

# Solid-Phase Microextraction as a Novel Air Sampling Technology for Improved, GC-Olfactometry-Based, Assessment of Livestock Odors

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## Summary and Implications

Air sampling and characterization of odorous livestock gases is one of the most challenging analytical tasks. This is due to low concentrations, physicochemical properties, and problems with sample recoveries for typical odorants. Livestock operations emit a very complex mixture of volatile organic compounds and other gases. Many of these gases are odorous. Relatively little is known about the link between specific VOCs/gases and specifically, about the impact of specific odorants downwind from sources. In this research, solid-phase microextraction (SPME) was used for field air sampling of odors downwind from swine and beef cattle operations. Sampling time ranged from 20 min to 1 hr. Samples were analyzed using a commercial GC-MS-Olfactometry system. Odor profiling efforts were directed at odorant prioritization with respect to distance from the source. Results indicated the odor downwind was increasingly defined by a smaller number of high priority odorants. These 'character-defining' odorants appeared to be dominated by compounds of relatively low volatility, high molecular weight, and high polarity. In particular, *p*-cresol alone appeared to carry much of the overall odor impact for swine and beef cattle operations. Of particular interest was the character-defining odor impact of *p*-cresol as far as 16 km downwind of the nearest beef cattle feedlot. The findings are very relevant to scientists and engineers working on improved air sampling and analysis protocols and on improved technologies for odor abatement. More research evaluating the use of *p*-cresol and a few other key odorants as a surrogate for overall odor dispersion modeling is warranted.

## Introduction

Livestock operations are sources of aerial emissions of gases, odor, and particulate matter. A large body of excellent analytical work has been reported during the past three decades relative to the volatile compounds emitted by confined animal feeding operations (CAFOs). The challenge relative to the CAFO odor issue is to extract from this large field of 'potential' odorants the compounds which carry primary responsibility for the downwind odor complaints relative to these operations.

Identification and quantification of the major key odorants downwind of CAFOs is needed to develop and evaluate effective technologies and approaches to control odor. Proper sampling and analysis protocols are needed to facilitate both of these tasks. Prioritization of individual odorants relative to odor impact at downwind receptors can be an extremely important consideration in the development of odor assessment sampling and analysis protocols.

The primary objective was to prioritize odorous gases responsible to swine odor downwind from typical finisher site in central Iowa. The secondary objective was to compare these results with the odor prioritizations previously reported for beef cattle feedlots for shorter distances. We used SPME for field air sampling of odorants downwind from a swine finisher site in Iowa. All analyses were done using GC-MS-O. The long term goal of this research is to address three major challenges confronting on-going efforts to develop objective and quantitative instrument-based odor assessment protocols for CAFO environments. These include: (1) validation of the concept of odorant prioritization, (2) refinement and expansion of the initial prioritizations to other livestock and poultry CAFOs, and (3) development of sampling and analytical protocols which more closely reflect the population 'consensus' prioritizations which emerge from successfully addressing the first two challenges.

## Materials and Methods

MDGC-MS-O is an integrated approach combining olfactometry and multidimensional GC separation techniques with conventional GC-MS instrumentation. A commercial, integrated AromaTrax™ system (Microanalytics, Round Rock, TX) was used for the GC-olfactometry profiling work.

SPME utilizing a 1 cm Carboxen modified PDMS - 75 µm and the PDMS - 100 µm fibers (Supelco, Bellefonte, PA) was used for ambient air sampling in this odor profiling study. SPME collections were carried out by exposing the fiber to ambient air at the source and several downwind locations relative to a commercial swine operation in central Iowa. Downwind air sampling was performed in the Fall 2004 in central Iowa. We compared resulting odorant prioritization with our earlier published work on downwind odorants from beef cattle feedlots in Texas.

## Results and Discussion

SPME was very useful in extracting livestock odorants from ambient air. It interfaced well with the GC-MS-Olfactometry system that in turn, facilitated simultaneous

chemical and sensory analyses. Based upon past and current GC-O based odor profile efforts, *p*-cresol appears to be the key ‘character-defining’ odorant relative to downwind, distance separation from swine CAFOs. These results were consistent with our earlier published work in beef cattle feedlot odor. If these preliminary prioritizations can be proven consistently across a broader sampling of similar environments and analytical parameters, there will be increasing impetus for critical review of current sampling, analytical, and odor abatement strategies. Particular attention appears to be warranted for *p*-cresol and other high priority semi-volatile odorants such as 4-ethyl phenol and 2'-aminoacetophenone due to their apparent odor impact prominence. In addition, improved sampling and analysis methodologies need to be developed for these compounds due to their well-documented sensitivity to

adsorption driven loss to the walls of plastic sample containers. SPME could be very useful as one possible alternative to current methods. Success in identifying this minimal critical odorant set from CAFOs simplifies the challenge of translating current, subjective, human ‘detector’-based odor assessment protocols to objective, instrument-based alternatives. The results reported here serve as added impetus for critical review of current odor assessment sampling and analysis protocols for the CAFO odor application.

**Acknowledgements**

The authors would like to thank the Iowa swine producer for the access to the site and cooperation on this research.

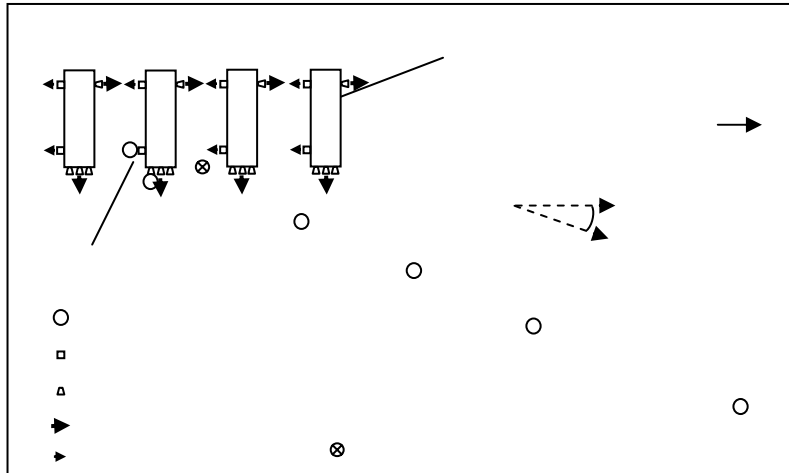


Figure 1. Schematic of field air sampling downwind from 4-barn swine finishing operation in Iowa with deep pit manure management system.

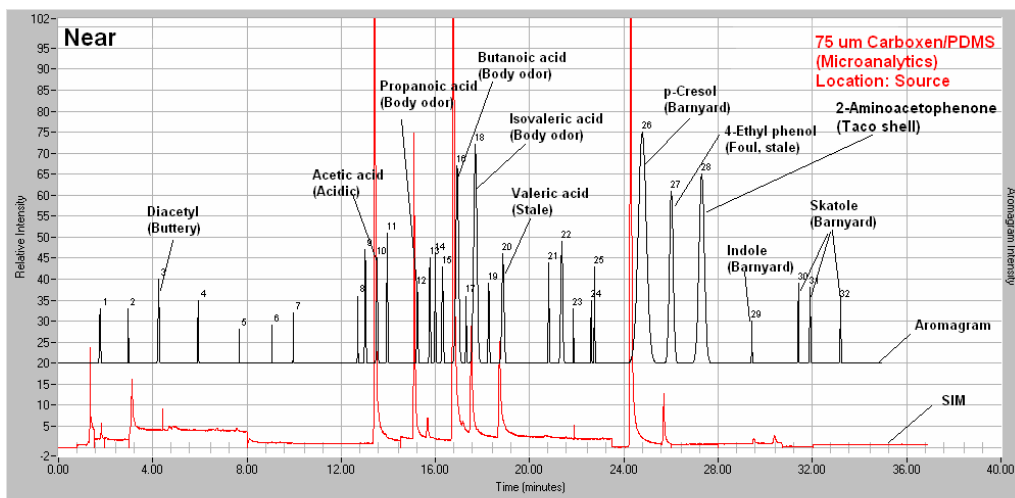


Figure 2. Comparison of chromatogram (lower, red line) and aromagram (upper, black line) of swine barn ambient air at source (“Near” plot) location using SPME. Similar plots were obtained at sampling locations 1, 2, 3, and 4, respectively. *P*-cresol was the odorous compound most closely associated with the characteristic swine barn odor at near and far locations downwind from the site.