Improved quantification of livestock associated odorous volatile organic compounds in a standard flow-through system using solid-phase microextraction and gas chromatography–mass spectrometry

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ABSTRACT

Aerial emissions of odorous volatile organic compounds (VOCs) are an important nuisance factor from livestock production systems. Reliable air sampling and analysis methods are needed to develop and test odor mitigation technologies. Quantification of VOCs responsible for livestock odor remains an analytical challenge due to physicochemical properties of VOCs and the requirement for low detection thresholds. A new air sampling and analysis method was developed for testing of odor/VOCs mitigation in simulated livestock emissions system. A flow-through standard gas generating system simulating odorous VOCs in livestock barn emissions was built on laboratory scale and tested to continuously generate ten odorous VOCs commonly defining livestock odor. Standard VOCs included sulfur VOCs (S-VOCs), volatile fatty acids (VFAs), and *p*-cresol. Solid-phase microextraction (SPME) was optimized for sampling of diluted odorous gas mixtures in the moving air followed by gas chromatography–mass spectrometry (GC-MS) analysis. CAR/PDMS 85 μm fiber was shown to have the best sensitivity for the target odorous VOCs. A practical 5-min sampling time was selected to ensure optimal extraction of VFAs and *p*-cresol, as well as minimum displacement of S-VOCs. Method detection limits ranged from 0.39 to 2.64 ppbv for S-VOCs, 0.23 to 0.77 ppbv for VFAs, and 0.31 ppbv for *p*-cresol. The method developed was applied to quantify VOCs and odorous VOC mitigation with UV light treatment. The measured concentrations ranged from 20.1 to 815 ppbv for S-VOCs, 10.3 to 315 ppbv for VFAs, and 4.73 to 417 ppbv for *p*-cresol. Relative standard deviations between replicates ranged from 0.67% to 12.9%, 0.50% to 11.4%, 0.83% to 5.14% for S-VOCs, VFAs, and *p*-cresol, respectively. This research shows that a simple manual SPME sampler could be used successfully for quantification of important classes of odorous VOCs at concentrations relevant for real aerial emissions from livestock operations.

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1. Introduction

Worldwide proliferation of intensive large-scale livestock production systems has focused the attention on aerial emissions of odor, VOCs, NH_3, H_2S, and bioaerosols, including pathogens [1]. Livestock air emissions are a complex mixture of very dilute odorous VOCs, among which several key volatile organic compounds (VOCs and semi-VOCs) were found to be responsible for odor nuisance [2–8]. Previous studies reported three main categories of chemicals as the key odorants from swine operations, i.e., sulfur-containing VOCs (S-VOCs), volatile fatty acids (VFAs), and phenolics/indoles [2,8]. Ammonia, which is characterized by relatively higher odor threshold compared to most of these VOCs, and typically present at higher concentrations, may or may not correlate with odor concentrations [9]. Hydrogen sulfide and methanethiol were reported to represent 70–97% of the total sulfuric gases and

volatiles in manure [10]. The most dominant sulfuric gases and volatiles in cattle manure were found to be hydrogen sulfide (39%), methanethiol (34%), and dimethyl sulfide (21%) [11]. VFAs were reported to be major odorants for emissions associated with animal production systems, more specifically, about 60% of total VFAs in manure were present as acetic acid, followed by propanoic acid, butyric acid, isobutyric acid and isovaleric acid [12–14]. Bulliner et al. [2] reported p-cresol as the key compound responsible for the characteristic smell of swine odor. It is generally accepted that the key odorous VOCs responsible for livestock odor are typically present at very low levels (ppbv to pptv).

Quantification of odorous VOCs from livestock operations is necessary in order to develop and test various odor mitigation technologies. However, there are challenges in quantifying target odorous VOCs because of their low concentrations (typically in the ppbv range) and the extremely low odor threshold of some of these compounds (which can be in the pptv range). Moreover, the majority of odorous VOCs are present at such trace levels in a complex matrix of odor-insignificant volatiles.

Several studies reported analytical detection limits of livestock odorants (Table 1). However, most of these were done in a static system; fewer studies aimed at quantifying VOCs in livestock air applying flow-through systems [15]. Moreover, in most studies summarized in Table 1, samples were stored in a polymeric bag (e.g. Tedlar) or a metal canister [19]. Such storage devices were reported to suffer from sample contamination and sample loss [26]. Finally, most of reported studies focused on a few target compounds, such as S-VOCs or VFAs only.

Notably, human odor detection threshold of target VOCs selected in the present study were reported at very low concentrations, mostly below 4 ppbv except acetic (145 ppbv) and propanoic acid (35.5 ppbv), as shown in Table 2. To fulfill the experimental needs, a system capable of producing gas mixtures at such low concentrations is required and an appropriate sampling and analytical method has to be established to achieve method detection limits (MDLs) as low as possible.

Characteristic VOCs were introduced into a standard gas generation system through emission at constant rates from Teflon permeation tubes. Emissions of VOCs were diluted by constant air flow to reach required low concentrations. A method for sampling and analysis of odorous VOCs in moving air simulating concentrations present in exhaust air of livestock barns was optimized in this study. This method is based on solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (SPME–GC–MS). A mixture of 10 standard odorous VOCs was used to simulate air emissions of livestock barns. As an illustration of the application of this analytical method, the simulating gas mixture was treated in a flow-through reactor with UV light, thus lowering concentrations further and challenging the method for residual concentrations as well.

2. Materials and methods

2.1. Materials and supplies

Standard chemicals used in this study were H_2S and S-VOCs (methyl mercaptan, ethyl mercaptan, butyl mercaptan, and dimethyl sulfide (DMS)), VFAs (acetic, propanoic, butyric, and isovaleric acid), and a phenolic compound (p-cresol). All standards were in HPLC grade and purchased from Sigma–Aldrich (Milwaukee, WI, USA). Permeation tubes are made and calibrated in-house or purchased from KIN-TEK[TM] Laboratories (La Marque, TX, USA). Mass flow controllers are made by Aalborg (Orangeburg, NY, USA). SPME fibers coupled with manual holders are from Supelco (Bellefonte, PA, USA). The 6890N GC/5973 MS was from

Agilent (Wilmington, DE, USA). The instrument was equipped with SGE BP5 and BP20 WAX columns (SGE Analytical Science, Melbourne, Australia). The pre-column is non-polar SGE BP-5, 12 m length, 0.53 mm i.d., and 1 μm film thickness, with 5% phenyl methylpolysiloxane stationary phase; and the polar analytical column is SGE BP20 WA, dimension of fused silica capillary column was 25 m length, and 0.53 mm i.d., and coated with polyethylene glycol at a film thickness of 1 μm. Data analysis was performed with Bench-Top/PBM (from Palisade Mass Spectrometry, Ithaca, NY, USA).

2.2. Standard gas generation system

A standard gas generation system (SGG; Fig. 1) was built to generate mixtures of VOCs/H_2S at concentrations typical to air emissions from livestock barns. Target compounds are generally liquids at room temperature; thus permeation tubes were used. Each chemical was generated by one permeation tube. All permeation tubes were made from Teflon. The permeation is a process of the gas dissolving into the Teflon wall and evaporating from the outer surface, which is highly sensitive to temperature. The emission rate of each permeation tube was controlled by temperature [31,32].

Standard gas concentrations of each compound were calculated based on the emission rate (E) of the permeation tube, which was determined by Eq. (1),

$$E = \frac{\Delta m}{t} \tag{1}$$

where E (ng min^{-1}) is the emission rate of each compound, Δm (ng) is the average mass loss between two weighing times, and t (min) is the permeation period. The concentration of each compound was estimated using Eq. (2),

$$C_{gas} = \frac{E}{Q} \tag{2}$$

where C_{gas} is the concentration of compound of interest (ng mL^{-1}), Q is air flow rate in the system (mL min^{-1}).

To be comparable with most literature data, gas concentration were converted to volume concentration by Eq. (3),

$$C_{ppm} = C_{gas} \times \frac{R \times T}{MW \times P} \tag{3}$$

where C_{ppm} is gas concentration in parts per million (ppmv), R is ideal gas law constant, $R = 8.314$ (m^3 Pa K^{-1} mol^{-1}), P and T are atmospheric pressure ($P = 101.32$ kPa under atmospheric conditions) and temperature (K), respectively, and MW is the molecular weight of each compound (g mol^{-1}). Since experimental conditions were normalized to $T = 298$ (K) (25 °C), and $P = 101.32$ (kPa). Equation (3) can be simplified to Eq. (4):

$$C_{ppm} = C_{gas} \times \frac{8.314 \times 298}{MW \times 101.32} = 24.4 \times \frac{C_{gas}}{MW} \tag{4}$$

where C_{gas} was gas concentration in ng mL^{-1} calculated from Eq. (2).

Under constant temperature, different gas concentrations could be achieved by changing the airflow, according to Eq. (2). Successful generation of constant VOCs (VFAs and phenolics) emissions at trace levels deploying the permeation tube technology was reported previously [35].

Differing concentrations were achieved by changing the air flow rate, i.e., the maximum concentration corresponding to 300 mL min^{-1} of air flow and the minimum concentration corresponding to 5000 mL min^{-1} (Table 2). The carrier gas was 99.995% pure air (pure oxygen or pure nitrogen are optional carrier gases based on experimental needs). These concentrations were controlled precisely using mass flow controllers. The stability of