

Passive monitors to measure hydrogen sulfide near concentrated animal feeding operations

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Hydrogen sulfide (H₂S) is one of many airborne pollutants emitted by concentrated animal feeding operations (CAFOs). However, few studies have characterized ambient H₂S levels near these facilities, largely due to the lack of low-cost, reliable, and easily transportable instrumentation available to researchers. We determined intermediate environmental H₂S exposure near CAFOs using Radiello passive monitors. First, a laboratory study was performed to determine the accuracy of the device. Next, a total of eight passive H₂S monitors were deployed bi-weekly in close proximity (<40 m) to a medium-sized swine confinement for seven months in order to determine the temporal and spatial variability of H₂S. Finally, we measured H₂S concentrations across two rural Iowa counties to characterize ambient exposure near thirteen CAFOs and two schools. The value of the temperature-adjusted H₂S passive diffusion rate provided by the supplier was 29% larger than the 24 h rate determined experimentally. Concentrations of H₂S measured near the medium-sized confinement were varied and ranged from 0.2 to 48.6 ppb depending on the sampling period and proximity to a lagoon on the property. Two-week concentrations near the schools were low (<1 ppb), while concentrations near the thirteen CAFOs ranged from 0.1 to 42.9 ppb. The passive monitors were effective in measuring H₂S concentrations near a swine CAFO as long as they were exposed for a sufficient period of time (two weeks). Radiello passive monitors are a promising new device in measuring intermediate H₂S exposure in rural populations. Measured values in excess of an Iowa state limit of 30 ppb (24 h average) suggest that enforcement actions are needed to mitigate H₂S migration from swine CAFOs.

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Environmental impact

During the last half century large concentrated animal feeding operations (CAFOs) have become the model of livestock production throughout the United States. CAFOs can produce high concentration of gasses, bio-aerosols, and other odorous compounds within the building. These contaminants are ventilated outdoors and potentially expose individuals living near these facilities. Epidemiological studies have consistently shown an increase in adverse respiratory symptoms among workers at CAFOs and surrounding residents. Due to the lack of low-cost sensitive instrumentation, few studies have characterized ambient exposure near these facilities. In this study we determined the effectiveness of using Radiello passive monitors to measure hydrogen sulfide, a surrogate measurement compound for a host of extremely odorous vapors, near CAFOs.

Introduction

Modern swine concentrated animal feeding operations (CAFOs) typically house more than 2000 head in a single facility.^{1,2} High animal density coupled with reduced air exchanges can produce high concentration of gasses, bio-aerosols, and other odorous compounds within the building.³ These contaminants are ventilated outdoors and potentially expose individuals living near these facilities to dangerous pollutants. Community-based studies have found that individuals living or going to school

near CAFOs have an increased prevalence of asthma, wheeze, and upper respiratory tract irritation.^{4–8} However, these studies relied on distance from the CAFO as a surrogate for exposure and did not include quantitative measurements. The availability of low-cost, precise samplers may allow researchers to better evaluate the relationship between environmental exposure to CAFOs and adverse health outcomes.

CAFOs generally store waste in pits underneath the confinement and/or in lagoons adjacent to the facility. Waste slurry is stored in these structures until it can be pumped out and applied to the nearby fields as fertilizer or hauled away. While in the pit, this slurry undergoes anaerobic fermentation which can produce high concentrations of noxious gasses. One gas of concern is hydrogen sulfide (H₂S), a poisonous, colorless gas with a distinct rotten egg smell.⁶ The odor threshold of H₂S is low and can be

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detected in the 10–300 ppb range.⁹ The amount of H₂S emitted from a CAFO is variable and dependent on numerous factors including type of animal feed, animal weight, manure management system, ventilation system, and ambient temperature.^{10,11} H₂S concentrations can approach 1000 ppb in air exhausted from pit fans¹⁰ but decreases exponentially, with measured mean concentrations of 3.2 ppb 30 m downwind from a confinement³ and generally below 2 ppb in areas with intensive hog production.¹² H₂S is also a surrogate measurement compound for a host of extremely odorous vapors arising from hog manure slurry.¹

Acute exposure to high concentrations of H₂S (>500 ppm) can cause loss of consciousness and death.¹³ Occupationally, H₂S is the second leading cause of fatality by gas inhalation.⁹ Epidemiological studies have shown a variety of adverse health outcomes to individuals environmentally exposed to low levels of H₂S (<100 ppb) including dyspnea, nasal irritation, exacerbation of asthma, and increased hospital visits for various respiratory complaints.^{14–16} Due to health effects related to environmental exposure to H₂S various states have begun to enact standards for livestock facilities including Iowa, California, Minnesota, Missouri, and Nebraska.^{1,3,17} The Agency for Toxic Substances and Disease Registry (ATSDR) lists a minimum risk level (no adverse health effect) of 70 ppb for an acute exposure (1–14 days) and 20 ppb for an intermediate exposure (15–364 days).¹³

Although there is the potential for H₂S exposure from swine CAFOs to surrounding residents, there are still only a small number of published studies with quantitative exposure measurements. This paucity of data is the result of limited instrumentation with a high analytical sensitivity (<100 ppb). H₂S direct reading instruments have a high initial startup cost, need a constant source of power, and need to be calibrated frequently.¹⁸ Since CAFOs are typically located near agricultural fields, the availability of power sources near the facilities can be limited. Furthermore, CAFOs can include multiple buildings that together span hundreds of meters in width and length, making multiple receptors cost prohibitive.

Passive monitors are a promising alternative to direct reading instruments. Passive gas monitors operate according to Fick's first law of diffusion, which states that gaseous molecules move from areas of high concentration to low concentrations.¹⁹ Using this phenomenon, passive samplers are able to trap molecules onto an adsorbing matrix without the need for a pump. Radiello (Fondazione Salvatore Maugeri-IRCCS, Pavia, Italy) has produced a new generation of H₂S monitors with a larger sampling rate due to a radial design. Unlike passive badges, the Radiello monitor has a larger surface area and allows for adsorption of H₂S throughout the 360° diffusive body. According to the manufacturer, these monitors have greater sensitivity, which allows for deployments in environmental settings where concentrations are generally low.²⁰

This study had three objectives. First, to assess the accuracy of Radiello passive monitors by exposing the monitors to known concentrations of H₂S during a laboratory study; second, to determine the effectiveness of using the monitors to measure ambient H₂S near a single swine CAFO over an extended period of time (7 months); and finally, to characterize H₂S exposure at multiple receptors across an area with a large number of CAFOs.

Material and methods

Radiello passive monitors

The passive monitor is comprised of three components: the adsorbent cartridge, diffusive body, and support plate. A white micro-porous high-density polyethylene diffusive body with radial design (6.0 cm high × 1.6 cm dia.) is attached at one end to a polycarbonate supporting plate (Fig. 1). Prior to mounting on the plate, a 60 mm × 5.8 mm dia. adsorbent cartridge is placed inside the diffusive body. The adsorbent cartridge is made of polyethylene impregnated with zinc acetate. When H₂S comes in contact with the zinc acetate, it is converted to stable zinc sulfide which is later extracted and assayed for sulfide ion. The H₂S adsorbent cartridge is a one-time use sampler, although the diffusive body and support plate can be used multiple times.²⁰

According to the manufacturer's instructions, the sampling rate (Q) of the adsorbent cartridge at 25 °C is 0.096 ng ppb⁻¹ min⁻¹ which is invariant in humidity ranges of 10–90% and wind speeds between 0.1 and 10 m s⁻¹. Using eqn (1), supplied by the manufacturer, Q can be adjusted to varying temperatures. The recommended exposure duration is 1 hour to 15 days with a stated limit of detection of 30 ppb for 1 hour exposures and 1 ppb for 24 hour exposures.²⁰

$$Q = 0.096 \left(\frac{K}{298} \right)^{3.8} \quad (1)$$

where Q = sampling rate (ng ppb⁻¹ min⁻¹), 0.096 = manufacturer sampling rate, K = ambient temperature (°K).

The concentration (C) of H₂S, in parts per billion (ppb), can be determined using eqn (2), which factors in the mass of sulfide adsorbed onto the cartridge (m), Q adjusted for the ambient temperature, and exposure time (t).²⁰

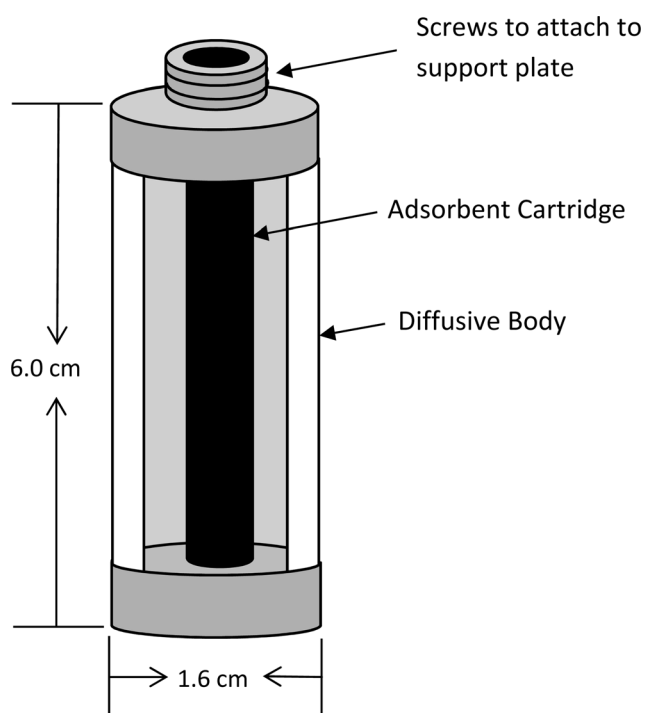


Fig. 1 Radiello passive diagram schematic.

$$C = \frac{m}{Qt} 1000 \text{ ng } \mu\text{g}^{-1} \quad (2)$$

where C = concentration (ppb), m = mass of sulfide ion (μg), t = time (min).

Laboratory analysis

Sulfide was recovered from the cartridges according to the manufacturer's specified guidelines.²⁰ Immediately following exposure, the monitors were sealed in test tubes provided by the manufacturer. During analysis, cartridges were desorbed with 10 mL of de-ionized water followed by 0.5 mL of ferric-chloride-amine solution. After vortexing for 30 seconds, the samples were allowed to react for 30 minutes. Aliquots of the analyte were then transferred to a microplate and diluted three-fold.

H_2S samples were analyzed with a spectrophotometer (SpectraMax 384 Plus, Molecular Devices, Inc., Sunnyvale, CA) at an absorbance of 665 nm. A calibration curve was prepared for each analysis using methylene blue (Sigma-Aldrich, St. Louis, MO). All calibration curves had a $R^2 > 0.995$. Results obtained from the spectrophotometer were in $\mu\text{g mL}^{-1}$ of sulfide ion and the range of the method was 0.115–1.145 $\mu\text{g mL}^{-1}$. The analytical detection limit, determined by 3σ of the 11 field blank samples, was 0.030 $\mu\text{g mL}^{-1}$. The concentration of the sulfide ion was converted to mass by multiplying by the volume of de-ionized water (10 mL). H_2S concentration, in ppb, was calculated from adsorbed mass using eqn (2).

Calibration study

A calibration study was conducted to evaluate the sampling rate for the devices. Two certified H_2S gas cylinders (14.21 ppm and 15.31 ppm) with an accuracy of $\pm 5.0\%$ were used to prepare known concentrations inside a 2 L glass chamber. H_2S was diluted with compressed air that was passed through a HEPA filter and desiccant prior to entry into the chamber. The flow rates of H_2S and air were controlled using needle valves and indicated with rotameters. Flow rates were pre- and post-calibrated using a Gilibrator bubble flow meter (Gilian Instrument Corp, Wayne, NJ). Average H_2S chamber concentrations were determined from the pre- and post-calibration measurements.

H_2S and air were mixed inside the chamber using a baffled glass screen placed at the entry into the chamber, and passive monitors were placed directly downstream of the screen in order to ensure mixing of the gasses. The monitors were exposed to four concentrations ranging from 17 to 145 ppb. The majority of samples ($n = 14$) were exposed for 24 h, while single measurements were made at 48 and 72 h in the 35 ppb range. The concentrations determined from the passive monitors were compared to the metered concentrations. Laboratory conditions during each test were relatively stable with temperature ranging from 18 to 22 °C.

We conducted the laboratory experiments under the assumption H_2S was adsorbed onto the cartridge linearly and was not influenced by concentration or duration of exposure. Therefore, H_2S levels inside the chamber were intentionally set at high concentrations over a short time period to produce the

same mass absorbed as those obtained with low concentrations over a long time period. We used the manufacturer's temperature adjusted sampling rate to predict the total mass adsorbed at concentrations ranging from 17–145 ppb. At these concentrations approximately 2350–20 045 ng of sulfide is expected to be adsorb onto the cartridge. This range of mass is equivalent to a 14 day exposure (20 160 min) at concentrations of 1.24–10.35 ppb, which is the range we expected to find in the field.

Environmental monitoring

All monitors deployed during the field studies were placed under a plastic canopy to protect them from rain and snow and were attached to a fence post approximately 1.5 m off the ground. Ambient H_2S sampling was conducted in two separate phases. In Phase I, monitors were deployed outside a single swine finishing facility to determine the temporal and spatial variability of H_2S near a CAFO, as well as the duration required to consistently measure detectable levels of H_2S . Phase I occurred from April 2010 until October 2010 outside a single medium-sized CAFO. The facility was composed of two buildings; the south building was the larger of the two structures with roughly 1500 swine, while the smaller north building housed approximately 750 swine. The buildings each employed different types of manure management and ventilation systems. The naturally ventilated north building used a deep pit system, whereas the south building operated a shallow pit system and had natural and mechanical ventilation. Manure in the south building was scraped out of the pit daily while waste from the north building was emptied monthly. The manure from the buildings was emptied into a lagoon (64 m dia. \times 2.3 m deep) located approximately 15 m west of the structures. A home was located 72 m east of the CAFO.

A total of eight H_2S passive monitors were arranged in a grid approximately 50 m from each other and <40 m from the edge of the structures, with three monitors to the north, three to the south, one to the east, and one to the west of the structures. The selection of <40 m was to allow comparison with other studies and accommodate topographic and property characteristics. For the first two rounds of sampling cartridges were changed every 7 days; however, due to a large percentage of samples being below the limit of detection (LOD) sampling was increased to 14 days for the remaining sampling periods.

In Phase II, conducted from July to November 2011, H_2S monitors were deployed at the fence-line of 13 CAFOs and two schools in order to characterize intermediate environmental exposure to H_2S . Monitors were deployed and retrieved on the same day and within three hours of one another. CAFOs were selected based on permitted live weight and spatial distribution throughout the area. The monitors were positioned at the property fence-line generally within 50 m of the CAFO with two monitors positioned 100 m or further from the CAFO. We also sampled outside two schools that were located 195 m and 1930 m from the nearest permitted-CAFO.

Meteorological measurements

In Phase I of this study temperature (°C), wind speed (m s^{-1}), and wind direction were obtained from a field station located

Table 1 Metered vs. supplier's H₂S derived concentrations and calculated uptake rates

Sample ID	Exposure time (min)	Concentration of certified gas cylinder (ppm)	Metered concentration (ppb)	Supplier's concentration (ppb)	Percent difference (metered vs. supplier's)	Calculated uptake rate (ng ppb ⁻¹ min ⁻¹)
1	1484	15.31	145	112	−23%	0.070
2	1410	14.21	144	150	4%	0.095
3	1415	14.21	143	133	−7%	0.085
4	1435	14.21	142	123	−13%	0.079
5	1438	14.21	73	71	−2%	0.089
6	1444	14.21	73	69	−5%	0.087
7	1416	14.21	69	57	−17%	0.076
8	1571	15.31	37	27	−26%	0.067
9	2876	15.31	37	26	−31%	0.063
10	5762	15.31	36	33	−10%	0.082
11	1454	14.21	36	18	−50%	0.046
12	1445	14.21	34	25	−28%	0.066
13	1420	14.21	34	22	−36%	0.059
14	1410	14.21	18	3	−82%	0.016
15	1600	14.21	17	8	−56%	0.040
16	1440	14.21	17	4	−74%	0.024

Table 2 Summary of temperature, wind speed, and wind direction by sampling period for Phase I

Period	Dates sampled	Mean temperature (°C)	Mean wind speed (m s ⁻¹)	Predominant wind direction (blowing towards)
1	4/2/10–4/9/10	14	5.57	North
2	4/9/10–4/16/10	17	4.90	North
3	4/16/10–4/29/10	14	4.71	South
4	4/29/10–5/14/10	14	5.48	East
5	6/4/10–6/18/10	24	3.48	Northwest
6	6/23/10–7/7/10	25	3.70	North
7	7/7/10–7/21/10	27	3.05	North
8	7/21/10–8/4/10	28	3.22	North
9	8/12/10–8/25/10	23	3.01	North
10	8/25/10–9/8/10	21	3.83	North
11	9/8/10–9/22/10	20	3.77	North
12	9/22/10–10/6/10	16	3.85	South

approximately 40 km from the study area and hourly measurements were averaged over each sampling period (Table 2). The one- or two-week averaged temperature was applied to eqn (1) to determine the sampling rate for each period. From these data a wind rose was created from data averaged over the entire study using WRPLOT (Lakes Environmental, Waterloo, Ontario). In Phase II of the study temperature (°C) and wind speed (m s⁻¹) were obtained from a weather station within a 30 km radius of all samplers. Daily measurements were averaged over each sampling period. Two-week averaged temperature was applied to eqn (1) to determine the sampling rate for each period.

Statistical analysis

Statistical analysis was performed using SAS version 9.2. Normality of the H₂S measurements was assessed using the Kolmogorov–Smirnov statistic, and data were determined to be log-normally distributed. Since the amount of data that was left-censored was considered low, measurements below the LOD were substituted with the LOD/√2 (0.021 µg of sulfide).²¹

Because sampling rate is conditional on temperature, each sampling period in the field study had a unique H₂S concentration LOD. Descriptive statistics including range, geometric mean (GM), and geometric standard deviation (GSD) were determined.

Results

Calibration study

There was a strong correlation between metered H₂S concentrations (24 h exposure only) and measured H₂S concentrations ($r = 0.98$). However, in general, concentrations obtained from the manufacturer's specified equations significantly underestimated exposure ($p < 0.001$) by approximately 30% (Table 1). A secondary check of H₂S concentrations inside the exposure chamber was not performed because we are unaware of an H₂S sampling method with a higher accuracy than that obtained by diluting a certified span gas. The mean absolute percent difference between the pre- and post-calibrated metered H₂S was 2.7%.

Experimental sampling rates were determined by quantifying the mass of sulfide ion (ng) adsorbed onto the cartridge and dividing this value by the concentration of H₂S metered into the chamber (ppb) and the duration of exposure (min). The average 24 h experimental sampling rate was 0.064 ng ppb⁻¹ min⁻¹ which was significantly ($p < 0.001$) lower than the supplier's temperature adjusted sampling rate (0.091 ng ppb⁻¹ min⁻¹). At exposure concentrations above approximately 70 ppb there was only a -9% average difference between the supplier's and the experimentally derived sampling rate (0.083 ng ppb⁻¹ min⁻¹). At lower concentrations (≤ 37 ppb) there was a much greater difference (-50%) between these rates (0.045 ng ppb⁻¹ min⁻¹). Samples that were exposed to the lowest concentration of H₂S (≤ 18 ppb) had the lowest accuracy and sampling rate of the concentration ranges studied.

The effect of exposure duration on sampling rate was evaluated for a limited number of samples. Samples 8–10 were removed sequentially from the exposure chamber at 24, 48, and 96 h. The samples came from the same lot, analyzed using the same reagents, and H₂S concentration were produced from the same gas cylinder. At 96 h there was only a -10% difference between the specified and experimentally determined sampling rate; however, at 48 h the percent difference was -31% which was similar to percent difference at 24 h (-26%).

Phase I environmental monitoring

Over the seven-month sampling period, 96 measurements were taken at eight locations along the perimeter of the swine CAFO. The majority of samples were above the LOD, with only 3% of samples being left-censored. An additional 3 samples were lost due to lab error and 1 sample was damaged by high winds. At the beginning of the study we hypothesized that seven-days would be sufficient to consistently measure concentration above the LOD. However, sampling time was increased to 14 days after the second round of sampling when 38% of samples were below the LOD and 100% of the samples were below the range of the method. After the increase in sampling duration, none of the remaining samples were below the detection limit and only 12% were below the range of the method.

Summary data of concentrations by sample location are presented in Table 3. The range of concentrations spanned three orders of magnitude (supplier derived concentrations: 0.2–48.6 ppb) depending on location and period. The geometric

mean (GM) concentration measured at all locations at the facility was 2.4 ppb with a GSD of 3.5. Location 4, north of the lagoon, had the largest GM (9.6 ppb), while the smallest was at location 1 (0.9 ppb), west of the confinement building. In general, the variability of the measurements at each location was moderate, with five of the eight locations having a geometric standard deviation (GSD) less than 3.0. However, at location 5 the GSD was 4.7 indicating a large degree of variability between measurements.

The spatial variability in H₂S concentrations appears to be the result of regional wind patterns and proximity to the lagoon. During the months of April–October the dominant wind direction was from the south (Table 2). Based on this pattern, the facility was divided into two sections, upwind and downwind. Monitors at locations 2, 3, and 4 were designated downwind while locations 6, 7 and 8 were considered upwind. *t*-Tests were conducted on each pair of monitors (2 vs. 8; 3 vs. 7; and 4 vs. 6) and downwind concentrations were significantly higher ($p < 0.001$). H₂S concentrations also increased as proximity to the lagoon decreased. The average concentration at the monitor closest to the lagoon (location 5) was more than 8-times larger than the average level measured at the monitor farthest from the lagoon (location 1).

Phase II environmental monitoring

Table 4 contains summary data for Phase II of this study. H₂S was measured across fifteen locations ($n = 128$) for five months in Johnson County and Washington County, Iowa. Only 2% of the measurements were below the limit of detection. However, the majority of samples (78%) collected at the two schools were below the range of the method. The size of the CAFOs we studied was varied with a permitted live weight range of 21 722–487 158 kg and a mean of 164 950 kg.

Concentrations were generally small at the schools, with no measurements exceeding 1 ppb. Levels near the confinements were comparatively larger, with one location recording a maximum two-week concentration of 42.9 ppb. The CAFO at that location had the largest permitted weight of any facility sampled. Although two-week concentrations could be large at some sites, especially during certain periods, the mean concentration measured outside the thirteen CAFOs over the entire study period was 4.1 ppb.

Table 3 Descriptive statistics of H₂S measurements around a single CAFO during Phase I of the study

Location	Direction of the monitor relative to the CAFO	Distance of the monitor to the lagoon (m)	n (<LOD)	Range (ppb)	Mean (ppb)	GM (ppb)	GSD
1	West	120	11(1)	0.2–4.7	1.3	0.9	2.4
2	North	89	11(0)	0.6–8.1	3.6	2.7	2.5
3	North	61	11(0)	0.6–14.8	6.6	3.9	3.3
4	North	33	11(0)	0.9–47.2	15.6	9.6	3.4
5	East	17	12(0)	0.5–48.6	11.1	4.8	4.7
6	South	33	12(1)	0.2–5.3	2.4	1.8	2.4
7	South	64	12(0)	0.5–3.3	1.7	1.4	2.0
8	South	97	12(1)	0.2–4.0	1.3	1.0	2.0

Table 4 Range, geometric mean (GM), and geometric standard deviation (GSD) of H₂S measurements by sampler location

Facility	Distance to CAFO (m)	Permitted weight (kg)	<i>n</i> (<LOD)	Range (ppb)	Mean (ppb)	GM (ppb)	GSD
1	30	161 025	8(0)	1.3–11.6	4.8	3.8	2.1
2	195	n/a ^a	9(1)	0.1–0.8	0.5	0.4	1.8
3	1930	n/a ^a	9(1)	0.1–0.6	0.4	0.4	1.6
4	30	207 518	9(0)	2.1–12.4	4.7	4.2	1.7
5	40	152 407	9(1)	0.1–6.1	1.6	1.0	2.7
6	245	21 772	9(0)	2.0–5.2	3.2	3.1	1.4
7	35	152 407	9(0)	0.7–15.1	8.6	6.7	2.5
8	50	146 964	9(0)	1.3–10.6	6.0	5.1	1.9
9	50	146 964	9(0)	0.3–11.1	3.7	2.4	2.9
10	40	487 158	9(0)	0.8–42.9	6.7	2.4	3.6
11	30	163 293	9(1)	0.1–11.1	5.7	3.6	4.0
12	25	136 078	9(0)	0.4–2.6	0.9	0.8	1.7
13	100	134 717	5(0)	0.4–0.9	0.7	0.7	1.4
14	40	87 090	9(0)	1.9–7.0	4.8	4.3	1.6
15	25	146 964	7(0)	1.6–32.3	9.1	5.7	2.8

^a Samples collected at a school.

Discussion

One of the objectives of this study was to assess the accuracy of Radiello H₂S passive monitors when using the specified sampling rate. Results showed the 24 h exposed monitors consistently underestimated H₂S levels in the concentration range we studied. However, the accuracy of the monitors increased with increasing exposure concentrations and duration. Mason *et al.* (2011) assessed the accuracy and precision of H₂S Radiello monitors (*n* = 3) by exposing them for seven-days at low concentrations (2.1 ppb). Researchers observed only a –5% difference between the reference and passive monitor concentrations when using the specified sampling rate.²² This value is similar to the percent difference (–9%) observed in this study for monitors exposed at concentrations above 70 ppb for 24 hours.

A previous validation study had also found decreased sampling rates with short-term exposure durations. Experimental sampling rates for Radiello NO₂ passive monitors were 20–30% smaller than the specified rate when exposing the samplers to varying concentrations (73–293 ppb) of NO₂ for 24 hours.²³ However, when one monitor was exposed for 14 days to low concentrations (11.9 ppb) the experimental sampling rate was comparable to that specified by the manufacturer. Although more data are needed, accuracy of the monitors for non-volatile compounds may be dependent on mass accumulation on the cartridge as well as exposure duration. Since, we were unable to either validate or conclusively reject the specified sampling rate we decided to use the specified sampling rate in the environmental portion of this study. As a result of this, concentrations measured outside the confinements may be underestimated, especially in samples outside the range of the method.

Results from the calibration study showed Radiello H₂S monitors would not be sufficiently sensitive or accurate to measure short-term exposures to low H₂S concentrations (<10 ppb). According to the manufacturer, the monitor will measure H₂S concentrations as small as 1 ppb over a 24 hour period.

However, using the calibration protocol provided by the manufacturer and the sampling rate determined experimentally, concentrations need to exceed 17.7 ppb over 24 hours for a measurement above range of the method. Researchers considering these devices should understand these limitations and determine expected concentrations prior to deployment. Additionally, according to the manufacturer, the sampling rate decreases with decreasing temperature. Therefore, any studies using H₂S monitors outside hog CAFOs in the wintertime need to account for the decreased sampling rate. It is also not clear whether these devices, at this deployment interval, would be useful at distances greater than 40 m, where H₂S concentrations are anticipated to be smaller than those measured here. Future studies, also need to consider prevailing wind direction when deciding where to position the monitors.

The monitors performed as expected in the field. In Phase I of the study, all downwind monitors recorded significantly larger H₂S concentrations than upwind and there was an increase in H₂S concentrations as sampler distance to the lagoon decreased. Downwind H₂S concentrations measured in this study were on the same order of magnitude as measurements previously recorded outside a swine confinement at a similar sampling distance. Thorne *et al.* (2009) sampled a medium sized confinement (<5000 swine), without a lagoon, at 10 different occasions over a 15 month period. A direct reading instrument, stationed 30 m downwind from the confinement recorded a geometric mean concentration of 3.2 ppb.³ This is similar to the geometric mean value recorded at location 2 (2.7 ppb) and 3 (3.9 ppb), which were downwind from the CAFO, but away from the lagoon.

The monitors performed well against a large range of environmental conditions and only one of 216 samples was lost due to meteorological factors. Unlike direct reading instruments, the passive monitors required no on-site calibration and could be deployed for weeks at a time. Laboratory assay of the samples was straightforward and required only minor training. When evaluating the cost and benefits of passive monitors *versus*

direct reading instruments, one must consider the variety of reagents, laboratory equipment, and training that goes along with analysis, not just the devices themselves.

Mean H₂S levels measured at the schools (Phase II) and away from the lagoon (Phase I) were relatively small (~1 ppb) and would not represent a chronic health risk. The ATSDR has developed minimum risk levels (MRLs) for contaminants commonly found at superfund sites. Although these levels are not enforceable, they are useful in evaluating the potential risk to populations exposed to contaminants. In its 2006 Toxicological Profile, ATSDR determined the MRL for an intermediate exposure (>14 days to 365 days) to H₂S to be 20 ppb in order to protect against adverse respiratory health.¹³ All measured concentrations at the two schools in our study were an order of magnitude smaller throughout the entire study.

In order to protect residents living near CAFOs, The Iowa Department of Natural Resources has established a H₂S standard of 30 ppb at the required set-back distance. This concentration is a one-hour time weighed average and cannot be exceeded more than seven times per year without prior notification. In Phase II of this study, we measured two-week concentrations above 30 ppb at the fence line at two different confinements. This suggests that there were multiple exceedences of the 1 h standard during the 24 h sampling period. Further research is needed to establish methods to mitigate H₂S exposure to residents living near these facilities and greater enforcement action is needed to ensure compliance with the standards.

When evaluating potential adverse health effects from CAFOs it is important to consider all contaminants emitted by these facilities, not just H₂S. While it is difficult to predict accurate concentrations of various contaminants based on only one measured pollutant, relationships between them can be assessed from previous studies. Ammonia concentrations measured inside a hog finishing facility were approximately an order of magnitude larger than H₂S levels during winter, spring, and fall, and almost two orders of magnitude larger during the summer months.¹⁰ Another study found ammonia emissions 3 to 4 orders of magnitude larger than H₂S emissions from a swine lagoon.²⁴ In addition to ammonia, bio-aerosols are also a concern outside these facilities. Measured downwind concentrations of endotoxin were found to be 59.5 EU m⁻³, while H₂S concentrations averaged 3.2 ppb 30 m downwind from a confinement.³ These findings show that epidemiological studies which use quantitative data to evaluate health effects need to consider numerous contaminants when evaluating potential adverse health effects, which were beyond the scope of this study.

This study had several limitations. First most monitors in the calibration study were exposed for 24 hours, while monitors in the field were exposed for 7–14 days. Concentrations measured at the CAFO could be inaccurate if H₂S mass does not accumulate linearly over time. Second, the known concentrations produced inside the chamber generally exceeded upwind levels recorded in the field study. Third, the effect of temperature and humidity on sampling rate was not evaluated in this study. Sampling was conducted from the spring through fall, and ambient temperatures fluctuated considerably over the

study, however only a single temperature value could be applied to eqn (1). According to the manufacturer, temperature has a large influence on sampling rate and not evaluating this experimentally may have limited the results. Humidity and wind speed averaged over each sampling period were within the manufacturer's specifications, but their effects on the sampling rate were not validated. Fourth, neither a direct reading instrument nor active sorbent tubes were used to evaluate the accuracy of the monitors in the chamber or in field studies. Finally, this study did not allow for evaluation of lot differences. Future studies need to take into consideration these limitations in order to validate these monitors.

Conclusions

Radiello passive monitors can be used effectively to measure intermediate H₂S concentrations in close proximity to swine CAFOs. We found a significant difference between the 24 h experimentally derived sampling rate and the specified sampling rate. Further laboratory validation is still needed to determine if H₂S is absorbed onto the cartridge linearly as time increases. H₂S exposure outside some of the CAFOs exceeded legal limits but two-week concentrations measured outside the schools rarely exceeded 1 ppb. Concentrations of H₂S near CAFOs can vary an order of magnitude depending on wind direction and proximity to the source. Compared to direct reading instruments, passive monitors were inexpensive and could be deployed with minimal maintenance in rural settings.

Conflicts of interest

The authors declare no conflict of interest.

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