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

Jacek A. Koziel
Iowa State University, koziel@iastate.edu

Lingshuang Cai
Iowa State University

Donald W. Wright
Microanalytics, Inc.

Steven J. Hoff
Iowa State University, hoffer@iastate.edu

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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.

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

Jacek A. Koziel¹, Lingshuang Cai¹, Donald W. Wright², Steven J. Hoff¹

¹ Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, Iowa. *Corresponding author: koziel@iastate.edu. Tel: 515-294-4206. ² Microanalytics, A MOCON Company, Round Rock, TX.

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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.
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 SPME (18-20). A relatively small subset of previous studies involved actual field measurements downwind from these facilities (5,6,20). 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 (3,11).

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 (3,7,20).

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 (1). Past and recent (20-22) 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. (23). Wright et al. (2005) used the SPME and a GC-MS-O approaches for beef cattle and swine operations in Texas (20). 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 (20).

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. 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 which are based upon Tedlar\textsuperscript{TM} (or alternate plastic) bags. Unfortunately, the propensity for plastic films to rapidly adsorb semi-volatile 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 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 (24). The standard gas contained volatile fatty acids (from C2 to 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 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. (2002) reported on quantification of C2 to C7 volatile fatty acids in ambient air using portable SPME samplers equipped with Carboxen/PDMS coating (33). 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. (2003) (35). Qualitative applications of SPME can be very useful in odor investigations conducted in ambient air. Wright et al. (2005) showed the use of Carboxen/PDMS 85 μm fibers to collect air samples in several locations downwind from beef cattle and swine operations (20). Field air samples collected on SPME were then analyzed on a GC-MS-O system for odorant ranking and prioritization.

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.
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.

Experimental

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 from 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, 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 Iowa State University (ISU) campus and the Microanalytics laboratory in Round Rock, TX. Samples were analyzed in the SIM mode at Microanalytics and in the scan mode at ISU. 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. Spectra were collected at 6/sec and electron multiplier voltage was set to 1000 V. The MS detector was auto-tuned weekly.

Compounds were identified with 3 sets of criteria: (1) match of the retention time on the MDGC capillary column with the retention time of pure compounds run as standards, (2) matching mass spectra of unknown compounds with BenchTop/PBM (from Palisade Mass Spectrometry, Ithaca, NY, USA) MS library search system and spectra of pure compounds, and (3) 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 Aromatrax software. 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 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. 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 sampling site. Special care was taken
while collecting 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 since 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, 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. These odor events occur typically in late afternoon/early evening hours when the atmospheric mixing is reduced compared to midday atmospheric conditions. 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. The hourly average wind direction was 213 deg (generally S-SW 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 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, red line) and aromagram (upper, black line) of swine barn ambient air at the source (“Near” plot) and at the most distant downwind location (“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 above. No sample at location 4 was collected due to the limited number of SPME fibers available. 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. This natural dilution effect relative to one representative swine CAFO is demonstrated in Figure 3 summarizing 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 #1, #2, #3, and #4, respectively.

Comparison of the total odor and the number of odor/aroma events in Figure 3 results in a few interesting observations. Two sample series collected with identical SPME fiber coating resulted in similar decreasing trends discussed above. However, the series analyzed in the Microanalytics laboratory had generally lower total odor and a higher number of odor events. The former is likely due to the possible sample loss during shipment to the Microanalytics laboratory. The second series was not shipped. The latter is likely due to 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 Carboxen/PDMS coating at location #4. The total odor associated with the pit exhaust air was in the same order of magnitude compared to the source (barn exhaust). Additional comparison can be made between the PDMS and Carboxen/PDMS coatings. The Carboxen/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.

\( \text{P-cresol (4-methyl phenol) with the characteristic “barnyard” odor character} \)

represented the dominant odorant relative to both near-source and at-distance downwind sampling locations (Figure 2 and Figure 4 Part A and B, respectively). 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 (Figure 4, Part B). This prioritization of \( \text{p-cresol relative to at-distance separation from the swine CAFO source} \) 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 response (i.e., ‘onion’ and 'fecal' character) (Figure 4). There were no significant odor responses for \( \text{H}_2\text{S} \) or the lower MW organic sulfide compounds. The profile of odorants which were secondary to \( \text{p-cresol in odor impact prioritization} \) was found to be in good agreement with that previously shown for cattle CAFOs (20). These included: isovaleric acid, \( \text{2’-aminoacetophenone} \) (‘taco shell, urinous’), 4-ethyl phenol, butyric acid and diacetyl (Figure 4 Part B).

Odor impact prioritization was estimated based upon the data presented above for near source and downwind from source (location #4) (Table 1). \( \text{P-cresol and isovaleric} \)
acids 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 (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 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 #1 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 considerable similarity is shown in these comparative odor profiles, there were also points of significant difference. Particularly noteworthy was an apparent reduction in the odor impact significance for trimethyl amine (not shown here) for the swine CAFO in comparison to 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 hr).

**Beef Cattle Odor**

Chromatogram (lower, red line) and aromagram (upper, black line) of ambient air from a cattle feedlot source is shown in Figure 5. 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. 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 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 (Figure 7).

Comparison of panelist responses to 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 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) (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 SPME fiber (Figure 7). Also, panelist #1 was much less experienced than panelist #2.

The observations presented above 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-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. 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 (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 critical review of the current odor assessment sampling and analysis protocols for the CAFO odor application.

Acknowledgements

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References


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) and the most distant downwind location #4 (“Far”) location using Carboxen/PDMS 75 µm 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 Carboxen/PDMS coating at location #4. Samples were analyzed at Iowa State University. The total odor was estimated as the sum of products of odor duration and odor intensity for all odor events in a sample.
Figure 4. Comparison of selected odorous compounds (Part A) and the panelist response to odor (Part B) from air samples collected for 20 min at and downwind from swine operation. Samples were analyzed at Microanalytics.
Figure 5. Chromatogram (lower, red line) and aromagram (upper, black line) of ambient air in Amarillo, Texas during characteristic odor event in March 2004. The nearest beef cattle feedyard was 16 km upwind from the sampling location. Samples were collected using Carboxen/PDMS 75 µm SPME and 1 hr 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, Texas. Samples were collected with 75 µm Carboxen/PDMS SPME for 1 hr. Samples were analyzed at Microanalytics.
Figure 7. Comparison of panelist responses to several characteristic odors and aromas collected in ambient air during odor event Amarillo, Texas using 75 µm Carboxen/PDMS SPME and 1 hr sampling time. Samples were analyzed at Microanalytics.
Figure 8. Comparison of panelist responses measured as the sum of all odors and aromas detected in ambient air during odor event Amarillo, Texas. Samples were analyzed at Microanalytics.
Table 1. Approximate odor impact priority rankings for a swine CAFO.

<table>
<thead>
<tr>
<th>Odor Priority Ranking</th>
<th>Near source</th>
<th>Downwind from source</th>
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<tbody>
<tr>
<td>1</td>
<td>$p$-cresol</td>
<td>$p$-cresol</td>
</tr>
<tr>
<td>2</td>
<td>isovaleric acid</td>
<td>isovaleric acid</td>
</tr>
<tr>
<td>3</td>
<td>$2'$-aminoacetophenone</td>
<td>guaiacol</td>
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<td>4</td>
<td>butyric acid</td>
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