Characterization of Volatile Organic Compounds and Odorants Associated with Swine Barn Particulate Matter Using Solid-Phase Microextraction and Gas Chromatography-Mass Spectrometry-Olfactometry

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Summary and Implications

Swine operations can affect air quality by emissions of odor, volatile organic compounds (VOCs) and other gases, and particulate matter (PM). Particulate matter has been proposed to be an important pathway for carrying odor. In this research, continuous PM sampling was conducted simultaneously with three collocated TEOM (tapered element oscicllating microbalance) analyzers inside a 1000-head swine finish barn located in central Iowa. Each TEOM was fitted with total suspended particulate (TSP), PM-10, PM-2.5 and PM-1 preseparators. Used filters were stored in 40 mL vials and transported to the laboratory. Carboxen/polydimethylsiloxane (PDMS) 85 µm solid phase microextraction (SPME) fibers were used to extract VOCs. Simultaneous chemical and olfactometry analyses of VOCs and odor associated with swine PM were completed using a gas chromatography-mass spectrometer-olfactometry (GC-MS-O) system. Fifty VOCs categorized into nine chemical function groups were identified and confirmed with standards. Five of them are classified as hazardous air pollutants. VOCs were characterized with a wide range of molecular weight, boiling points, vapor pressures, water solubilities, odor detection thresholds, and atmospheric reactivities. All characteristic swine VOCs and odorants were present in PM and their abundance was proportional to PM size. However, the majority of VOCs and characteristic swine odorants were preferentially bound to smaller-size PM. The findings indicate that a significant fraction of swine odor can be carried by PM.

Introduction

Airborne PM inside barns consisting of swine skin cells, feces, feed, bacteria, and fungi contribute to potentially poor indoor air quality. The dust sources are feed, fecal matter, dander, mold, mineral ash, pollen, and insect parts. Most of the odor of swine barns is carried on dust. Previous studies focused mainly on total PM in swine housing. To date, little is known about odor-VOCs-PM interactions, particularly for PM sizes of interest to regulatory agencies. In this study, headspace (HS) SPME combined with GC-MS-O system was used to identify VOCs and characterize the key odors adsorbed/absorbed on different size swine barn dust (PM-1, PM-2.5, PM-10, and the total suspended particulate (TSP)).

Materials and Methods

Tapered element oscillating microbalance (TEOM, Model 1400a, Rupprecht & Patashnick, East Greenbush, NY, USA), is a commercially available device for the continuous real-time measurement of airborne particles (TSP, particulate matter less than PM-10, PM-2.5, and PM-1, respectively).

SPME extractions were performed with a manual fiber holder from Supelco (Bellefonte, PA). Three commercially available fibers—PDMS 100 µm, 85 µm Carboxen/PDMS, and 70 µm Carbowax /DVB—were used to select the SPME coating capable of extracting maximum amounts of VOCs typically associated with swine odor. Multidimensional GC-MS-O (from Microanalytics, Round Rock, TX) was used for simultaneous chemical and sensory analyses.

Results and Discussion

HS-SPME coupled with GC-MS-Olfactometry is a novel and effective analytical tool for identifying VOCs and odor associated with swine barn PM. The most effective SPME fiber for HS-SPME is the Carboxen/PDMS.

A total of 50 different compounds were identified using HS-SPME-GC-MS–O approach, 21 of which have been reported to be present in swine barn PM for the first time. The 50 compounds covered a wide range of polarity and molecular weight (34.08-234.39) and belong to nine chemical classes: alkanes (4), alcohols (4), aldehydes (8), ketones (7), acids (8), amines and nitrogen heterocycles (8), sulfides and thiols (3), aromatics (7), and furans (1). Five compounds are classified as HAPs: styrene, acetamide, N, N-dimethyl formamide, phenol, and 4-methyl phenol.

The 50 compounds detected in swine barn PM were characterized by a wide range of physicochemical parameters including carbon number, b.p., v.p., sol., log Kow, and atmospheric lifetime. Sixty percent of compounds were within the C5-C8 range, 68% had b.p. between 80 and 230 ºC, 48% had v.p. > 0.52 mmHg, 64% were very soluble in water (500 to 5E+05 mg/L), 78% had a log Kow < 3, and 58% had τOH < 24 hr.

Key malodorants associated with swine barn PM include methyl mercaptan, isovaleric acid, 4-methyl-phenol, indole, and skatole. Twenty-four odorous compounds were selected for comparing the adsorption capacity between PM-1, PM-10, and TSP, including H2S, methyl mercaptan, trimethylamine, acetone, diacetyl, 7 aldehydes, 7 volatile fatty acids, phenol, 4-methyl- and 4-ethyl phenol, indole, and skatole. TSP adsorbed a much more absolute amount of those compounds and odors than PM-10 and PM-1, respectively. However, when absolute amounts of compounds and odors were normalized by the PM mass and the total surface area, the values (area count/M/TSA) of those compounds showed a significant difference. PM-1 had a greater capacity for characteristic VOCs and odors relative to PM-10 and TSP.

Acknowledgements

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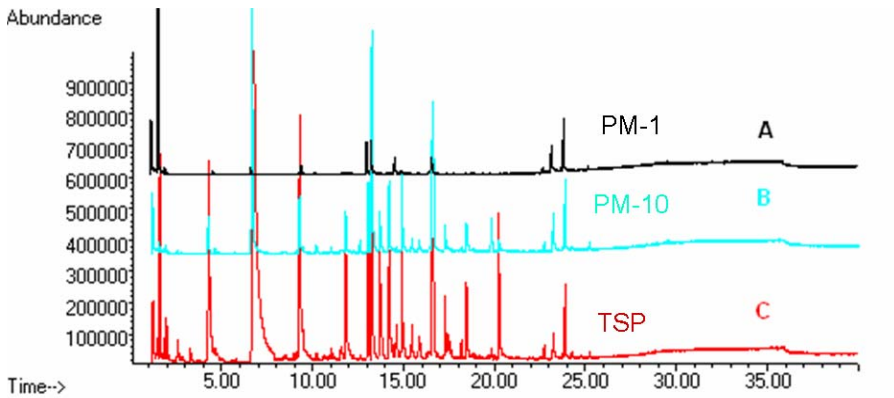

Figure 1. Comparison of adsorption capacity between difference size PM.

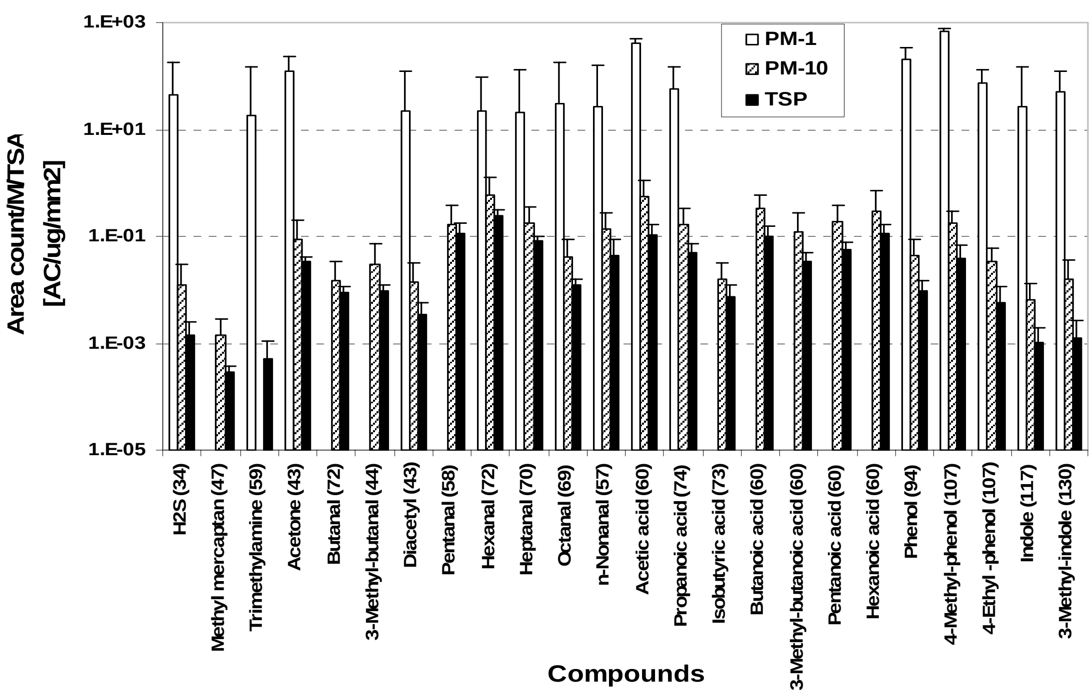

Figure 2. Comparison of peak area count / Mass $_{PM}$/total surface area (TSA) of selected VOCs in swine barn TSP, PM-10, and PM-1. Error bars show the plus standard deviation of the mean. Number in parentheses is the single ion of each compound used for peak area count integration.