HYDROGEN SULPHIDE GAS PRODUCTION FROM SPENT MUSHROOM COMPOST UNDER FIELD AND LABORATORY CONDITIONS

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ABSTRACT

Hydrogen sulphide (H_2S) gas production was monitored during the disturbance of four heaps of Spent Mushroom Compost (SMC) that were stored for up to 12 months either outdoors or under cover (indoors). QRAE (www.raesystems.eu) and ITX (www.indsci.com) gas monitors with data logging facilities were used to measure the 10-second average concentration of H_2S released into the air above the heaps of SMC as they were being disturbed. The highest concentrations of up to 2083 ppm were detected for the outdoor stored material in comparison to concentrations of up to 687 ppm detected for indoor stored material. Outdoor stored SMC had higher moisture contents (66-72%) compared to indoor stored material (53-65%). Laboratory studies were conducted to study the effects of moisture content (69 – 85%) and temperature (35ºC or 45ºC) on H_2S production from fresh un-steamed and steamed samples of SMC. The H_2S gas concentration in the head space of the incubation vessels was measured every 24 hours for 3 days. Un-steamed SMC produced higher levels of H_2S than steamed SMC and in general the higher the moisture content the higher the H_2S concentration. Higher concentrations of H_2S were also produced with the higher incubation temperature of 45 ºC. These results suggest that the high levels of H_2S detected during disturbance of stored SMC are heavily influenced by moisture content. The higher rates of H_2S production at 45 ºC also suggest that thermophilic microorganisms are involved in the process. Health and Safety aspects of H_2S production from stored SMC are discussed

Keywords: Hydrogen Sulphide, Spent Mushroom Compost, Health and Safety

INTRODUCTION

Hydrogen sulphide (H_2S) gas is a by product of the anaerobic decomposition of organic matter and is produced when stored spent mushroom compost (SMC) is disturbed and removed for spreading on land or other uses[1]. It is a toxic gas which can cause respiratory paralysis and death within a few minutes following exposure to concentrations in the region of 1000 ppm. Occupational exposure limits (OEL's) are important regulatory instruments to protect employees from exposure to toxic chemicals in the workplace. The short term exposure limit (STEL) for H_2S is currently 10 ppm for a period of 15 minutes, and for no more than 4 times a day[2].

Organic sulphur can be found in amino acids and is usually attached to organic material through carbon or ester bonds [2]. In aerobic environments, the oxidation of organic sulphur to sulphates includes the production of sulphides as an intermediate step in the mineralization process. Sulphides are easily adsorbed to organic material and are oxidized in aerobic conditions by *Thiobacillus* bacteria. In extremely low oxygen environments, bacteria such as *Clostridium*, *Salmonella* and *Desulfovibrio* spp. reduce sulphate to sulphides [2, 3]. If aerobic bacteria do not oxidize the sulphides then inorganic sulphur, such as hydrogen sulphide gas, can accumulate.

Hydrogen sulphide (H_2S) is a toxic and colourless gas, which has a characteristic odour similar to rotten eggs at low concentrations. At higher concentrations H_2S is odourless and, depending on the concentration, it can cause rapid loss of consciousness, neurological and respiratory impairment or sudden death [4]. H_2S is a common cause of fatal gas inhalation exposures in the workplace. In many cases, additional deaths of co-workers occur when attempts are made to rescue the first victim [5]. Occupational exposure limits (OEL's) are important regulatory instruments to protect employees from exposure to toxic chemicals in the workplace. In Europe, there are two OEL's in place for H_2S exposure to protect workers against adverse effects of this toxic gas: the time-weighted average (TWA), which is currently 5 mg kg^{-1} for a conventional 8 hour day/40 hour week and the short term exposure limit (STEL), which is 10 mg kg^{-1} over a period of 15 minutes for up to 4 times per day [6, 7, 8].

At the end of a mushroom crop most growers steam the compost at 60-70 ºC for 8-12 hours in order to kill off all pathogens and pests. Thus the microbial population of steamed SMC is considerably lower than un-steamed SMC. In addition, fresh SMC that has been steamed has a higher moisture content compared to fresh SMC that has not been steamed. The mushroom growing substrate is then removed and is stored as SMC until needed. During storage outdoors, the SMC is exposed to rain and wind (evaporation) so the moisture content may fluctuate depending on the weather during storage. SMC stored under cover is largely protected from rainfall but the open sides of the storage barns will allow evaporation to occur. Thus SMC stored indoors, under cover is likely to be drier than SMC stored outdoors. The primary objective of this work was to monitor the emissions of H_2S from stored SMC at existing commercial storage sites at the time when the SMC was being disturbed and removed for spreading on nearby farmland. A secondary objective was to identify what factors, if any, may influence the concentration of H_2S produced from SMC under controlled laboratory conditions.

MATERIALS AND METHODS

SMC Storage Sites. Four commercial SMC storage sites were selected and H_2S emissions were monitored when the SMC was being disturbed and removed for land spreading or other uses in 2009. Sites 1 & 2 were outdoors and consisted of heaps of SMC stored on a concrete platform with retaining side walls to approx 3 m. Sites 3 & 4 were indoors and consisted of heaps of SMC stored under cover in an open-sided Apex-roofed barn with concrete floor and retaining side walls to approx 3 m. SMC was delivered weekly to each site and, on the day of H_2S measurement, the heaps consisted of material varying in age from 1-8, 1-12, 1-6 and 1-12 months for Sites 1- 4, respectively. Average monthly rainfall during the storage period was 97, 116, 102 and 90 mm, for Sites 1-4, respectively (some rainfall lands on SMC stored undercover via the open sides of the storage barns). On the day when H_2S was measured, as the day progressed the SMC was removed from older to younger material at the outdoor sites and from younger to older material at indoor sites. The age of the SMC was estimated based on heap dimensions. SMC samples (3-5 kg) were taken throughout the day at middle depths of each heap for moisture content determination (n = 25, 9, 45 and 20 for Sites 1-4, respectively). The temperature of the SMC heap at middle depths was measured throughout the day at 28, 18, 25 and 25 locations for Sites 1-4, respectively, as the SMC was being progressively removed.

H_2S Measurement. Hydrogen sulphide (H_2S) gas production was monitored during the disturbance of the heaps of SMC which had been stored for up to 12 months. QRAE (www.raesystems.eu) and ITX (www.indsci.com) gas monitors with data logging facilities were used to measure the 10-second average concentration of H_2S released into the air above the heaps of SMC as they were being disturbed.

Laboratory Studies. A 6 kg sample of fresh un-steamed SMC was collected in June 2009 from the mushroom research unit at Teagasc at the end of a mushroom crop. The crop was then steamed at 70 ºC (compost temperature) for 8 hours to kill off any pests and pathogen and, when it had cooled down, a further 6 kg sample of fresh steamed SMC was then taken. . The moisture content of the fresh un-steamed SMC was 69% and of the steamed SMC was 74%. Each batch of SMC was subdivided into 3 x 2 kg sub-samples and the moisture content of two of the subsamples was adjusted to give higher moisture contents as indicated in Table 1.

Table 1. Moisture content of SMC samples used in laboratory experiments

	% moisture content		
	Sub sample 1	**Sub sample 2**	**Sub sample 3**
Un-steamed SMC	69 (fresh)	75	80
Steamed SMC	74 (fresh)	80	85

The SMC samples were then stored at 4 ºC until needed for laboratory experiments in June and July 2009. Four separate experiments were conducted:

- un-steamed SMC at different moisture contents incubated at 35ºC,
- un-steamed SMC at different moisture contents incubated at 45ºC,
- steamed SMC at different moisture contents incubated at 35ºC and
- steamed SMC at different moisture contents incubated at 45ºC.

In each experiment SMC (140 g) was placed in a sterile 500 ml glass bottle. The cap of each bottle was fitted with an airtight tube that could be connected directly to an ITX gas monitor. Three replicates were prepared for each SMC at each moisture content The prepared bottles of SMC were incubated for a total of three days. An ITX gas monitor was used to measure the H_2S gas concentration in the head space of the bottles once every 24 hours over 3 days.

Personal Safety. A full face gas mask (EN 136:1998 CL 1) fitted with a H_2S filter code EN 141 A1B1E1K1 (www.northsafety.com) was worn during H_2S measurements.

RESULTS AND DISCUSSION

Maximum peaks of H_2S concentration of 680, and 2083 ppm were detected during disturbance of 4-12 month-old, outdoor-stored SMC (Sites 1, and 2, respectively), in comparison to maximum peaks of 687, and 89 ppm for indoor-stored material of the same age (Sites 3, and 4, respectively) (Table 2). Most SMC in Ireland is stored for between 4-12 months so these results highlight a significant risk of H_2S exposure for those working with SMC during its disturbance and removal from the storage site. Younger SMC (1-3 months) generally produced lower H_2S readings (280-610 ppm) compared with older material but exposure to these concentrations would still be considered a health and safety risk. The lowest concentrations of H_2S were detected at indoor Site 4, which was a much smaller heap of SMC compared to the others, and this would suggest that smaller heaps are better from a health and safety perspective.

Outdoor stored SMC had a higher average moisture content (69-70%) compared to indoor stored material (61-65%), reflecting the fact that it would have absorbed any rainfall during the storage period. This is likely to have had a significant influence on the peaks of H_2S detected at the outdoor locations as H_2S would be produced more readily in the wetter, more anaerobic, SMC. The SMC heap that had been exposed to the highest monthly rainfall (Site 2) had the highest H_2S levels.

The average internal temperature of the outdoor-stored SMC heaps was lower at 28-30 ºC compared to the indoor stored heaps at 37-46 ºC. This suggests that there may have been greater microbial activity occurring in the indoor stored SMC, compared to the outdoor stored material, or that more heat was retained within the heap when there was a protective roof overhead. The large indoor-stored SMC heap at Site 2 had a much higher temperature than all other heaps and this factor may have contributed to the high levels of H_2S detected during its disturbance

Further studies on outdoor and indoor stored heaps of SMC, where heap size, storage conditions and SMC age are controlled, would highlight more clearly the relative importance of individual factors on H_2S emissions.

Table 2. Characteristics of SMC heaps and peaks of H_2S detected during disturbance and removal.

Site No	**Type of storage**	**Heap size** (approx) m^3	**Age of SMC** (months)	**Date of Visit**	**Average [1] % moisture** (Min-Max)	**Average[1] Temperature** (Min-Max)	**Max H_2S conc. (ppm)** SMC Age: 1-3 months	**Max H_2S conc. (ppm)** SMC Age: 4 -12 months
1	Outdoor	2000	1 - 8	Feb-09	69 $\pm$ 1.9 (66-72)	30 $\pm$ 6.7 (22-41)	280	680
2	Outdoor	2300	1 - 12	Feb-09	70 $\pm$ 1.4 (68-72)	28 $\pm$ 3.3 (23-33)	610	2083
3	Indoor	1800	1 - 6	Oct-09	65 $\pm$ 3.7 (55-68)	46 $\pm$ 3.3 (41-54)	395	687
4	Indoor	600	1 - 12	Oct-09	61 $\pm$ 7.3 (43-68)	37 $\pm$ 3.7 (30-43)	49	89

[1] Mean $\pm$ standard deviation; (Min-Max) = minimum and maximum values.

In the laboratory studies, H_2S gas was detected in the head space of the sealed bottles after 24 to 48 hours. More H_2S was produced from un-steamed SMC incubated at 35^{o}C, compared to steamed SMC (Fig. 1), suggesting that the steaming process reduced the sulphate-reducing bacteria (SRB) population significantly. The level of H_2S produced from both the un-steamed and steamed SMC incubated at 45^{o}C were more similar, suggesting that although the numbers of sulphate reducing bacteria may have been reduced by steaming, they survived the steam treatment through the formation of endospores, which would allow the SRB population to rapidly re-establish itself in the SMC under favourable thermophilic growth conditions.. The fact that H_2S production from steamed SMC was highly enhanced at 45^{o}C compared with 35^{o}C confirms (a) the thermophilic nature of the SRB population and (b) that the SRB population responds favourably to the process of steaming.

Increasing the moisture content of the fresh SMC (un-steamed or steamed) to 80% significantly increased the H_2S production by approximately three to eight fold. This highlights the fact that by increasing the moisture content, the SMC becomes more anaerobic, resulting in higher levels of H_2S production. However, when the moisture content was increased to 85% the H_2S accumulation in the head space of the incubation vessels was reduced to very low levels. Although it might have been expected that H_2S production at 85% moisture content would be

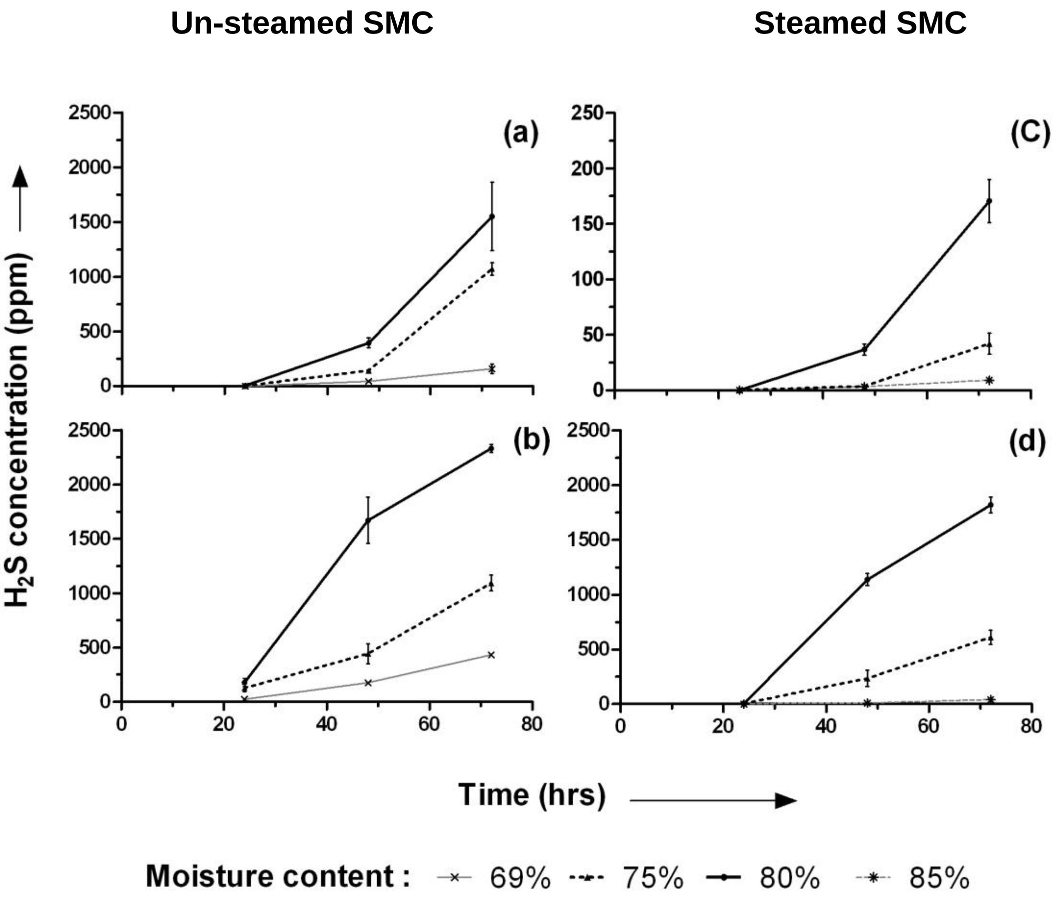

Figure 1. H_2S production from un-steamed and steamed SMC during incubation at 35°C (a and c) and 45°C (b and d).

very high, the SMC in this treatment was semi-liquid in consistency. It is likely therefore, that any H_2S, produced by the 85% SMC, was trapped within the semi-liquid substrate and not released into the head space of the incubation vessel. It is possible that high H_2S concentrations would have been detected if the 85% SMC had been physically disturbed, allowing the release of H_2S.into the atmosphere.

Further research is required to confirm the role of thermophilic SRB in H_2S emissions from stored SMC

CONCLUSION

The level of H_2S released from stored SMC during its disturbance is influenced by its age as well as its moisture content and temperature. The practise of steaming mushroom compost, before its disposal and storage as SMC, does not eradicate populations of SRBs; they recover rapidly, especially if the SMC temperature increases above 35°C. The best conditions for SMC storage to minimise high levels of H_2S during disturbance would appear to be in small heaps under cover where the lower moisture content and moderate temperature do not enhance H_2S production.

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