Simultaneous Chemical and Sensory Characterization of VOCs and Semi-VOCs Emitted from Swine Manure Using SPME and Multidimensional Gas Chromatography-Mass Spectrometry-Olfactometry

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Summary and Implications

Swine manure is associated with emissions of odor, volatile organic compounds (VOCs), and other gases that can affect air quality on local and regional scales. In this research, solid phase microextraction (SPME) and novel multidimensional gas chromatography-mass spectrometry-olfactometry (MDGC-MS-O) system were used to simultaneously identify VOCs and related odors emitted from swine manure. Gas samples were extracted from manure headspace using Carboxen/polydimethylsiloxane (PDMS) 85 µm SPME fibers. The MDGC-MS-O system was equipped with two columns in series with a system of valves allowing transfer of samples between columns (heartcutting). The heartcuts were used to maximize the isolation, separation, and identification of compounds. The odor impact of separated compounds was evaluated by a trained panelist for character and intensity. A total of 295 compounds with molecular weights ranging from 34 to 260 were identified. Seventy-one compounds had a distinct odor. Nearly 65% of the compounds for which reactions rates with OH• radicals are known had an estimated atmospheric lifetime < 24 hrs.

Introduction

Swine operations are sources of aerial emissions of odors, volatile organic compounds (VOCs), particulate matter, and other gases including NH_3, H_2S, and methane. A number of studies have been conducted to identify compounds emitted from swine manure. However, a limited number of studies have attempted to determine the relationship between VOCs and corresponding odor.

The overall objective of this research was to identify and characterize VOCs emitted from swine manure using SPME and MDGC-MS-O. To date, no studies related to VOCs emitted from livestock operations have been conducted using the MDGC-MS-O system. The advantages of using MDGC-MS-O are enhanced VOC separation and simultaneous odor identification. It is critical to characterize swine manure VOCs and malodorous gases to improve the understanding of the environmental impact of swine operations. This knowledge is also needed to develop and evaluate odor and gas mitigation strategies and technologies.

Materials and Methods

Manure samples were collected from the nursery pit, the finisher pit, and outside storage pit at the Swine Nutrition and Management Research Farm (Ames, IA). Four commercially available SPME fibers, including Carboxen/PDMS 85 µm, PDMS 100 µm, Polyacrylate 85 µm, and PDMS/DVB 65 µm (Supelco, Bellefonte, PA) were used to select the most efficient fiber coating in extracting VOCs and semi-VOCs emitted from swine manure. Simultaneous chemical and sensory analyses of gases emitted from swine manure were completed using the MDGC-MS-O (Microanalytics, Round Rock, TX) system. The MDGC-MS-O system with heart cut was capable of working in 3 modes, i.e., GC-FID only, GC-FID-O, and GC-MS-O. The MultiTrax (Microanalytics, Round Rock, TX) software was used to control the timing of valves and heartcuts (HC) for each mode.

Results and Discussion

SPME combined with MDGC-MS-O was a powerful tool used to extract 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.

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. Sixteen of the compounds identified were listed as HAPs. The six compounds with DT less than 1 ppb were 2-bromo-phenol, indole, 2,4-hexadienal, skatole, 2-chloro-phenol, and 2,6-dimethyl-phenol.

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).

Physical and chemical properties of the compounds emitted from swine manure were studied and summarized.

The 295 compounds identified were classified into 12 chemical classes: 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).

Nearly 65% of the total 218 compounds (for which the reaction rate with OH• was known) had an estimated atmospheric lifetime (τ) < 24 hrs. Dimethyl disulfide (τ = 1.22 hrs) was the most reactive in this group.

Acknowledgements

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Figure 1. Simultaneous chemical and olfactory analysis of odor and VOCs emitted from swine manure using GC-MS-O.

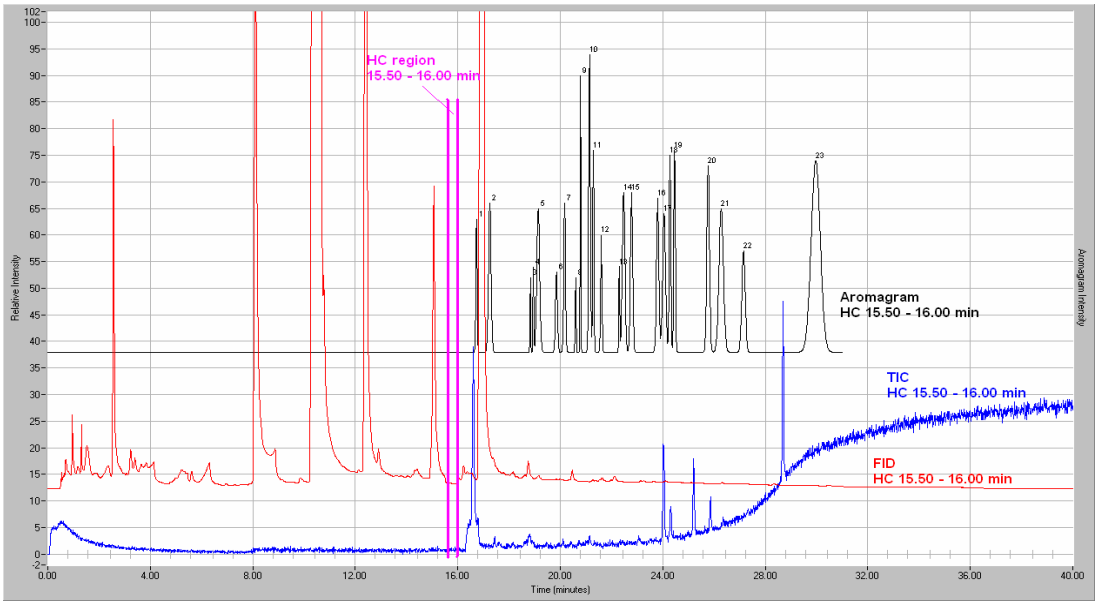

Figure 2. Example of the enhanced chemical and olfactrometry separation for identification of most offensive odorants. Comparison of aromagram, FID, TIC signals with HC between 15.50 min to 16.00 min.