMENTAL PROCEDURE



APPENDIX C: EXPERIMENTAL PHOTOS

Photos were taken to document procedures and notable events throughout the study.

Figure C1. Close view of internal chamber between runs, with chamber door open.

Figure C2. Upon initial charging of chamber during Run 7 (on equivalent barn day 64), the chamber was filled to a concentration of 10.5 ppm H_2S, according to the ToxiRae inside. In response, the secondary Altair went into low alarm mode, but the primary Altair did not respond. This was the first alarm discrepancy observed between the two monitors.

Figure C3. Activated simultaneously, the BW Clip on the left was the primary and on the right was the secondary monitor, which was stored within the hibernation chamber during the study. This photo shows the difference in countdown of 'months remaining' on the monitors' displays. The hibernation case had extended the life of the secondary by 3 months at this point in the study.

APPENDIX D: RAW SUPPORTING DATA

Table D1. Summary of test run timelines.

Run	Start Date	Start Time	End Date	End Time	Minutes	Gap min after	Total min at start of run	Avg Conc	"Barn Days" Cumulative
1	3/1/2016	11:32:55 PM	3/7/2016	6:41:55 PM	8350	1451	0	3.20	18
2	3/8/2016	6:53:52 PM	3/11/2016	5:24:52 PM	4232	3086	9801	3.84	30
3	3/13/2016	8:51:59 PM	3/16/2016	10:18:59 AM	3688	11256	17119	2.43	36
4	3/24/2016	5:55:51 PM	3/27/2016	4:41:51 PM	4247	3113	32063	3.33	46
5	3/29/2016	8:34:10 PM	4/2/2016	11:01:10 AM	5188	79	39423	2.95	56
6	4/2/2016	12:21:53 PM	4/4/2016	5:13:53 PM	3173	62	44690	3.63	64
7	4/4/2016	6:16:35 PM	4/7/2016	7:17:35 PM	4382	1349	47925	4.47	78
8	4/8/2016	5:47:43 PM	4/11/2016	5:24:43 PM	4298	3018	53656	3.44	88
9	4/13/2016	7:43:24 PM	4/17/2016	10:57:24 AM	5235	617	60972	2.73	98
10	4/17/2016	9:15:51 PM	4/19/2016	11:43:51 PM	3029	43	66824	3.89	106
11	4/20/2016	12:28:24 AM	4/22/2016	11:10:24 AM	3523	2194	69896	3.89	115
12	4/23/2016	11:45:20 PM	4/26/2016	6:22:20 PM	3998	8807	75613	3.61	125
13	5/2/2016	9:11:07 PM	5/6/2016	5:13:07 PM	5523	24	88418	3.57	139
14	5/6/2016	5:38:49 PM	5/10/2016	8:28:48 PM	5931	36	93965	3.79	155
15	5/10/2016	9:05:29 PM	5/14/2016	10:52:29 AM	5148	470	99932	3.59	167
16	5/14/2016	6:43:50 PM	5/19/2016	7:15:50 AM	6513	702	105550	3.99	185
17	5/19/2016	6:58:36 PM	5/21/2016	10:37:36 PM	3100	12485	112765	4.03	194
18	5/30/2016	2:43:36 PM	6/1/2016	9:58:36 PM	3316	5282	128350	4.04	203
19	6/5/2016	2:01:04 PM	6/9/2016	7:58:04 AM	5398	601	136948	3.29	216
20	6/9/2016	6:02:22 PM	6/15/2016	3:32:22 PM	8490	8135	142947	4.65	243
21	6/21/2016	7:08:46 AM	6/28/2016	6:48:46 AM	10061	12	159572	4.39	273
22	6/28/2016	7:06:45 AM	6/30/2016	10:41:18 PM	3816	20	169645	5.91	289
23	6/30/2016	11:02:39 PM	7/6/2016	9:04:39 PM	8523	149	173481	6.02	324
24	7/6/2016	11:34:12 PM	7/15/2016	7:21:12 AM	11988		182153	5.91	373

Table D2 shows bump test results for the monitors that displayed quantitative concentration measurements. The BW Clip RT was released by the manufacturer after the study began and was added later, so the equivalent barn days (EBD) were calculated separately, shown in the right column.

Table D2. Bump test results for quantitative monitors.

Date	Time	Barn Day	ToxiRae	Pac 3500	Rattler	BW Clip RT	BW Clip RT EBD
3/13/2016	2100	29.68	24.2	16.6	21		
3/24/2016	1630	35.88	20.3	19	25		
3/29/2016	2000	45.63	19.6	17.4	25		
4/2/2016	1200	56.23	20.3	16.4	23		
4/4/2016	1800	64.18	19.4	18.6	22		
4/8/2016	1730	77.72	19.4	17.4	22		
4/13/2016	1700	87.94	18.6	17	23		
4/17/2016	2030	97.82	19.2	16.8	23		
4/19/2016	2355	105.97	20.7	16.6	22		
4/23/2016	2300	115.44	21.5	16.8	22		
5/2/2016	2100	125.42	21.6	17	23		
5/6/2016	1715	139.05	18.8	16.2	23		
5/10/2016	2040	154.58	19	16	22		
5/14/2016	1810	167.37	19.4	16	22	20	0
5/19/2016	705	185.35	20.1	16.2	22	19	17.98
5/30/2016	1415	193.97	21.3	17.2	21	20	26.61
6/5/2016	1335	203.22	20.4	17	19		
6/9/2016	1725	215.48	19.4	16.2	22	19	48.12
6/21/2016	640	242.53	20.6	16.6	22	19	75.17
6/28/2016	630	273.03	18.5	15.8	21	19	105.67
7/6/2016	2245	288.62	19.5	15.2	23	18	121.26
7/25/2016	1945	373.04		16.6	21	19	205.67

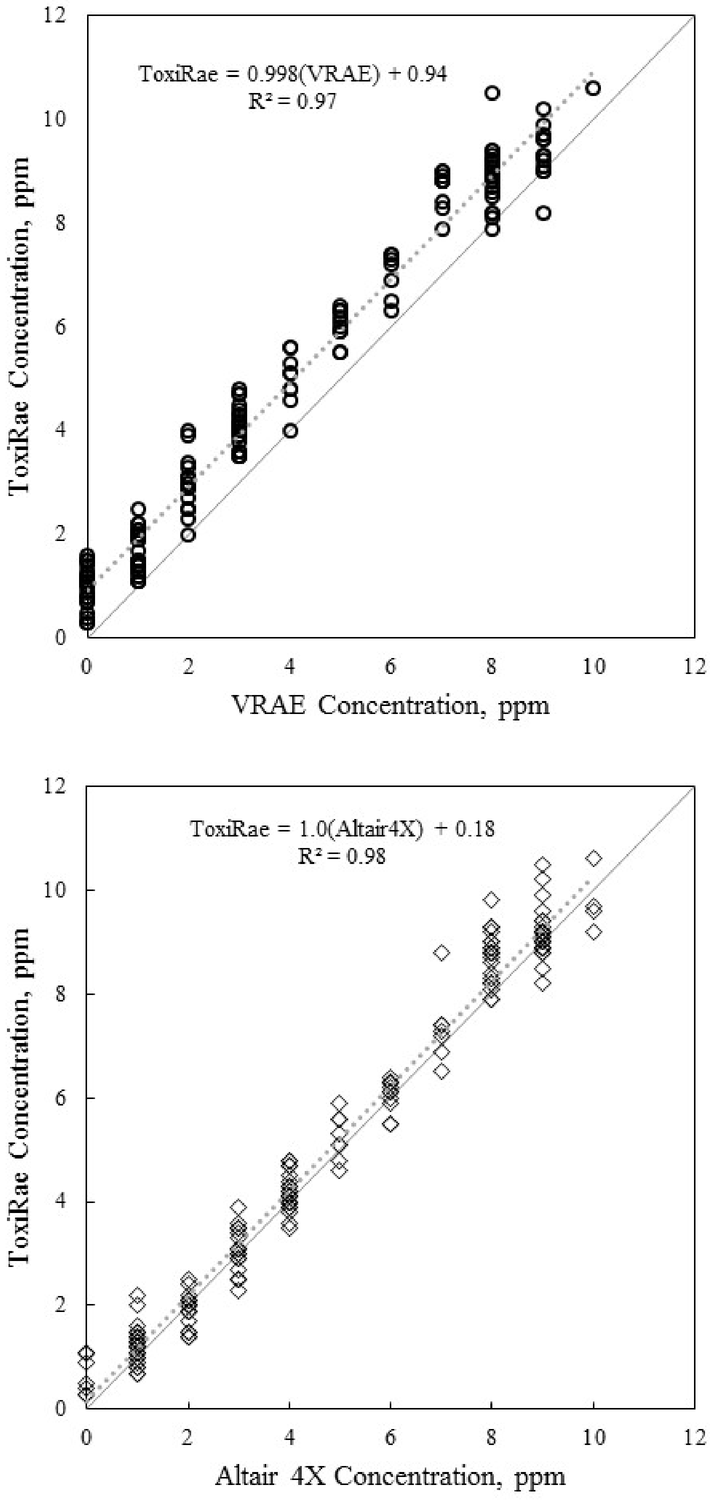


Figure D1. Results of concentration checks for comparison between ToxiRae (inside chamber continuously) and VRAE and Altair 4X (maintained outside of the chamber). All monitors were calibrated between each test run, and all monitors were shown to provide consistent measurements of concentration throughout testing. No sensor drift was noted for the ToxiRae.

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