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Simultaneous Characterization of VOCs and Livestock Odors Using Solid-Phase Microextraction - Multidimensional Gas Chromatography- Mass Spectrometry-Olfactometry

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Livestock manure is a very complex source of odor, volatile organic compounds (VOCs) and other gases that can affect local and regional air quality. Identification of VOCs responsible for odor can be used to solve livestock odor problem. In this research solid phase microextraction (SPME) and a multidimensional (MD)-GC-MS-Olfactometry system was used for the separation, isolation and identification of compounds in swine manure headspace. Olfactometry analyses using human nose as a detector were simultaneous with chemical analysis via the MS. Odor analyses including odor character and odor intensity were performed in both modes. Several SPME fiber coatings were compared for their extraction efficiency for a wide range of compounds extracted from manure headspace. The Carboxen/PDMS 85 μm coating was the best overall SPME fiber coating for extractions of a wide range of analytes emitted from swine manure. As many as 295 compounds were identified as emitted to headspace from swine manure using the SPME-MDGC-MS-O. Seventy one compounds were recognized as odorous compounds. Sixteen of the compounds identified were listed as hazardous air pollutants. Among the 295 compounds identified, 188 were not reported in previous studies and physical and chemical properties of the compounds emitted from swine manure were also studied and summarized.

1. Introduction

1.1 Livestock odor and VOCs

Swine operations are sources of aerial emissions of odors, VOCs, particulate matter, and other gases. The main source of malodor is microbial degradation in the anaerobic environment of manure storage. A limited number of studies have attempted to determine the relationship between VOCs and corresponding livestock odor (Schaefer, 1977; Yasuhara et al., 1984; Kai and Schafer, 2004; Zahn et al., 1997; Schiffman et al.

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2001. Most recently, Lo et al. (2008) published a list of 295 compounds identified in swine manure headspace.

1.2 Properties of VOCs

VOCs identified in and around swine operations can be classified into many different chemical groups including acids, alcohols, aldehydes, amines, VFAs, hydrocarbons, ketones, indoles, phenols, N-containing compounds, S-containing compounds, and other compounds. Thus, the chemical/sensory characterization of these compounds is challenging due to the wide range of physicochemical properties. Large uncertainties are associated with published detection thresholds (DTs) (e.g., Devos et al., 1990).

1.3 Measurements of livestock VOCs

No standard method is available for odor-causing VOCs in livestock environments. Part of the challenge is due to polar and reactive VOCs undergoing reactions, interacting with sampling lines and containers, and the presence of moisture (Koziel et al. 2005). Some researchers attempted to modify USEPA methods to sample the VOCs in and around swine operations (Schiffman et al., 2001; Blunden et al., 2005, Zhang et al, 2010). SPME is an alternative for air sampling (Koziel and Pawliszyn, 2001).

1.4 Solid-phase microexctraction

SPME combines sampling and sample preparation into one step. Larreta et al., (2006) quantified VOCs in cow slurry and Cai et al., (2007) used SPME to evaluate the effectiveness of zeolite to control VOCs and odors emissions from poultry manure. SPME has been useful for qualitative characterization and screening of livestock gases. Sampling of livestock VOCs and odorants with SPME has been used to characterize swine dust odorants (Cai et al., 2006), downwind odor impact of beef cattle feedlot and of swine finisher operation (Koziel et al., 2006; Bulliner et al., 2006), and characterization of dairy manure (Laor et al., 2007). Lo et al., (2008) used SPME to for sampling of swine manure headspace and analysis with multidimensional GC-MS-O.

1.5 Gas chromatography – olfactometry (GC-O)

Gas chromatography coupled with a FID has been used for chemical separation and analysis of VOCs emitted from livestock operations (Schiffman et al., 2001; Begnaud et al., 2003; Kai and Schafer, 2004). Addition of sniff port enables simultaneous chemical and olfactometry analysis of livestock odor (Kai and Schafer, 2004; Cai et al., 2006). Another option is to use olfactometry with GC-mass spectrometry (MS). Cai et al. (2006) reported partitioning of odorants to various fractions of swine dust. Koziel et al. (2006) used GC-MS-O to analyze air samples downwind from swine finisher barns. A single-column cannot always separate a complex air sample. Thus, multidimensional GC provides powerful way to resolve the complex livestock air.

1.6 Multidimensional GC

Multidimensional GC (MDGC) utilizing multiple columns represents the state-of-the-art refinement for the separation of VOCs and semi-VOCs. Recently, multidimensional (MD)-GC-MS-O approach was used to analyze complex odorous samples from swine, poultry and dairy operations (Bulliner et al., 2006; Laor et al., 2007; Lo et al., 2008).

The overall objective of this research was to identify and characterize VOCs emitted from swine manure using SPME and MDGC-MS-O. The advantage is the enhanced

VOC separation and the simultaneous odor identification for improved the understanding of the environmental impact of livestock farming.

2. Methods

Manure samples were collected from the nursery, finisher and the outside storage pits, respectively, at the swine research farm in Ames, Iowa. Manure samples were then dispensed (15 mL) into 40 mL vials with PTFE-lined silicone septum (Lo et al., 2008).

2.1 Sampling and sample preparation of swine manure headspace with SPME

Four SPME fibers, i.e., Carboxen/PDMS 85 µm, PDMS 100 µm, Polyacrylate 85 µm and PDMS/DVB 65 µm were first used to select the most efficient fiber coating in extracting VOCs/semi-VOCs emitted from manure. For practical reasons, a 24 hr SPME extraction at room temperature was selected (Lo et al., 2008).

2.2 Analyses of swine manure headspace samples with MDGC-MS-O

Simultaneous chemical and sensory analyses of gases emitted from swine manure were completed using the MDGC-MS-O system (Lo et al., 2008). The system components, the software, and GC oven programs are described in Cai et al. (2006). MD capability was used for better separation of gases and odors of compounds associated with swine manure. Heartcut (HC) is defined a part of a sample “cut” from the pre-column and transferred to the column with a Dean’s switch. Compounds were further separated on the column and then simultaneously analyzed on the MSD and the sniff port. A series of 30 sec-wide HCs starting from 0.05 to 24 min were used to methodically separate and enhance identification of new compounds.

2.3 Data analysis and interpretation

Three sets of signals were generated for each sample including the total ion chromatogram (TIC), the FID signal, and the aromagram (Lo et al., 2008). Data were analyzed using the AromaTrax, BenchTop/PBM, and NIST library software. Selected physicochemical properties for the identified compounds were selected to better characterize compounds emitted from swine manure (Lo et al., 2008).

3. Results

3.1 SPME fiber selection

Based on the comparison of both the chemical and olfactometry data analysis, Carboxen/PDMS fiber coating was the most effective coating for extraction in terms of number of compounds extracted, number of odor events recorded, odor intensity and odor event peak area count (Lo et al., 2008). Therefore Carboxen/PDMS 85 µm coating was selected for subsequent extractions of gases from swine manure headspace.

3.2 Multidimensional GC-MS-O

Headspace samples were analyzed with the MDGC-MS-O mode utilizing 30 sec-wide HCs. An example of a 30 sec HC is shown in Figure 1. The aromagram recorded was only for the odors detected from the 30 sec-wide HC. It is interesting to note that 23 odor events were recorded, which allowed for easier matching of odor events and chemical compounds. The chromatographic separations were improved. Sample background from co-eluting compounds was also lower, allowing for improved spectral matches.

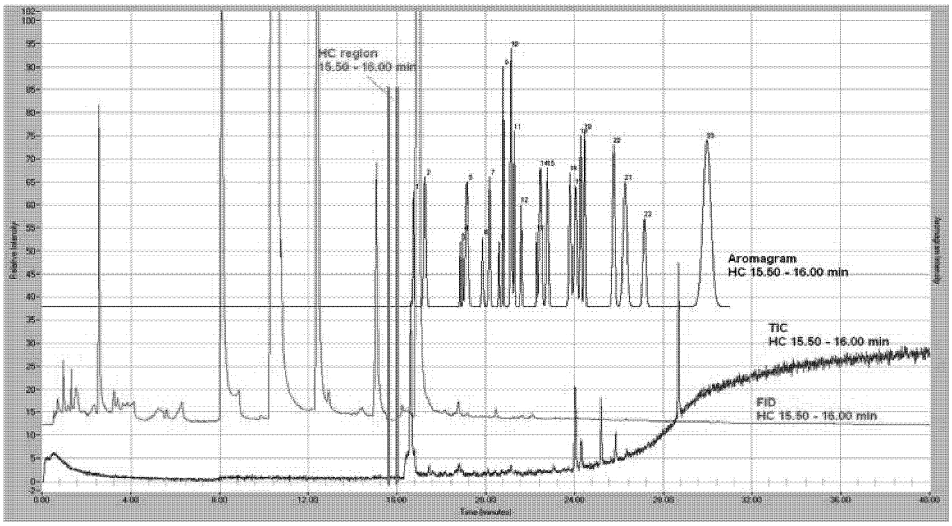

Figure 1. Comparison of aromagram, flame ionization detector (FID), total ion chromatogram (TIC) signals with heartcut (HC) between 15.50 min to 16.00 min.

3.3 Identification of VOCs and semi-VOCs

Summary of all 295 compounds identified in swine manure headspace is provided in full in Lo et al., 2008 and cannot be provided here due to page limit. The summary contains the chromatographic retention time, compound name, the CAS number and the heartcut timing for which a compound was first detected. Whenever applicable, published or detected odor character, detection threshold (e.g., Devos et al., 1990), and estimated atmospheric lifetime were also listed. Odor descriptors recorded by the panelist was presented, along with odor descriptors obtained from literature.

A total of 295 compounds emitted from swine manure were identified. These compounds can be classified into 12 chemical classes with the numbers of compounds in each class , i.e., acids (9), alcohols (33), aldehydes (4), aromatics (32), esters (6), ethers(10), fixed gases (2), hydrocarbons (36), ketones (71), nitrogen-containing compounds (35), phenols (19) and sulfur-containing compounds (38). Molecular weights ranged from 34 to 260. Of these 295 compounds, 113 were positively confirmed with pure standards. Approximately 25% of the total compounds had distinct odor. Approximately 107 compounds had been reported in previous studies. The total of 188 compounds were reported here for the first time and 26 of them had a distinct odor. Sixteen compounds found in this research are listed as hazardous air pollutants by the US EPA. Only 77 compounds identified had DTs published in previous studies (e.g., Devos et al., 1990). The majority (~80%) of compounds had their DTs between 1 nL/L to 1 μL/L. The six compounds with a DT less than 1 nL/L were 2-bromo-phenol, indole, 2,4-hexadienal, skatole, 2-chloro-phenol and 2,6-dimethyl-phenol. Approximately 47% of odorous compounds had odor character that can be considered "offensive.

3.4 Characterization of physicochemical properties of VOCs

VOCs emitted from manure represent very wide ranges of physicochemical properties. Summary of all findings was presented by Lo et al (2008). Approximately 89% of the compounds identified fell into the category of VOCs and semi-VOCs (< 12C) with about 74% within C5 – C10. The compound identified with the highest carbon number was heptadecane ($C_{17}H_{36}$), and the compounds with the lowest carbon number included methanethiol (CH_4S) and carbon disulfide (CS_2). It is remarkable that the Carboxen/PDMS SPME fiber was capable of extracting these compounds. The b.p. of 215 compounds (for which boiling points were known or published) ranged from -60.3 to 322 ˚C with a mean b.p. of 168 ˚C. Vapor pressure and sol. of 219 compounds (for which vapor pressure was known or published) were summarized (Lo et al., 2008). As many as 86% of compounds had a Henry's law constant, defining the solubility of gases in pure water < 0.01 (atm-m3/mole). Water-octanol partitioning coefficients ranged from -2.2 to 9.26. More than half of compounds (approximately 68%) had an estimated atmospheric lifetime τ less than 24 hrs, which are considered as very reactive, with dimethyl disulfide (τ = 1.224 h) being the most reactive compound emitted from swine manure.

4. Conclusions

The following conclusions can be drawn from this research:

a) SPME combined with MDGC-MS-O was a powerful tool for extraction and separate VOCs and gases emitted from swine manure, to identify compounds and to determine their odor characters. The use of heartcut improved chromatographic separations and compound identification.
b) A wide range of VOCs and gases were emitted from swine manure. As many as 295 compounds were identified from the gas samples using MDGC-MS-O. Seventy one compounds were recognized as odorous compounds.
c) Among the 295 compounds identified, 188 were not reported in previous studies. This total number (295) also represents an improvement by 44 of the total number of compounds listed in the most comprehensive summary of compounds present in swine manure and/or air around swine operations (Schiffman et al., 2001).

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