Field Air Sampling with SPME for Ranking and Prioritization of Downwind Livestock Odors with MDGC-MS-Olfactometry

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Abstract
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Keywords
air pollution, chemical analysis, chemical sensors

Disciplines
Agriculture | Bioresource and Agricultural Engineering

Comments
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Citation: AIP Conf. Proc. 1137, 333 (2009); doi: 10.1063/1.3156540
View online: http://dx.doi.org/10.1063/1.3156540
View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1137&Issue=1
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Field Air Sampling with SPME for Ranking and Prioritization of Downwind Livestock Odors with MDGC-MS-Olfactometry

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Abstract. 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. The 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 the overall odor dispersion modeling is warranted.

Keywords: Odor, VOCs, livestock, air sampling, SPME.

PACS: 01.30.Cc.

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).¹,² A variety of sampling and sample preparation techniques have been utilized in the extractions of scores, if not hundreds, of volatile compounds in these environments. These include acid traps, solvent extraction, sorbent tubes and thermal desorption, whole air sampling in canisters or sampling bags, and SPME.¹-³ A relatively small subset of previous studies involved actual field measurements downwind from these facilities.²,³ Yet, the downwind impact of volatile compounds affects air quality and subsequently often results in nuisance complaints from an affected population. Included among these volatiles are a large number of compounds which are known to be potent individual odorants.¹ 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.²

There is a popular ‘school of thought’ which states that there are no odorants emitted by CAFO environments which are sufficiently dominant to be utilized as quantitative odor markers. As a result, much of the odor assessment work to date has been restricted to qualitative assessment utilizing ‘human’ detectors in conjunction with techniques such as dynamic dilution olfactometry. Past and recent GC-Olfactometry (GC-O) work which has been carried out by these and other authors suggests that CAFO odor assessment should, in fact, be translatable to objective, instrument-based protocols such as those proposed by Pollien at al.²,⁵ Wright et al. (2005) used the SPME and a GC-MS-O approaches for beef cattle and swine operations in
This work suggested that the key odorants that significantly contribute to the characteristic malodor of swine barn relative to distance separation from high density CAFOs are dominated by just a few compounds (i.e., 4-methyl phenol a.k.a. p-cresol, 4-ethyl phenol, isovaleric acid, 2'-aminoacetophenone, indole and skatole), which are characterized by relatively low volatility, high polarity and extreme odor potency.

The identification of and quantification of the major key odorants downwind of CAFO’s 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. There is absolute truth to the old adage that ‘the analysis is only as good as the sample to which it is applied’. This consideration is especially pertinent to the question of environmental odor assessment in general and CAFO odor assessment in particular. For example, much of the odor monitoring work to date has been carried out utilizing sampling protocols which are based upon Tedlar™ (or alternate plastic) bags. Unfortunately, the propensity for plastic films to rapidly adsorb semi-volatile compounds from contained gas samples has been well documented.

Other air sampling and sample preparation techniques have a potential for better sample recovery of odorous VOCs. Koziel et al. (2005) showed that the Carboxen/PDMS SPME coating and sorbent Tenax TA/thermal desorption are capable of recovering an average of 98.3% and 88.3%, respectively, of 11 odorous analytes from a standard gas mixture at 24 hrs sample preservation time at room temperature. To date, relatively few published data exist on the quantitative use of SPME for characterization of ambient air.

In this research, we used SPME for field air sampling of odorants downwind from a swine CAFO in Iowa. In addition, we used SPME for far downwind odor impact of a beef cattle feedlot in Texas. The secondary objective was to compare these results with the odor prioritizations previously reported for beef cattle feedlots for shorter distances.

EXPERIMENTAL AND METHODS

Multidimensional Gas Chromatography-Mass Spectrometry-Olfactometry

MDGC-MS-O is an integrated approach combining olfactometry and multidimensional GC separation techniques with conventional GC-MS instrumentation. A commercial, integrated AromaTrax™ system (from Microanalytics, Round Rock, TX) was used for the GC-olfactometry profiling work as presented below. The system integrates a conventional GC-MS (Agilent 6890N GC / 5973 MS with the addition of an olfactory port, MDGC control, flame ionization detector (FID) and olfactory data acquisition software. The SIM mode targeted H₂S, mercaptans, VFAs, phenolics, indolics, and phenones. Mass/molecular weight to charge ratio (m/z) range was set between 34 and 250 in the scan mode.

Air Sampling with SPME

SPME utilizing a Carboxen modified PDMS 75 µm and the PDMS 100 µm fibers was used for ambient air sampling in this odor profiling study. Before sampling, fibers were desorbed for 5 min at 260 °C, then wrapped in clean aluminum foil, enclosed in a clean jar, placed in a cooler with blue ice and carried to sampling site. SPME fibers were transported to the laboratory enfolded in clean, aluminum foil, placed inside a clean jar with a tight cover and then in a cooler with blue ice.

Swine Odor Sampling

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. All air samples were collected on the afternoon of November 9, 2004 at 1 m height and utilized variations in downwind distance for cross-comparison purposes (Figure 1). Samples were collected at the source (continuous barn exhaust fan) and at four locations downwind, i.e., approximately at 109, 159, 214, and 294 m, respectively, from the center of the emission site, at the tunnel end of the barns (Figure 1). Three rounds of samples consisting of 20-min sampling periods with one SPME fiber per location were collected consecutively. The first two rounds utilized the Carboxen/PDMS coating and the last one utilized the PDMS coating. In addition, one sample was collected with a PDMS coating at the pit fan. Wind was S-SW and steady during sampling. No other CAFOs were present upwind from this facility within at least 16 km. All SPME collections were carried out under ambient conditions.
BeeF Cattle Odor Sampling

Downwind sampling during the characteristic odor event was conducted on March 18, 2004 in Amarillo, Texas. The characteristic odor events occur a few times a year, typically within a few days following rain or snow-thawing. The subjective far-downwind perception of odor during these odor events is typically comparable to perception of odor at a large beef cattle feedlot, i.e., at the source. Two rain events occurred prior to this sampling event. On March 12 and 13, 1.5 and 0.5 mm of rain fell, respectively, followed by several days of cold weather. One day prior to this odor event, the ambient air temperature maximum increased by 5 °C from the day before to 25 °C, creating the appropriate conditions for the odor event to occur. For this event, 1-hr long sampling with Carboxen/PDMS 75 µm was completed between 8 and 9 P.M. at the Texas Agricultural Experiment Station grounds in Amarillo.

RESULTS

Swine Odor

Each air sample analysis resulted in simultaneous collection of a chromatogram and aromagram. The data shown emphasizes the relationship between the distance of the downwind separation from the source showing the two extreme locations, i.e., at the exhaust fan and 294 m downwind. As expected, locations at or near these source facilities appear to be characterized by greater odor complexity with a greater number and variety of individual odorants rising above their individual odor detection thresholds. Chromatograms and aromagrams for air samples collected in between, i.e., locations 1 to 3, were progressively less complex and consistent with the trend described above. The natural dilution effect associated with increasing distance from these sources had the effect of simplifying the resulting odor profiles, i.e., by reducing both the number of individual odorants detected and the relative intensities of those odorants that are detected. The total odor and the number of distinct odor/aroma events were generally decreasing with distance from the source, e.g., 32, 26, 18, 18, and 12 odors for series (II) at the source, location #1, #2, #3, and #4, respectively.

P-cresol (4-methyl phenol) with the characteristic “barnyard” odor character represented the dominant odorant relative to both near-source and at-distance sampling locations. This was true for all 3 sample series and locations. This dominance was reflected in responses by the GC-O panelist to both perceived odorant intensity as well as perceived odor character. This prioritization of p-cresol relative to at-distance separation from the swine CAFO source is in agreement with earlier profiles developed for beef cattle CAFOs. Relative to the near-site collection, only the dimethyl trisulfide (DMTS) homolog of the sulfide series caused a distinct individual odor response (i.e., ‘onion’ and ‘fecal’ character). There were no significant odor responses for H₂S or the
lower MW organic sulfide compounds. The profile of odorants which were secondary to p-cresol in odor impact prioritization was found to be in good agreement with that previously shown for cattle CAFOs. These included: isovaleric acid, 2'-aminoacetophenone (‘taco shell, urinous’), 4-ethyl phenol, butyric acid and diacetyl.

Odor impact prioritization was estimated based upon the data presented above for near source and downwind from source (location #4). P-cresol and isovaleric acid were ranked as #1 and #2, respectively. They were followed by 2'-aminoacetophenone, and butyric acid, and guaiacol and DMTS for near and downwind locations, respectively. Somewhat surprisingly, in contrast to previous swine CAFO odor profile efforts, skatole and indole were not shown to be significant secondary odorants relative to this current series in downwind locations. It is assumed that this absence resulted from the extremely short SPME sampling times (20 min). Short exposure time bias relative to increasing molecular weight of volatiles is a well established characteristic of SPME sampling. These odor profile results were shown to be consistent with those previously reported by these authors for cattle CAFOs. P-cresol was also #1 prioritization odor impact odorant for beef cattle feedlots. These similarities serve as additional evidence supporting the suggestion that p-cresol is the odorant of greatest individual odor impact relative to either cattle or swine CAFOs.

**Beef Cattle Odor**

Samples were collected using Carboxen/PDMS 75 µm SPME and 1-hr sampling time. As many as 44 distinct odor events were recorded in one of the samples. Many of the important odorants were present, e.g., p-cresol, isovaleric acid, butyric acid, 4-ethyl phenol, and H2S. Acetic acid was one of the most abundant compounds detected. Sample #1 was significantly different than samples #2 and #3. The reason for this was likely differences in sample preservation during the transportation to the laboratory. These variations in replicates were likely the reason behind the apparent differences in odor analysis. Comparing of panelist responses to several characteristic odors and aromas collected in ambient air during an odor event in Amarillo. P-cresol was then the characteristic ‘barnyard’ odorant of the highest individual impact downwind, followed by butyric and isovaleric acids, and 4-ethyl phenol. It is remarkable to note that these samples were collected very far downwind from the nearest cattle feedyard (~16 km) and yet, the odor impact prioritization is very similar to those reported for much shorter distances (up to 2 km). In addition, the ranking of odorants is consistent between two panelists analyzing three samples.

**CONCLUSIONS**

SPME was very useful in extracting livestock odors 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 beef cattle and swine CAFOs. If these preliminary prioritizations can be proven consistent 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. 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.

**ACKNOWLEDGMENTS**

The authors would like to thank the Iowa swine producer for the access to the site. This work as published in reference #6.

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