

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

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Abstract

Air sampling and characterization of odorous livestock gases is one of the most challenging analytical tasks. This is because of low concentrations, physicochemical properties, and problems with sample recoveries for typical odorants. Livestock operations emit a very complex mixture of volatile organic compounds (VOCs) and other gases. Many of these gases are odorous. Relatively little is known about the link between characteristic VOCs/gases and, specifically, about the impact of characteristic odorants downwind from sources. In this research, solid-phase microextraction (SPME) is used for field air sampling of odors downwind from swine and beef cattle operations. Sampling time ranges from 20 min to 1 h. Samples are analyzed using a commercial gas chromatography–mass spectrometry–olfactometry system. Odor profiling efforts are directed at odorant prioritization, with respect to distance from the source. The results indicate the odor downwind is increasingly defined by a smaller number of high-priority odorants. These “character defining” odorants appear to be dominated by compounds of relatively low volatility, high molecular weight, and high polarity. In particular, *p*-cresol alone appears to carry much of the overall odor impact for swine and beef cattle operations. Of particular interest is the character-defining odor impact of *p*-cresol as far as 16 km downwind of the nearest beef cattle feedlot. The findings are highly 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 (1–3). 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) (2–20). 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 (4,5), solvent extraction (6–11), sorbent tubes and thermal desorption (11–16), whole air sampling in canisters or sampling bags (11,17), and solid-phase microextraction (SPME) (18–20). A relatively small subset of previous studies involved actual field measurements downwind from these facilities (5,6,20). However, 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 that are known to be potent individual odorants (3,11). The challenge relative to the CAFO odor issue is to extract from this large field of “potential” odorants, the compounds that carry primary responsibility for the downwind odor complaints relative to these operations (3,7,20).

There is a popular “school of thought” that states that there are no odorants emitted by CAFO environments that 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 (1). Past and recent (20–22) gas chromatography (GC)–olfactometry (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 et al. (23). Wright et al. (20) used the SPME and a GC–mass spectrometry (MS)–O approaches for beef cattle and swine operations in Texas. 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 (also known as *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 (20).

The identification and quantitation of the major key odorants downwind of CAFOs is needed to develop and evaluate effective

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technologies and approaches to control odor. Proper sampling and analysis protocols are needed to facilitate both of these tasks. The 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. It is impossible to overstate the importance of sampling quality to the overall validity of an analytical procedure. 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 that are based upon Tedlar (or alternate plastic) bags. Unfortunately, the propensity for plastic films to rapidly adsorb semivolatile compounds from contained gas samples has been well documented (16,24).

Other air sampling and sample preparation techniques have a potential for better sample recovery of odorous volatile organic compounds (VOCs). Koziel et al. (2005) showed that the carboxen (CAR)-polydimethylsiloxane (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 h sample preservation time at room temperature (24). The standard gas contained volatile fatty acids (C2–C7), *p*-cresol, 4-ethyl phenol, 2'-aminoacetophenone, and indole. SPME is a viable technology for quantitative indoor air sampling of aromatic VOCs, alkanes, and reactive gases such as formaldehyde (25–33). A review of SPME applications to indoor air sampling is presented elsewhere (33). To date, relatively few published data exist on the quantitative use of SPME for the characterization of ambient air (34). This is because calibrations in ambient air may be affected by changes in wind velocity, air temperature, competitive adsorption, and others. Lin et al. (33) reported on quantitation of C2 to C7 volatile fatty acids in ambient air using portable SPME samplers equipped with CAR-PDMS coating. This sampling protocol was developed based on the concept of rapid air sampling using SPME in constant forced cross flow (29,30), which was later improved upon by Chen et al. (35). Qualitative applications of SPME can be very useful in odor investigations conducted in ambient air. Wright et al. (20) showed the use of 85- μ m CAR-PDMS fibers to collect air samples in several locations downwind from beef cattle and swine operations. Field air samples collected on SPME were then analyzed on a GC-MS-O system for odorant ranking and prioritization.

In this research, SPME was used for field air sampling of odorants downwind from a swine CAFO in Iowa. In addition, SPME was used to determine the 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 (20). All analyses were carried out using GC-MS-O. The long-term goal of this research was to address three major challenges confronting ongoing efforts to develop objective and quantitative instrument-based odor assessment protocols for CAFO environments. These include: (i) validation of the concept of odorant prioritization; (ii) refinement and expansion of the initial prioritizations to other livestock and poultry CAFOs; and (iii) development of sampling and analytical protocols, which more closely reflect the popula-

tion “consensus”, prioritizations that emerge from successfully addressing the first two challenges.

Experimental

Multidimensional GC-MS-O

Multidimensional GC (MDGC)-MS-O is an integrated approach combining O and MDGC separation techniques with conventional GC-MS instrumentation. A commercial, integrated AromaTrax system (Microanalytics, Round Rock, TX) was used for the GC-O profiling work as presented later. The system integrates a conventional GC-MS (Agilent 6890N GC with a 5973 MS) (Agilent, Wilmington, DE) with the addition of an olfactory port, MDGC control, flame ionization detector (FID), and olfactory data acquisition software (MultiTrax V. 6.00 and AromaTrax V. 6.61 from Microanalytics and ChemStation from Agilent). The general run parameters used were as follows: injector, 260°C; FID, 280°C; column, 40°C initial, 3 min hold, increased 7°C/min, 220°C final, 10 min hold; carrier gas, He. Details regarding hardware and operational parameters have also been described in detail in the previous publication (20). Samples were analyzed using nearly identical instrumentation at the Atmospheric Air Quality Laboratory at the Iowa State University (ISU) campus and the Microanalytics laboratory in Round Rock, TX. Samples were analyzed in the selected ion monitoring (SIM) mode at Microanalytics and in the scan mode at ISU. The SIM mode targeted H₂S, mercaptans, VFAs, phenolics, indolics, and phenones. The *m/z* range was set between 34 and 250 in the scan mode. The spectra were collected at 6 scans/s, and the electron multiplier voltage was set to 1000 V. The MS detector was autotuned weekly.

Compounds were identified with three sets of criteria: (i) match of the retention time on the MDGC capillary column with the retention time of pure compounds run as standards; (ii) matching mass spectra of unknown compounds with BenchTop/PBM (Palisade Mass Spectrometry, Ithaca, NY) MS library search system and spectra of pure compounds; and (iii) matching odor character. Qualitative assessment of VOC abundance was measured as area counts under peaks for separated VOCs. Human panelists were used to sniff separated compounds simultaneously with chemical analyses. Odor caused by separated VOCs was evaluated with a 64-descriptor panel and intensity scale in Aromatraz software (Microanalytics, Round Rock, TX). Odor evaluations consisted of comparisons of the number of odor/aroma events, with odor intensity measured as the area under odor/aroma peaks in aromagrams.

Air sampling with SPME

SPME (32,33), utilizing a 1-cm CAR modified PDMS 75- μ m fiber and PDMS 100- μ m fibers (Supelco, Bellefonte, PA), was used for ambient air sampling in this odor profiling study. Fibers were conditioned according to the manufacturer's directions. No SPME holders were used, (i.e., SPME fiber assemblies had their tensioning spring removed and samples were collected manually). 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 the sampling site.

Special care was taken during the collection of air samples. The operator wore nitrile gloves and avoided direct contact with the SPME needle to minimize interferences. 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. Tight wrapping of SPME assemblies in aluminum foil sealed the fibers from the ambient environment.

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. The swine operation consisted of four identical deep-pit swine finishing barns. Each barn was designed to house 1000 pigs ranging in weight between approximately 20 and 120 kg. Slurry was stored in a 2.4-m deep holding concrete basin below a fully-slatted concrete floor and was designed to store this manure for one calendar year. The manure pit was only partially filled because the slurry was removed prior to sampling in October. Each barn was fan-ventilated with pit and end-wall (or tunnel) fans (Figure 1). The pit exhaust fans draw air from the headspace between the deep manure pit and the slatted floor. The barn exhaust fan at the end-wall is designed to draw the main fraction of the total air going through the barn.

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, locations 1, 2, 3, and 4, 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 CAR-PDMS coating, and the last one utilized the PDMS coating. In addition, one sample was collected with a PDMS coating at the pit fan. The wind was south-southwest 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

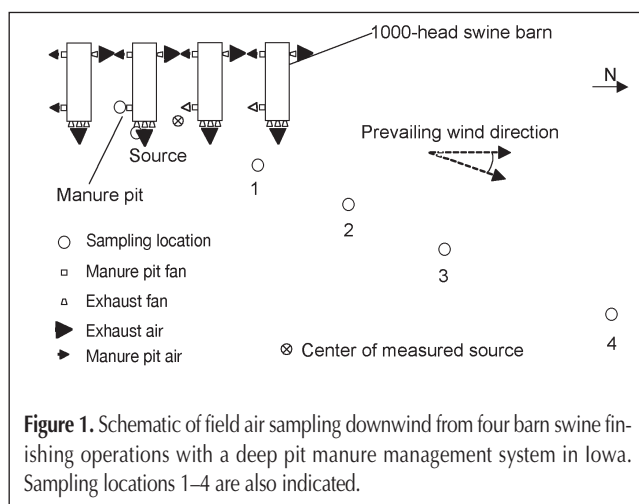
Downwind sampling during the characteristic odor event was conducted on March 18, 2004 in Amarillo, TX. The characteristic odor events occur a few times a year, typically within a few days following rain or snow thawing. These odor events occur typically in late afternoon/early evening hours when the atmospheric mixing is reduced compared with midday atmospheric conditions. The subjective, far-downwind perception of odor during these odor events is typically comparable with 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-h long sampling with CAR-PDMS (75 µm) was completed between 8 and 9 P.M. at the Texas Agricultural Experiment Station grounds in Amarillo. The hourly average

wind direction was 213 deg (generally south-southwest winds). The average wind velocity at 2 and 10 m was 2.4 and 4.5 m/s, respectively. The nearest 55,000-head capacity beef cattle feedlot was located approximately 16 km upwind from the sampling location. No other sources of this characteristic odor were present between the feedyard and the sampling location. Samples were handled and preserved in the same manner as for the swine CAFO.

Results and Discussion

Swine odor

Each air sample analysis resulted in the simultaneous collection of a chromatogram and aromagram. The aromagram was generated by the panelist sniffing and monitoring the odor impression of the separated compounds eluting from the chromatographic column. The width of each peak in the aromagram reflected the start and end time for the individual odor responses, and the peak height was related to the perceived intensity of these responses. Odor events resulting from separated analytes eluting from the column were characterized for odor character and odor intensity. Comparison of the chromatogram (lower line) and aromagram (upper line) of swine barn ambient air at the source ("near" plot) and at the most distant downwind location (location 4) ("far") is shown in Figure 2. 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 previously. No sample at location 4 was collected because of the limited number of SPME fibers available. The natural dilution effect associated with increasing the 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 intensi-



ties of those odorants that are detected). This natural dilution effect, relative to one representative swine CAFO, is demonstrated in Figure 3, which summarizes the total odor and the total number of odor events for the series of aromagrams. The total odor was estimated as the sum of areas under the curve for all odor events for each aromagram obtained from samples that were collected at the source, the pit fan, and four locations downwind from the swine operation. Three series are shown in Figure 3. 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 number 1, 2, 3, and 4, respectively].

Comparison of the total odor and the number of odor/aroma events in Figure 3 resulted in a few interesting observations. Two

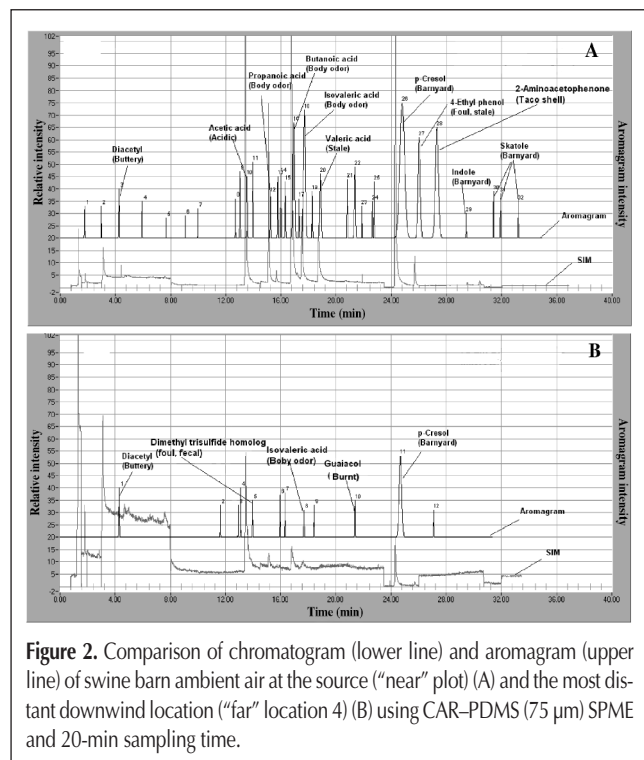


Figure 2. Comparison of chromatogram (lower line) and aromagram (upper line) of swine barn ambient air at the source ("near" plot) (A) and the most distant downwind location ("far" location 4) (B) using CAR-PDMS (75 μ m) SPME and 20-min sampling time.

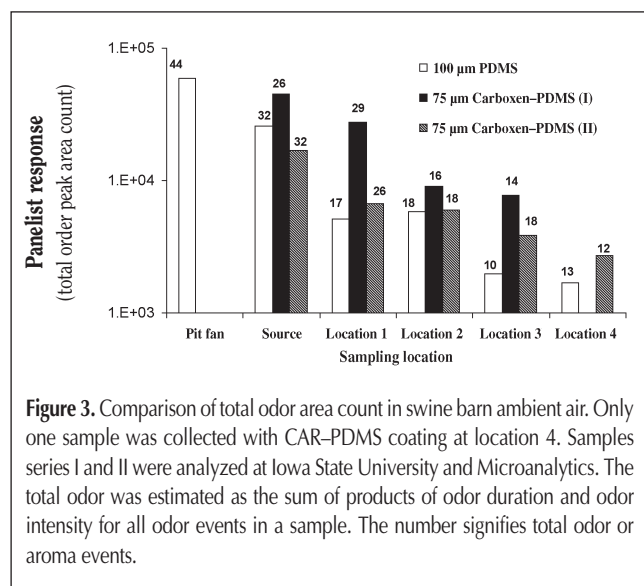


Figure 3. Comparison of total odor area count in swine barn ambient air. Only one sample was collected with CAR-PDMS coating at location 4. Samples series I and II were analyzed at Iowa State University and Microanalytics. The total odor was estimated as the sum of products of odor duration and odor intensity for all odor events in a sample. The number signifies total odor or aroma events.

sample series collected with identical SPME fibers resulted in the similar decreasing trends discussed previously. However, the series analyzed in the Microanalytics laboratory had generally lower total odor and a higher number of odor events. The former is likely because of the possible sample loss during shipment to the Microanalytics laboratory. The second series was not shipped. The latter is likely because of more experienced panelists analyzing samples at Microanalytics, who were able to detect more individual odor events in the same sample. Only one sample was collected with the CAR-PDMS coating at location 4. The total odor associated with the pit exhaust air was in the same order of magnitude compared with the source (barn exhaust). Additional comparison can be made between the PDMS and CAR-PDMS coatings. The CAR-PDMS coating was much more effective at extracting odorous analytes from air. Many odorants associated with manure and odorants present in ambient air at livestock operations are highly volatile and polar.

p-Cresol (4-methyl phenol), with the characteristic "barnyard" odor, represented the dominant odorant relative to both near-source and at-distance downwind sampling locations (Figures 2A and 4B). This was true for all three 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 (Figure 4B). 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 (20). Relative to the near-site collection, only the dimethyl trisulfide (DMTS) homolog of the sulfide series caused a distinct individual odor

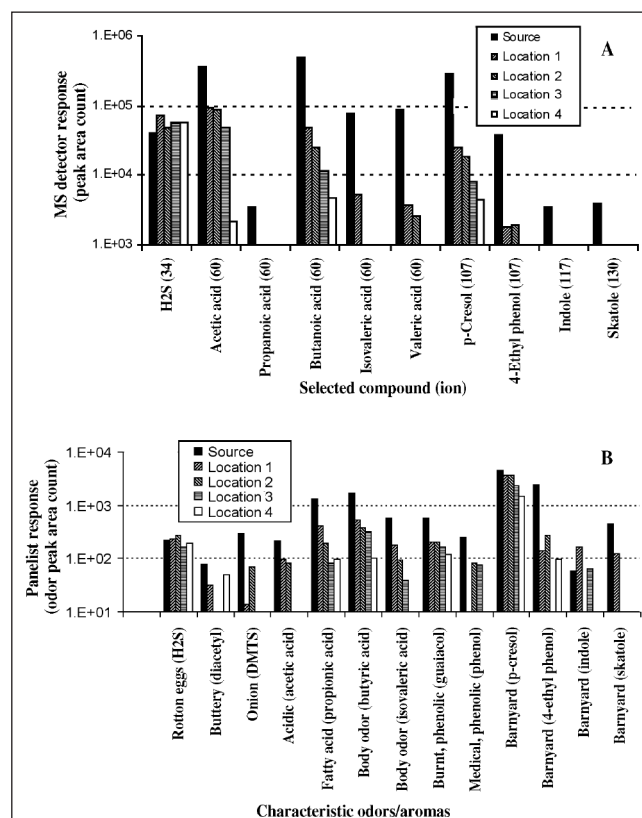


Figure 4. Comparison of selected odorous compounds (A) and the panelist response to odor (B) from air samples collected for 20 min downwind from the swine operation. Samples were analyzed at Microanalytics.

response (i.e., “onion” and “fecal” character) (Figure 4). There were no significant odor responses for H₂S or the lower molecular weight 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 (20). These included isovaleric acid, 2'-aminoacetophenone (“taco shell, urinous”), 4-ethyl phenol, butyric acid, and diacetyl (Figure 4B).

Odor impact prioritization was estimated based upon the data presented previously for near source and downwind from source (location 4) (Table I). *p*-Cresol and isovaleric acid were ranked as having the highest odor impact, respectively, for both near and downwind sources. They were followed by 2'-aminoacetophenone

Odor priority ranking	Near source	Downwind from source
1	<i>p</i> -Cresol	<i>p</i> -Cresol
2	Isovaleric acid	Isovaleric acid
3	2'-Aminoacetophenone	Guaiacol
4	Butyric acid	Dimethyl trisulfide

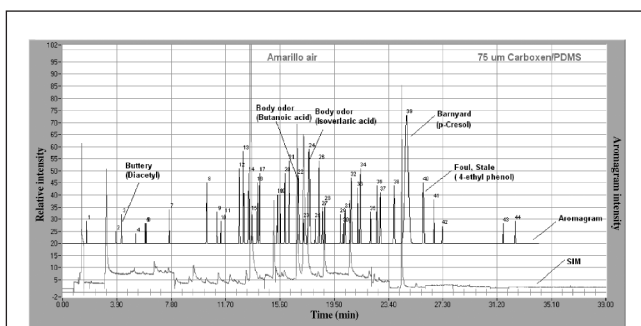


Figure 5. Chromatogram (lower line) and aromagram (upper line) of ambient air in Amarillo, TX during characteristic odor event in March 2004. The nearest beef cattle feedyard was 16 km upwind from the sampling location. Samples were collected using CAR-PDMS (75 μm) SPME and 1-h sampling time. Numbers signify odor events.

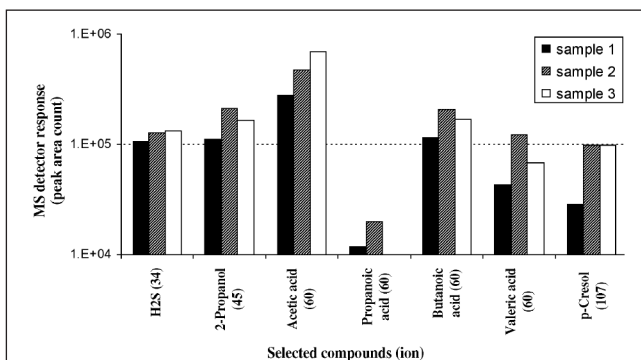


Figure 6. Comparison of several characteristic compounds in replicate samples of ambient air during odor event in cattle feedyard in Amarillo, TX. Samples were collected with CAR-PDMS (75 μm) SPME for 1 h. Samples were analyzed at Microanalytics.

and butyric acid for near source locations and guaiacol and DMTS for downwind locations, respectively. Somewhat surprisingly, in contrast to previous swine CAFO odor profile efforts (data not published), 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 the increasing molecular weight of volatiles is a well-established characteristic of SPME sampling (36). These odor profile results were shown to be consistent with those previously reported by these authors for cattle CAFOs (20). *p*-Cresol was also the highest prioritization odor impact odorant for beef cattle feedlots (20). 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.

Although a considerable similarity is shown in these comparative odor profiles, there were also points of significant difference. Of particular note was an apparent reduction in the odor impact

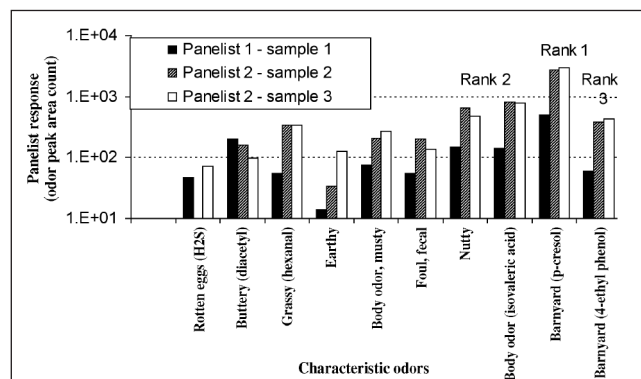
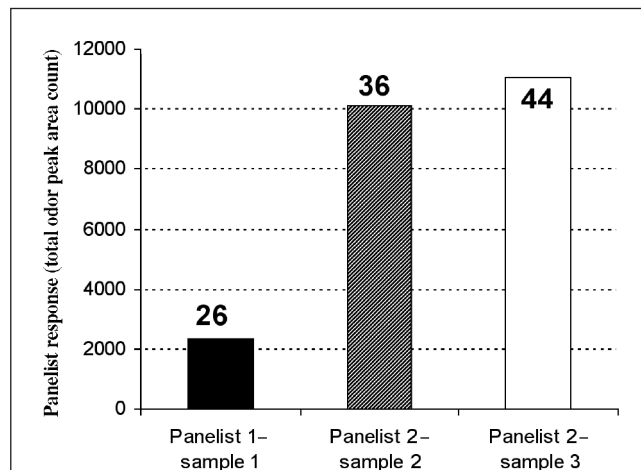


Figure 7. Comparison of panelist responses to several characteristic odors and aromas collected in ambient air, during an odor event in Amarillo, TX using CAR-PDMS (75 μm) SPME and 1-h sampling time. Samples were analyzed at Microanalytics.



Note: Number signifies total odor and aroma events in a sample

Figure 8. Comparison of panelist responses measured as the sum of all odors and aromas detected in ambient air during an odor event in Amarillo, TX. Samples were analyzed at Microanalytics.

significance for trimethyl amine (not shown here) for the swine CAFO in comparison with the previous beef cattle CAFO results (20). As stated previously, this apparent difference may be accounted for by the short sample collection time (i.e., 20 min) relative to that of the previous beef cattle CAFO series (i.e., 1 and 4 h).

Beef cattle odor

Chromatogram and aromagram of ambient air from a cattle feedlot source is shown in Figure 5. Samples were collected using CAR-PDMS (75 μ m) SPME and 1-h 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). The response of the MS detector to several characteristic compounds is presented in Figure 6. Acetic acid was one of the most abundant compounds detected. Sample 1 was significantly different from 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 (Figure 7). Comparison of panelist responses with several characteristic odors and aromas collected in ambient air during an odor event in Amarillo is shown in Figure 7. *p*-Cresol was again the characteristic “barnyard” odorant of the highest individual impact downwind, followed by butyric acid, isovaleric acid, 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 was very similar to those reported for much shorter distances (up to 2 km) (20). In addition, the ranking of odorants in Figure 7 is consistent between two panelists analyzing three samples. Some variation between the samples and responses of the panelists is also evident for the total odor and the number of distinct odor events (Figure 8). Analysis of sample 1 resulted in much lower odor and also a lower number of compounds detected. The reason for this could be related to the amount of odorous analytes on the SPME fiber (Figure 7). Also, panelist 1 was much less experienced than panelist 2.

The observations presented previously do not purport to represent a definitive qualitative assessment of the complex field of CAFO odor. However, these assessments are believed to be sufficiently compelling and consistent to warrant a more comprehensive GC-O-based odorant prioritization study. Far downwind impact of specific livestock odorants can be critically important information needed to propose strategies to solve the livestock odor problem.

Conclusion

SPME was very useful in extracting livestock odorants from ambient air. It interfaced well with the GC-MS-O 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 consis-

tent across a broader sampling of similar environments and analytical parameters, there will be increasing impetus for a critical review of current sampling, analytical, and odor-abatement strategies. Particular attention appears to be warranted for *p*-cresol and other high priority, semivolatile odorants such as 4-ethyl phenol and 2'-aminoacetophenone because of their apparent odor impact prominence. In addition, improved sampling and analysis methodologies need to be developed for these compounds because of their well-documented sensitivity to adsorption driven loss to the walls of plastic sample containers (24). 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 a critical review of the current odor assessment sampling and analysis protocols for the CAFO odor application.

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