Hydrogen Sulfide Gas Emissions during Disturbance and Removal of Stored Spent Mushroom Compost

B. Velusami, T. P. Curran, H. M. Grogan

ABSTRACT. Spent mushroom compost (SMC) is a by-product of the mushroom industry that is used as an agricultural fertilizer. In Europe, SMC storage and use are governed by EU Nitrates Directive 91/676/EEC to protect waterways against pollution by nitrates. A health and safety risk was identified during the removal of stored SMC for land application, as the stored SMC released high levels of toxic H_2S gas into the atmosphere when disturbed. In this study, emissions of H₂S were monitored at two outdoor and two indoor locations where stored SMC was being removed for land application. A repeating peaktrough pattern of $H_{2}S$ emissions was detected at all sites, with peaks corresponding to periods of active disturbance of SMC. The highest H_2S concentrations (10 s average) detected at the SMC face were, respectively, 680 and 2083 ppm at outdoor sites 1 and 2, and 687 and 89 ppm at indoor sites 3 and 4. Higher concentrations of H_2S were released from older SMC compared to newer material. Indoor-stored SMC had lower moisture content (53% to 65%) compared to outdoor-stored material (66% to 72%), while the temperature of indoor-stored SMC was higher (33°C to 51°C) compared to outdoorstored material (24°C to 36°C). The current short-term exposure limit (STEL) of 10 ppm was exceeded at all sites except site 4, which was smaller than the other sites, indicating a significant health and safety risk associated with working in the vicinity of stored SMC when it is being actively disturbed. Results suggest that SMC stored under cover in small heaps (600 m³) emits less H_2S during disturbance and removal compared to SMC stored outdoors in large heaps (>1500 m^3). This should be taken into consideration in the design, construction, and management of SMC storage facilities. Health and safety protocols should be in place at SMC storage facilities to cover the risks of exposure to toxic H_2S gas during disturbance of stored SMC.

Keywords. Compost storage, Gas emission, Health and safety, Hydrogen sulfide, Spent mushroom compost.

Spent mushroom compost (SMC) is a by-product of the mushroom industry that is used as an organic fertilizer for agriculture. In Europe, SMC storage and use are governed by EU Nitrates Directive 91/676/EEC to protect waterways against pollution by nitrates. In Ireland, the Nitrates Directive is implemented through Statutory Instruments (SI), the most recent of which is SI No. 610 of 2010 (DOE, 2010), otherwise

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known as the Nitrates Regulations. This directive prohibits SMC application to land for 13 to 16 weeks from October to January; therefore, SMC must be stored during this period. Under earlier regulations, SI No. 378 of 2006 (DOE, 2006), the provision and management of storage facilities for organic fertilizers, such as SMC, were specified; they had to be "designed, sited, constructed, maintained, and managed so as to prevent runoff or seepage, directly or indirectly, into groundwater or surface water" of "specified substances," especially nitrogen and phosphorus. This requires concrete platforms with retaining walls, covered or uncovered, and if uncovered with underground storage tanks to collect runoff. The size of facilities had to be large enough to contain all the SMC generated during the "closed" 13 to 16 week winter period plus additional capacity in case adverse weather or conditions prevented land application as planned. In reality, SMC can be stored for up to 8 to 12 months, depending on the timing of its planned application to agricultural land.

In 2005, a fatality due to hydrogen sulfide (H₂S) gas poisoning occurred during the removal of stored SMC for application on nearby farmland (HSA, 2006; Khan, 2006). SMC that had been stored for several months was identified as the source of the H₂S. The fatality highlighted a heretofore unknown health risk for those working with SMC and identified a gap in our knowledge concerning H₂S emissions into the atmosphere from stored SMC. There was no information on H₂S emissions from stored SMC or what effect different types of storage would have on such emissions. This work was undertaken to address this gap in knowledge.

H₂S is a toxic gas that has a characteristic odor of rotten eggs at low concentrations. It is produced as a result of the anaerobic decomposition of sulfur-containing organic matter (Costigan, 2003). Its occurrence in confined spaces such as sewers and underground storage containers for solid-liquid animal manure (slurry) is well documented (Hooser et al., 2000; Chénard et al., 2003; Lenehan and Frost, 2005; Scully et al., 2007; Kim et al., 2008). Agitation of slurry prior to its removal from underground storage containers releases H_2S gas to the atmosphere. This results in a rapid increase in H_2S concentration in the animal housing facility above, which can result in fatalities of both livestock and personnel (Donham et al., 1988; Hooser et al., 2000; WorkSafeBC, 2010). A single exposure to H_2S gas in the region of 1,000 ppm can cause respiratory paralysis and death within a few minutes (Beauchamp et al., 1984; Costigan, 2003; Nikkanen and Burns, 2004; SCOEL, 2007). Deaths of animals and farm staff exposed to high concentrations of H₂S during the agitation of manure in animal housing facilities have been reported in the swine, poultry, and cattle industries (NIOSH, 1990; ASAE Standards, 1992; Shepherd, 1999; Hooser et al., 2000). In addition, there are cases of further H_2S toxicity and death of those who attempt to rescue coworkers in difficulty (Snyder et al., 1995; Hendrickson et al., 2004).

Mushroom compost is initially produced from wheat straw, poultry and/or horse manure, gypsum, nitrogen supplements, and water (Maher et al., 1993; Beyer, 2003). It goes through a process of mixing, high-temperature composting, pasteurization, inoculation with a pure mushroom culture, incubation, and finally mushroom production. At the end of the crop, the compost may be treated with steam to eradicate diseases before its removal and disposal, while other growers dispose of it without steaming. At this stage, the compost is known as "spent mushroom compost" or SMC (alternatively "spent mushroom substrate" or SMS), and it still has nutritional value (Maher et al., 1993; Mullen and McMahon, 2001). It is suitable as a natural organic fertilizer and soil amendment for ag-

Journal of Agricultural Safety and Health

riculture and horticulture (Fidanza et al., 2010), and it is frequently used as a soil conditioner and fertilizer for tillage crops and grasslands (Rynker, 2002). Roughly 180,000 tonnes of mushroom compost per year are used by the mushroom industry in Ireland (Teagasc, personal communication), which results in a similar quantity of SMC being generated. It is generally stored in large or small heaps, either indoors or outdoors, for periods of up to a year until it is used for land application.

In a preliminary study, 1 min average H_2S concentrations of 80 ppm (indoor) and >250 ppm (outdoor) were detected above the face of stored SMC during its removal for land application (Grogan et al., 2008). This confirmed that there was an H_2S health and safety risk for those working in the vicinity of stored SMC, particularly while it was being disturbed, and that indoor storage might be safer than outdoor storage. Occupational exposure limits (OELs) are an important regulatory instrument used to protect employees from the adverse effects of chemical exposure in the workplace (Topping, 2001; Schenk et al., 2008). In Europe, the time-weighted average (TWA) and short-term exposure limit (STEL) are used to identify safe working conditions for employees. The TWA for H_2S is currently 5 ppm for a conventional 8 h day and 40 h week, and the STEL is 10 ppm for a period of 15 min, for no more than four times per day. Exposure to H_2S within these limits should not cause adverse effects (HSE, 2005; EC, 2009; HSA, 2010).

The objective of this work was to quantify and characterize H_2S emissions into the atmosphere during the disturbance and removal of stored SMC of different ages and at different storage facilities. A second objective was to monitor H_2S levels in the human-occupied zone that SMC operators are exposed to (inside and outside tractor cabs, and at the periphery of SMC storage facilities) with a view to developing health and safety guidelines for this activity; that work will be reported separately.

Materials and Methods

SMC Storage Sites

Four SMC sites (fig. 1) were visited between February 2008 and October 2009. Two were uncovered outdoor sites (sites 1 and 2), and two were indoor sites under cover (sites 3 and 4). All four sites consisted of concrete platforms with retaining walls 2 to 2.5 m high. Site 1 (figs. 1a and 1b) had two retaining side walls, while the other sites had retaining walls on three sides. SMC at the outdoor sites was left uncovered and exposed to rainfall. The indoor sites (figs. 1e and 1f) were covered with an apex roof structure mounted on steel supports to produce a continuous opening above the retaining walls.

SMC storage conditions are summarized in table 1. SMC was stored from back to front at sites 1, 3, and 4, with older material at the back and newer material at the front. At site 2, SMC was stored in discrete heaps of different ages (figs. 1c and 1d), and runoff water was collected in an underground storage tank. Sites 1, 2, and 3 are considered "large" SMC storage facilities with a capacity of >1500 m³, while site 4 is a "small" storage facility with a capacity of about 600 m³.

The SMC at all four sites originated from two mushroom compost facilities that produce a similar type of compost based on wheat straw, poultry manure, and gypsum. One composter uses a small amount of horse manure when available. Sites 1 and 3 had compost from one supplier, while sites 2 and 4 had compost predominantly from the second supplier. Both composters produce and deliver compost on a weekly basis, so the SMC in storage would reflect any natural variations in compost from each supplier during the

19(4): 261-275



Figure 1. Schematic diagrams (overhead views) and images of SMC storage areas (not to scale): (a) site 1 during visit 1 in 2008, (b) site 1 during visit 2 in 2009, (c) site 2 during visit 1 in 2008, (d) site 2 during visit 2 in 2009, (e) site 3 during 2009, and (f) site 4 during 2009.

year. The analysis of fresh SMC taken from all four sites at the time of H_2S measurements is as follows (range of averages across the sites): pH 6.4 to 7.9, bulk density = 418 to 518 kg m⁻³, ash content = 28% to 37%, total N = 22 to 28 g kg⁻¹, total P = 6 to 7 g kg⁻¹, total K = 6 to 28 g kg⁻¹, and total S = 39 to 60 g kg⁻¹.

Journal of Agricultural Safety and Health

Table 1. Summary of SMC storage conditions.							
Site and		SMC Age	SMC Heap Size $L \times W \times H^{[a]}$	Weekly Delivery			
Location	SMC Storage Duration	(months)	(m)	(tonnes)			
1 (Outdoor)	Visit 1: Sept. 2007 to Feb. 2008	Up to 6	$30 \times 18 \times 2.8$	45 to 60			
	Visit 2: July 2008 to Feb. 2009	Up to 8	$47 \times 18 \times 3$				
2 (Outdoor)	Visit 1: Sept. 2007 to Aug. 2008	Up to 12	$43 \times 36 \times 3.5^{[b]}$	35 to 45			
	Visit 2: Feb. to Sept. 2009	Up to 8					
3 (Indoor)	Visit 1: May to Oct. 2009	Up to 6	$32 \times 18 \times 3.5$	80 to 120			
4 (Indoor)	Visit 1: Nov. 2008 to Oct. 2009	Up to 12	$16 \times 12 \times 3.4$	20 to 23			

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^[a] H = height of the SMC heap at the highest point.

^[b] SMC was stored in smaller heaps within the large storage area (see figs. 1c and 1d).

SMC Removal Process

SMC was removed from the storage areas using a tractor with a standard closed cab and front-end loader. At sites 1, 3, and 4, SMC was filled into a Jeantil EVR 18-14 or Jeantil EVR 14-11 manure spreader with vertical beaters (www.jeantil.com). The manure spreader was then driven to the fields, where the SMC was applied at a rate of approximately 10 to 12 tonnes per hectare. It took approximately 5 min to fill the spreader and 10 to 15 min to apply the SMC on nearby land. At sites 1 and 4, the loader operator filled the spreader first and then drove the spreader to the field. During visit 2 at site 1, SMC was removed from older to newer material. At site 3, one front-end loader and three spreaders were used during SMC removal, each with a dedicated driver, so the SMC removal operation was almost continuous. At sites 1, 3, and 4, from 6 to 42 combined loading and spreading operations were monitored during periods of up to 8 h. At site 2, the SMC was being turned to facilitate degradation and was not loaded into a trailer for removal. During the turning operations at site 2, the operator worked at the SMC heaps for periods of approximately 1.5 h at a time.

H₂S Monitoring during SMC Removal

ORAE II, EntryRAE, ORAE+ (www.raesystems.eu), and ITX (www.indsci.com) gas monitors with data loggers were used over the course of these studies. The sensors have low cross-sensitivity to other compounds, as outlined in the manufacturers' literature available on their websites. The H₂S concentrations detected by the different monitors were accurate up to 100, 250, 500, and 999 ppm, respectively, with resolution of 0.1 or 1 ppm. The H_2S gas concentration was recorded continuously by the data loggers, which were set to automatically calculate the average concentration at 60 s intervals (EntryRAE) or 10 s intervals (QRAE+, QRAE II, and ITX) for the duration of the SMC removal operations. The EntryRAE monitor could not be set to calculate a 10 s average, so it was replaced with the ITX monitor after the first visit to site 1. The EntryRAE and then the ITX monitor were used at the face of the SMC heap during disturbance in conjunction with PVC tubing and a 7 m fiberglass pole. A 6 m length of Tygon PVC tubing (formulation R-3603, 2.4 mm inner diameter) was connected to the monitor. A polytetrafluoroethvlene (PTFE) microfilter (0.45 μ m) was fitted to the air-inlet end of the tube to prevent dust and water vapor from entering and interfering with the gas sensor. The monitor and tubing were attached to the 7 m fiberglass pole so that 1 m of PVC tubing was hanging down from the top of the pole. The PVC tubing was then suspended above the SMC face, as the SMC was being removed, by manually positioning it with the fiberglass pole.

In addition to recording the 10 or 60 s average H₂S concentration, the monitors also

19(4): 261-275

calculated and recorded the short-term exposure value (STEV, 15 min average) and the time-weighted average value (TWAV, 8 h average) throughout the operations. All gas monitors were calibrated according to the manufacturers' instructions before the start of each site visit using a cylinder of H_2S gas of known concentration.

Personal Safety

 H_2S exposure in the workplace is governed by the EU Framework Directive (89/391/EEC) on Health and Safety, which is implemented in Ireland under the Code of Practice for Safety, Health, and Welfare at Work (Chemical Agents) Regulations (HSA, 2010). To prevent H_2S exposure, a Cen-Paq personal breathing apparatus with bottled air and full-face mask (www.seridan.com) was worn by research personnel during the first visits to sites 1 and 2 in 2008. It was subsequently decided that adequate protection from H_2S exposure could be obtained by wearing a full-face gas mask (EN 136:1998 CL 1) fitted with an H_2S filter (code EN 141 A1B1E1K1; www.northsafety.com), and these were used on all subsequent visits. Disposable Tyvek suits and QRAE II/QRAE+ personal monitors were worn by research personnel during H_2S measurements.

Temperature Measurement

The temperature of the SMC was measured at various locations across the length, width, and depth of the heaps. Measurements were taken at approximately 50 cm from the top and bottom surfaces of the heaps as well as at the middle. A Eurolec TH103 thermocouple (www.eurolec-instruments.com) with a modified probe length of 1.5 m was used to measure the temperature.

Moisture Content

Samples of SMC (3 to 5 kg) were taken from the top, middle, and bottom of the SMC heaps at intervals across the full length and width of the heaps and mixed well prior to subsampling. Two 150 g replicate subsamples per sample were dried in an oven at 105°C for 24 h. Moisture content was calculated on a wet weight basis.

Weather Data

Weather data were obtained from the two nearest Met Éireann (www.met.ie) weather stations for each site, which were located at 0.2 to 60 km distance from the sites. Records were obtained for wind direction (hourly average), wind speed (hourly average), and weather conditions on the days when the sites were visited. In addition, the total rainfall amount recorded for each site for the duration of the SMC storage periods was also obtained. An AV6 digital handheld vane anemometer (www.airflow.co.uk) was also used to measure wind speed during site visits in 2009 to compare against the wind speed data collected from Met Éireann.

Results

H₂S Detection above the SMC Face: Outdoor Storage Sites

 H_2S gas was consistently detected above the SMC face when outdoor-stored SMC was disturbed. The pattern of emissions was similar at both sites 1 and 2, with peaks of high concentration occurring at the times when the SMC was being actively disturbed and troughs of low concentration occurring when the disturbance ceased (figs. 2 and 3).

At site 1 in 2008, H₂S concentrations (60 s average) above the SMC face were fre-

Journal of Agricultural Safety and Health





Figure 2. Average H_2S concentration above the SMC face at site 1: (a) visit 1, 60 s average; (b) visit 2, 10 s average; and (c) visit 2, 60 s average. STEV (15 min average), date, wind direction, wind speed, and approximate age of SMC are also indicated.

quently 100 to 400 ppm for 3 to 6 month old SMC but <100 ppm for 1 to 2 month old SMC (fig. 2a). In 2009, a similar pattern was observed, but H_2S concentrations were generally lower than in 2008 (figs. 2b and 2c). Weather conditions were similar except that there were some periods of drizzling rain during the 2009 visit. The highest 60 s average concentrations of H_2S detected at the SMC face were 386 and 300 ppm in 2008 and 2009,

19(4): 261-275



— Hydrogen sulphide concentration (10 second average) — Short term exposure values (15 minute average)

Figure 3. Average H_2S concentration (10 s average) above the SMC face at site 2: (a) visit 1 and (b) visit 2. STEV (15 min average), date, wind direction and speed, and approximate age of SMC are also indicated.

respectively (figs. 2a and 2c). In 2009, the highest 10 s average concentration was 680 ppm (fig. 2b).

At site 2 in 2008, H_2S concentrations (10 s average) above the SMC face were much higher than at site 1, with peaks of 250 to 1000 ppm recorded for all material (fig. 3a). H_2S concentrations were even higher in 2009, with peaks of 400 to 2000 ppm frequently recorded (fig. 3b). In both years, disturbance of 1 to 3 month old SMC resulted in lower detected H_2S concentrations compared with older material. Weather conditions were similar on both occasions. The highest 10 s average concentrations of H_2S detected at the SMC face were 1064 ppm in 2008 and 2083 ppm in 2009.

The STEV (15 min average) above the SMC face during disturbance and removal was

Journal of Agricultural Safety and Health

Table 2. Exceedances of the STEL and TWA values, and maximum values recorded, above the SMC face at storage sites during SMC disturbance.

		Above SMC Face				
		STEV	Max. STEV	TWA	Max. TWA	
Site	Site Visit Dates	(>10 ppm)	(ppm)	(>5 ppm)	(ppm)	
1	Visit 1 (Feb. 2008)	Yes	95	Yes	16	
	Visit 2 (Feb. 2009)	Yes	94	Yes	7	
2	Visit 1 (Aug. 2008)	Yes	350	Yes	24	
	Visit 2 (Sept. 2009)	Yes	444	Yes	31	
3	Visit 1 (Oct. 2009)	Yes	50	Yes	17	
4	Visit 1 (Oct. 2009)	No	10	No	2.5	

greater than the statutory STEL of 10 ppm for most of the time at both outdoor sites and in both years, with the highest values being 95 ppm for site 1 and 444 for site 2 (figs. 2 and 3, table 2). The TWA value (8 h average) above the SMC face was also greater than the statutory limit of 5 ppm on many occasions at both sites during both years, with the highest values being 16 ppm for site 1 and 31 ppm for site 2 (table 2). This zone thus poses a high risk to the health and safety of workers in the vicinity.

H₂S Detection above the SMC Face: Indoor Storage Sites

 H_2S gas was also detected above the SMC face at both indoor sites (sites 3 and 4) in a peak-trough pattern that was similar to that recorded at the outdoor sites (fig. 4). At site 3, H_2S concentrations above the SMC face were frequently >80 ppm when 2 to 6 month old SMC was disturbed but <80 ppm (10 s average) when 1 month old SMC was disturbed (fig. 4a). The highest concentration of H_2S detected at the SMC face was 680 ppm (10 s average) (fig. 4a), and concentrations were generally similar to outdoor site 1. At site 4, H_2S concentrations above the SMC face were much lower than at sites 1, 2, and 3, with peaks of <90 ppm (10 s average) recorded for 3 to 12 month old material and <20 ppm (10 s average) recorded for 1 to 2 month old material (fig. 4b). The highest concentration of H_2S detected at the SMC face was 89 ppm (10 s average).

The STEV (15 min average) above the SMC face during disturbance and removal was greater than the statutory STEL of 10 ppm for most of the time at site 3, with the highest value being 50 ppm. The STEL was not exceeded at site 4, where the highest value was 10 (fig. 4, table 2). Similarly, the TWA values (8 h average) above the SMC face were also greater than the statutory limit of 5 ppm for most of the time at site 3, but the statutory limit was not exceeded at site 4 (table 2). Thus, the zone at site 3 poses a risk to the health and safety of workers in the vicinity, while the risk is much reduced at site 4.

H₂S Monitoring for Research Personnel

 H_2S gas was detected by the personal monitors worn by researchers working in the vicinity of the SMC face at both indoor and outdoor sites. The pattern of detection was similar at all sites, with peaks of high concentration detected at the times when the SMC was being actively disturbed and troughs of low concentration occurring when the disturbance ceased. The highest concentrations (10 s average) of H_2S detected were 154, 500, 117, and 17 ppm for sites 1 through 4, respectively. The highest STEVs (15 min average) were 25, 76, 9, and 2 ppm, while the TWAVs (8 h average) were 2, 4, 4, and 0 ppm for sites 1 through 4, respectively. The STEV for research personnel was >10 ppm on many occasions at sites 1 and 2 but was not exceed at sites 3 and 4, indicating a risk to the health and safety of workers in the vicinity of the SMC face, particularly at outdoor sites. The TWAV did not exceed 5 ppm at any site.

19(4): 261-275

Site 3



- Hydrogen sulphide concentration (10 second average) — Short term exposure values (15 minute average)

Figure 4. Average H₂S concentration (10 s average) above the SMC face at (a) site 3 and (b) site 4. STEV (15 min average), date, wind direction, wind speed, and approximate age of SMC are also indicated.

Temperature and Moisture Content of Stored SMC

Temperature and moisture content data for SMC stored at sites 1 to 4 are summarized in table 3. The temperature of indoor-stored SMC was higher than that of outdoor-stored SMC. Temperatures were highest in the top layer and lowest in the bottom layer. The moisture content was higher for outdoor-stored SMC compared to indoor-stored SMC, and the moisture content of the top layer was lower than the middle and bottom layers.

Weather during Storage and Removal

Total and average monthly rainfall during the various SMC storage periods are given in table 3. The highest rainfall was received at site 2 (outdoor), where monthly averages were 108 and 116 mm during the storage periods for 2008 and 2009, respectively. Although the indoor storage sites (sites 3 and 4) are covered, some rainfall reaches the stored

Journal of Agricultural Safety and Health

Table 3. Temperature and moisture content of stored SMC at time of sampling.^[a]

G ¹ /		Temperature		Moisture Content		SMC Storage		
Site	T	(°C)		(70) Moon (Min Mov)	(%)		(mm)	
and	Location	Mean (Mini-Max)		Mean (Min-Max)			Monthly	
Visit	ın Heap	±SD	n_1	±SD	n_2	Total	Average	
Site 1, Visit 1	Тор	32 (22-43) ±5.5	35	66 (65-68) ±1.2	5			
	Middle	30 (20-40) ±5.0	35	67 (65-68) ±1.5	5	388	65	
	Bottom	24 (16-30) ±3.6	35	67 (66-68) ±0.8	5			
Site 1, Visit 2	Тор	32 (23-44) ±8.0	28	68 (64-73) ±2.5	25			
	Middle	30 (22-41) ±6.7	28	70 (66-73) ±1.9	25	775	97	
	Bottom	27 (21-35) ±4.5	28	71 (68-74) ±1.7	25			
Site 2, Visit 1	Тор	36 (24-46) ±7.9	15	69 (65-71) ±2.6	6			
	Middle	32 (22-42) ±7.1	15	70 (67-72) ±1.8	6	1291	108	
	Bottom	31 (21-38) ±6.7	15	71 (69-73) ±1.6	6			
Site 2, Visit 2	Тор	31 (24-37) ±4.2	18	70 (69-72) ±1.1	9			
	Middle	28 (23-33) ±3.3	18	70 (68-72) ±1.2	9	931	116	
	Bottom	26 (20-33) ±3.6	18	72 (70-73) ±0.8	9			
Site 3, Visit 1	Тор	51 (46-54) ±2.1	25	62 (52-68) ±4.5	45			
	Middle	46 (41-54) ±3.3	25	65 (55-68) ±3.7	45	614 ^[b]	102 ^[b]	
	Bottom	36 (30-43) ±2.5	25	65 (57-70) ±4.2	45			
Site 4, Visit 1	Тор	41 (36-47) ±3.1	25	53 (35-66) ±11.5	20			
	Middle	37 (30-43) ±3.7	25	61 (43-68) ±7.3	20	1077 ^[b]	90 ^[b]	
	Bottom	33 (28-37) ±2.4	25	63 (50-68) ±5.3	20			

^[a] SD = standard deviation, n_1 = number of readings taken, and n_2 = number of SMC samples collected.

^[b] Some rainfall reaches the SMC through the open sides of the storage barns at the indoor sites.

SMC through the open sides of the storage barns (figs. 1e and 1f). Wind speeds during the SMC removal operations were generally lower at sites 2 and 4 but higher at sites 1 and 3 (figs. 2 through 4). In 2009, there were some periods of drizzling rain during removal operations at site 1. The wind speed data obtained from Met Éireann were broadly in agreement with measurements taken by the handheld vane anemometer.

Discussion

A peak-trough pattern of H_2S emissions into the atmosphere was detected repeatedly at four sites where stored SMC was being disturbed and removed for land application or other use. Similar peak-trough patterns have been recorded when managing stored animal slurry (Chénard et al., 2003; Hooser et al., 2000; Scully et al., 2007). High concentrations of H₂S were consistently detected in the air above the face of the SMC when it was being actively disturbed, but there were differences in the maximum concentrations detected at the four sites. Variations in concentrations seemed to relate to some of the storage conditions and site characteristics. Generally, the longer the SMC had been stored, the higher the concentration of H_2S released into the atmosphere when it was disturbed. This pattern was consistent across all four sites, whether the SMC was stored outdoors or under cover and whether the heap was large or small. However, the size of the heap seemed to be an important factor. The smallest heap (site 4) contained about 600 m³ of SMC up to 12 months old, while the other sites had more than 1500 m³ of stored SMC. Site 4 had by far the lowest H₂S emissions, with no H₂S peaks above 90 ppm and most peaks were <50 ppm. Thus, small heaps of SMC, stored under cover, are less likely to produce high H₂S emissions.

19(4): 261-275

Persistently high concentrations of H_2S of >500 ppm were detected in the air above the SMC face at outdoor site 2, which was located in an area with high rainfall and where the average moisture content of the SMC was generally 70% or higher. Lethal H_2S concentrations of >1000 ppm were detected at this site, particularly in 2009 when rainfall levels during the storage period were high. High moisture content in organic-rich soils leads to anaerobic conditions and anaerobic microbial activity, and in such low-oxygen environments sulfate-reducing bacteria will reduce the sulfates in the organic matter to volatile sulfur compounds such as H_2S (Kissel et al., 1992; Nassry, 2007). Lin et al. (2012) reported increased H_2S emissions from high-rise egg production facilities when the moisture content of the surface manure was high (64%). Preliminary studies by Velusami et al. (2011) indicated that with increasing moisture content of SMC from 69% to 80% there was a corresponding increase in H_2S production. Thus, it is not surprising that the highest H_2S concentrations recorded at the SMC storage sites in this study were detected where the moisture contents were highest.

Moisture content does not explain why the H_2S levels at indoor site 3 were quite similar to those at outdoor site 1, despite the fact that the average moisture contents at the two sites were different at <65% and >68%, respectively. Lower H_2S levels might have been expected from the drier SMC, due to the relatively more aerobic environment. However, the average temperatures of the two stored heaps were also quite different. The average temperature of the outdoor-stored SMC ranged from 24°C to 32°C, while that of the similarly sized indoor-stored heap ranged from 36°C to 51°C. Preliminary studies by Velusami et al. (2011) indicated that H_2S production from SMC was more rapid at 45°C than at 35°C, suggesting that thermophilic microbial activity is a significant factor in H_2S production from SMC even when moisture contents are not excessively high. Thus, indoor storage of SMC, by itself, does not eliminate the risk of high H_2S emissions.

Thermophilic microbial activity along with high moisture contents are likely to be two key factors influencing the level of H_2S that is released into the atmosphere when stored SMC is disturbed. This would explain why the H_2S levels for the small indoor heap at site 4 were so low, where average temperatures were moderate (33°C to 41°C) rather than high and where moisture contents were also relatively low (53% to 63%). Smaller heaps of SMC that are stored under cover, and thereby sheltered from rain, are likely to be drier and cooler than large heaps under cover, where the greater mass of compost will retain more moisture and heat. Large, outdoor heaps are more susceptible to rainfall and are therefore likely to have relatively high moisture contents, especially in areas with high rainfall, predisposing them to greater anaerobic microbial activity and H_2S emissions. Thus, factors such as heap size and storage conditions should be considered when planning SMC storage facilities.

Occupational exposure limits exist to protect the labor force from exposure to H_2S in the workplace. The 15 min STEL is currently set at 10 ppm, and the 8 h TWA is 5 ppm (HSA, 2010; EC, 2009). These limits were consistently exceeded at the SMC face of the three large SMC storage sites studied, but not at the smaller site. Although no person should be present in this location, the fact that freshly disturbed SMC can release toxic levels of H_2S into the atmosphere means that there is potential risk to operators working in proximity to this zone. Data on the H_2S levels recorded inside and outside the tractor cabs involved in removing the SMC at the four sites are reported separately.

The agricultural industry is increasingly aware of the practices that lead to agriculturerelated water pollution. In Ireland, SMC is currently stored in a way that protects

Journal of Agricultural Safety and Health

groundwater and waterways from pollution by nutrient-enriched runoff. However, storage of SMC in large covered or uncovered heaps on concrete platforms, which is in compliance with the Nitrates Regulations, is liable to release toxic H_2S gas into the atmosphere when the material is removed for land application. It is important that employers and employees at SMC storage facilities are made aware of the risks of H_2S emissions during SMC disturbance and removal and that appropriate health and safety protocols are in place to ensure the health and safety of all personnel.

Conclusion

In Ireland, SMC must be stored for a minimum of 13 to 16 weeks from October to January to comply with EU Nitrates Directive 91/676/EEC in order to protect waterways against pollution by nitrates. In reality, SMC is often stored for much longer periods until it is applied to land as an organic fertilizer. Storage periods of longer than three months increase the likelihood of toxic H_2S gas emissions into the atmosphere during the removal and application process. Factors such as heap size, moisture content, and temperature all influence H_2S levels, as well as whether or not the SMC is stored outdoors or under cover. The lowest H_2S risk appears to occur when SMC is stored under cover in small heaps, where low moisture contents and moderate heap temperatures favor reduced H_2S emissions. Thus, storage of SMC should be managed not only in accordance with the Nitrates Regulations but also in accordance with Health and Safety Regulations in view of the risks associated with H_2S emissions. This requires that employers evaluate the risks, combat them at the source to reduce the danger, provide information and training, adapt the workplace to avoid risk, and have appropriate health and safety protocols in place to protect operators and employees.

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19(4): 261-275