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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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Abstract

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. However, little is known about the odor–VOCs–PM interactions. In this research, continuous PM sampling was conducted simultaneously with three collocated TEOM 1400a 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. VOCs adsorbed/absorbed to dust were allowed to equilibrate with vial headspace. Solid-phase microextraction (SPME) Carboxen/polydimethylsiloxane (PDMS) 85 μm 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 spectrometry–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. Research of the effects of PM control on swine odor mitigation is warranted.

Keywords

VOCs, Odor, SPME, GC–MS–O, PM-10, PM-1, Swine

Disciplines

Agriculture | Animal Sciences | Bioresource and Agricultural Engineering | Environmental Sciences

Comments

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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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22 **Abstract**

23 Swine operations can affect air quality by emissions of odor, volatile organic compounds
24 (VOCs) and other gases, and particulate matter (PM). Particulate matter has been proposed to be
25 an important pathway for carrying odor. However, little is known about the odor-VOCs-PM
26 interactions. In this research, continuous PM sampling was conducted simultaneously with three
27 collocated TEOM 1400a analyzers inside a 1000-head swine finish barn located in central Iowa.
28 Each TEOM was fitted with total suspended particulate (TSP), PM-10, PM-2.5 and PM-1
29 pre-separators. Used filters were stored in 40 mL vials and transported to the laboratory. VOCs
30 adsorbed/absorbed to dust were allowed to equilibrate with vial headspace. Solid-phase
31 microextraction (SPME) Carboxen/polydimethylsiloxane(PDMS) 85 µm fibers were used to
32 extract VOCs. Simultaneous chemical and olfactometry analyses of VOCs and odor associated
33 with swine PM were completed using a gas chromatography-mass-olfactometry (GC-MS-O)
34 system. Fifty VOCs categorized into nine chemical function groups were identified and confirmed
35 with standards. Five of them are classified as hazardous air pollutants. VOCs were characterized
36 with a wide range of molecular weight, boiling points, vapor pressures, water solubilities, odor
37 detection thresholds, and atmospheric reactivities. All characteristic swine VOCs and odorants
38 were present in PM and their abundance was proportional to PM size. However, the majority of
39 VOCs and characteristic swine odorants were preferentially bound to smaller-size PM. The
40 findings indicate that a significant fraction of swine odor can be carried by PM. Research of the
41 effects of PM control on swine odor mitigation is warranted.

42
43 *Keywords:* VOCs; Odor; SPME; GC/MS-O; PM-10; PM-1; Swine

44

45 **1. Introduction**

46 In recent decades, intensive large-scale swine production has grown rapidly in the U.S. and
47 other parts of the world. Most modern swine operations raise hogs in confinement buildings. The
48 large number of animals raised in concentrated animal feeding operations (CAFOs) can affect air
49 quality by emissions of odor, volatile organic compounds (VOCs) and other gases, and particulate
50 matter (PM) [1]. Airborne PM inside barns consisting of swine skin cells, feces, feed, bacteria and
51 fungi contribute to potential poor indoor air quality [2]. The dust sources are feed, fecal matter,
52 dander, mold, mineral ash, pollen and insect parts [3].

53 Aerial PM in swine houses can cause respiratory distress symptoms in both humans and
54 pigs. Swine operation workers have a high prevalence of wheezing and symptoms of chronic
55 bronchitis [4] and an acute decrease in the lung function [5]. Deposition of inhaled PM in the
56 respiratory system is a function of the size of particles. Hatch and Gross [6] reported particles > 10
57 μm are deposited in the human nasal passages, 5-10 μm in the upper respiratory tract and < 5 μm
58 in the lungs themselves. Wathes et al. [7] found for animals PM of 5 μm as the critical size below
59 which the lungs are penetrated and emphasized that the degree of hazard depends on the site of
60 deposition, retention time and the nature of the PM.

61 Heber et al. [8] reported that 50% of all PM in swine finishing buildings were < 2.6 μm in
62 diameter. Most starch and grain meal PM had diameters > 5 μm . Nilsson [9] noted that although
63 80% of the dust (based on particle count) in a swine house was within the range of 0.5 to 2.5 μm ,
64 the mass of these particles were less than 10% of the total PM mass. The mass median diameter
65 (MMD) of PM from four finishing buildings was 10.7 μm , and 66% of the observed PM were $<$
66 4.6 μm and within the respirable range [3]. They found the predominant components of particles in
67 swine confinement buildings > 5 μm , and fecal material among particles between 0.4 to 2 μm .

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68 Day et al. [10] reported that most of the odor of swine barns was carried on dust. The odors
69 generated in animal facilities that are intense and detectable at perceivable distances are all
70 aerosols. Hammond et al. [11,12] indicated that PM plays a crucial role in transporting and even
71 magnifying swine odor. Honey and McQuitty [13] reported that the 5 to 20 μm diameter PM size
72 range in livestock buildings is mainly responsible for transporting odors. Hammond et al. [12]
73 found that the odor is concentrated on the aerosol and that all of the odors can be removed from an
74 air stream when a 0.8 μm dust filter was used to remove all PM. Similar results were found in a
75 series of experiments conducted by Hoff et al. [14] where particle count reduction by size using
76 various filter porosities resulted in corresponding levels of odor reduction. And Hammond et al.
77 [12] showed that concentrations of two odorants (butyric acid and phenol) were 4×10^7 greater on
78 PM than in ambient air. Only a few studies were published on comparing the adsorption capacities
79 of different PM sizes and the relationship between PM size and odor. Das et al. [15] reported that
80 significantly higher amounts of H_2S , octanal and nonanal were found in relatively small size
81 particles (5 to 20 μm) when compared to medium (20-40 μm) and large (40 to 75 μm) PM in
82 swine operations.

83 Livestock PM contains many different odorants [12,16,17]. Razote et al. [18] identified 84
84 compounds in swine barn PM using three extraction methods followed by GC-MS analysis:
85 solvent extraction, SPME and purge and trap. Most of the compounds in the airborne PM—
86 including volatile fatty acids (VFAs), aldehydes, alcohols, ketones, hydrocarbons, phenols, indoles,
87 N- and S-containing compounds, and esters—were present in the air as well as in also in lagoon
88 manure near swine barns. Five compounds were quantified using the purge and trap method.
89 Previous studies primarily adopted solvent extraction methods to extract the odorants from swine
90 barn PM [11,12,15,16,19]. However, solvent extraction may cause some losses of some of VFAs,

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91 phenolics and indolics during the procedure of extracting and concentrating [16]. SPME was first
92 used to characterize swine PM by Razote et al. [20]. Comparison of sampling and analytical
93 methods between the present and previous studies to characterize VOCs in swine barn PM, and
94 VOCs in ambient and indoor air for which SMPE was used is shown in Table 1. SPME is a simple,
95 solvent-free method that combines sampling and sample preparation of the VOCs [26]. SPME has
96 been used to characterize VOCs emitted from livestock operations [18,20,27,28,29,30,31].

97 Previous studies focused mainly on total PM in swine housing. To date, still little is known
98 about the odor-VOCs-PM interactions particularly for PM sizes of interest to regulatory agencies.
99 In this study, headspace (HS) SPME combined with GC-MS-O system was used to identify VOCs
100 and characterize the key odors adsorbed/absorbed on different size swine barn dust (PM-1, PM-2.5,
101 PM-10 and the total suspended particulate (TSP)).

102

103 **2. Materials and Methods**

104

105 The procedures of identification of odorants adsorbed/absorbed on swine barn PM include
106 the collecting of PM samples, the separation of the compounds from the dust, and the
107 qualification/quantification of the compounds using GC-MS-O.

108

109 *2.1. TSP, PM-10, PM-2.5 and PM-1 sampling inside swine finish barn*

110 Tapered element oscillating microbalance (TEOM, Model 1400a, Rupprecht & Patashnick,
111 East Greenbush, NY, USA) was used for continuous real-time measurement of airborne particles
112 (TSP, PM-10, PM-2.5 and PM-1, respectively). This PM monitor has the U.S. EPA Designation
113 No. EQPM-1090-079 for PM-10 measurements. The TEOM1400a is being used extensively by

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114 federal and state agencies for ambient PM monitoring. The sample flow passes through the filter,
115 where PM is collected. The TEOM measures the mass collected on an exchangeable filter
116 cartridge situated at the end of the oscillating tapered element. This is accomplished by monitoring
117 the corresponding frequency changes. As more mass collects on the exchangeable filter, the
118 frequency of oscillation changes. A direct relationship exists between the change in frequency and
119 mass on the filter. Dust concentration is estimated as the ratio of the mass on the filter to the
120 sampling air flow rate.

121 Three collocated TEOM samplers were placed in one 2.4 m × 6 m pen reserved for this
122 study. The building used for this study was designed to house pigs from 20 to 120 kg and during
123 this study pigs averaged 60 kg. Pigs were present in all pens surrounding the pen containing the
124 TEOM samplers. The feeders were wet-dry type feeders implying that the water and feed were
125 delivered to the pigs in one common trough for each pen. The set-point temperature maintained in
126 the barn was 23 °C and the relative humidity was controlled between 50 and 60%. The TEOM
127 filter housing was kept at 50 °C according to the manufacturer's recommendation. This was done
128 to minimize the effect of ambient water associated with hygroscopic salts. Because of hygroscopic
129 particles, the mass collected on the filter can be very sensitive to changes in the ambient water
130 vapor concentration. Details related to the building monitored can be found in Hoff et al. [32]. The
131 TEOM samplers were placed within 7 m of a continuously operating exhaust ventilation fan with
132 each TEOM sampling head within 1 m of each other, arranged triangular near the center of the pen.
133 Air surrounding the TEOM sampling heads was classified as still air with airspeeds less than 0.20
134 m/s. The TEOM samplers were sampled at 10 sec intervals and data was downloaded daily from
135 each TEOM.

136

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137 2.2. *Solid-phase microextraction*

138

139 SPME extractions were performed with a manual fiber holder from Supelco (Bellefonte, PA,
140 USA). Three commercially available fibers—PDMS 100 μm , 85 μm Carboxen/PDMS and 70 μm
141 Carbowax /divinylbenzene (DVB)—were first used to select the SPME coating capable of extracting
142 maximum amounts of VOCs typically associated with swine odor. Before use, each fiber was
143 conditioned in a heated GC splitless injection port under He flow according to the manufacturer's
144 instructions. Screw-capped vials from Supelco (40 mL) sealed with a polytetrafluoroethylene
145 (PTFE)-lined silicone septum were used for storing used TEOM filters and for HS-SPME sampling.
146 The vials were cleaned and dried at 110 °C overnight. Vials with used TEOM filters were placed in a
147 water bath at 25 °C for 24 hr prior to SPME sampling. During SPME extraction the septum was
148 pierced using the SPME needle and exposed the SPME fiber to the headspace for 3 hr. Preliminary
149 experiments using fiber exposition times between 10 sec and 24 hr at 25 °C were used to determine
150 the optimal extraction conditions. After extraction, the SPME fiber was removed from the vial and
151 immediately inserted into the injection port of GC for analysis. The desorption time of SPME fiber
152 was 40 min at 260 °C.

153

154 2.3. *Gas Chromatograph –Mass Spectrometry-Olfactory System*

155

156 Multidimensional GC-MS-O (from Microanalytics, Round Rock, TX, USA) was used for
157 all analyses. The system integrates GC-O with conventional GC-MS (Agilent 6890N GC / 5973
158 MS from Agilent, Wilmington, DE, USA) as the base platform with the addition of an olfactory
159 port and flame ionization detector (FID). The system was equipped with a non-polar precolumn

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160 and polar column in series as well as system automation and data acquisition software
161 (MultiTrax™ V. 6.00 and AromaTrax™ V. 6.61, from Microanalytics and Chemstation™, from
162 Agilent). The general run parameters used were as follows: injector, 260 °C; FID, 280 °C, column,
163 40 °C initial, 3 min hold, 7 °C /min, 220 °C final, 10 min hold; carrier gas, He. Mass/molecular
164 weight to charge ratio (m/z) range was set between 33 and 280. Spectra were collected at 6/sec and
165 electron multiplier voltage was set to 1000 V. The MS detector was auto-tuned weekly.

166 Compounds were identified with 3 sets of criteria: (1) match of the retention time on the
167 MDGC capillary column with the retention time of pure compounds run as standards, (2) matching
168 mass spectrums of unknown compounds with BenchTop/PBM (from Palisade Mass Spectrometry,
169 Ithaca, NY, USA) MS library search system and spectrums of pure compounds, and (3) matching
170 odor character. Qualitative assessment of VOC abundance was measured as area counts under
171 peaks for separated VOCs. Human panelists were used to sniff separated compounds
172 simultaneously with chemical analyses. Odor caused by separated VOCs was evaluated with a 64-
173 descriptor panel and intensity scale in Aromatrx software. Odor evaluations consisted of
174 comparisons of the number of odor/aroma events, with odor intensity measured as the area under
175 odor/aroma peaks in aromagrams.

176

177 **3. Results and Discussion**

178

179 *3.1. Optimization of sampling parameters for HS-SPME analysis*

180

181 *Selection of SPME fibers.* Three commercial SPME fiber coatings (85 µm
182 Carboxen/PDMS, 70 µm Carbowax /DVB and 100 µm PDMS) were evaluated for the

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183 determination of VOCs emitted from swine barn PM. Figure 1 indicates the comparison of
184 extraction efficiency between the three SPME fiber coatings for eight characteristic swine odor
185 compounds extracted from swine barn PM: H₂S, hexanal, octanal, acetic acid, phenol, 4-methyl
186 phenol, indole and skatole. All extractions were performed at 25 °C for 3 hr. Carboxen /PDMS
187 fiber was most effective for all target compounds except H₂S and skatole, for which the
188 Carboxen/DVB coating was more effective. Carboxen has small diameter (10A on average) pores
189 which are suitable to adsorb molecules in the C₂-C₁₂ range [33,34,35]. These results confirm the
190 observations of Popp and Paschke [36] and Shirey [37], who found the Carboxen /PDMS fiber
191 performed best for the analysis of VOCs extracted from air or water. In subsequent studies,
192 Carboxen/PDMS fiber was selected to concentrate the VOCs from swine barn PM.

193 *HS-SPME optimization.* The extraction time was varied from 10 sec to 24 hr with a fixed
194 extraction temperature (25 °C) and peak area of the analytes were plotted against time as shown in
195 Figure 2. The results demonstrated that as time increased so did the amount of most volatiles
196 extracted by SPME fiber, but the relationship was not the same for all. Most compounds—such as
197 isovaleric acid, phenol, 4-methyl phenol, indole and skatole—appeared to follow a linear trend.
198 Adsorption rates progressively increased with no evidence of reaching equilibrium with the test
199 time range (up to 24 hr). However, extraction amounts of H₂S, methyl mercaptan and hexanal
200 decreased with longer extraction time because the porous structure of the Carboxen/PDMS fiber
201 can easily become saturated when using prolonged extraction times [38,39]. Once this occurs,
202 compounds with higher affinity for the fiber will essentially displace those compounds with lower
203 affinity. This can be minimized when shorter extraction times are used [40,41]. In this study, 3 hr
204 was chosen as the extraction time for all compounds.

205

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206 3.2. Identification of the VOCs associated with swine barn PM

207

208 Sampling of VOCs associated with swine barn PM was performed by means of HS-SPME
209 followed with chemical and olfactometry analyses on a GC-MS-O system. Compounds were
210 identified using classic MS analyses and compared with the retention time of authentic standard
211 compounds. If no standards were available, compounds were identified by BenchTop/PBM mass
212 spectrometry library search system and their single odor event. A total of 50 different compounds
213 were identified, of which 21 have never been reported to be present in swine barn dust in previous
214 studies (Table 2). Some odorous compounds that have not been reported include pentane, methyl
215 mercaptan, trimethyl amine, 3-pentanamine, diacetyl, dimethyl sulfone, styrene, 2-pentyl furan,
216 and 2'-aminoacetophenone. The fifty compounds identified cover a wide range of polarity and
217 molecular weight (34.08-234.39) and belong to nine chemical classes: alkanes (4), alcohols (4),
218 aldehydes (8), ketones (7), acids (8), amines and nitrogen heterocycles (8), sulfides and thiols (3),
219 aromatics(7) and furans (1). The main chemical classes involved in odorous emissions from swine
220 buildings previous identified [42,43] were also identified in this study: volatile fatty acids,
221 aromatics (4-methyl phenol and 4-ethyl phenol), nitrogen heterocycles (indole and skatole), thiols
222 and mercaptans. Five of the compounds identified are classified as hazardous air pollutants (HAPs):
223 styrene, N, N-dimethyl- formamide, acetamide, phenol and 4-methyl phenol.

224 The 37 published odor threshold values (ODTs) for identified compounds ranged from
225 parts per trillion (ppt) to parts per million (ppm) for identified compounds, as shown in Table 2
226 [44,45,46,47,48]. For the remaining 13 compounds, no ODTs currently exist. As many as 31
227 compounds have an ODT < 1 ppm. Frequencies of occurrence of the compounds identified on all
228 seven sets of TSP (7), PM-10 (7), PM-2.5 (1) and PM-1 (6) are listed in Table 2. Ten of these

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229 compounds were present in all samples including H₂S, acetone, hexanal, acetic acid, 2-
230 ethylhexanol, phenol, 4-methylphenol, 4-ethylphenol, indole and skatole. Eight were only present
231 in PM-10 and TSP: methyl mercaptan, pentanal, 2-heptanone, 2-pentyl furan, 1-octanol, butanoic
232 acid, 3-methyl butanoic acid and pentanoic acid.

233

234 3.3. Physicochemical parameters of organic compounds detected in swine barn PM

235

236 VOCs are defined as those organic liquids or solids whose room temperature vapor pressures
237 are greater than about 0.01 psi (0.52 mmHg) and whose atmospheric boiling points are up to about
238 260 °C. This includes compounds with < 12 C atoms [49]. Selected physicochemical parameters
239 including C number, boiling point (b.p.), vapor pressure (v.p.), water solubility (sol.), log K_{ow} and
240 atmospheric lifetime (τ) based on reaction with the [OH·] are summarized in Figure 3 (parts a to f).

241 Figure 3a shows the distribution of the C number. Sixty percent of compounds fell within
242 C5-C8 and 28% were within the C1-C4. Only 10% were > C9 and one compound had 12 C atoms.
243 Organic compounds are commonly characterized by their b.p.. The b.p. ranged from -60.33 °C to
244 266 °C and the mean b.p. was 149 °C. Approximately 68% of the compounds had a b.p. ranging
245 from 80 to 230 °C. The b.p. of compounds < 80 °C and > 230 °C were 16% and 10%, respectively.
246 It is interesting to recall that all extractions were conducted at 25 °C. This indicates that airborne
247 PM in swine barn at ambient temperature can emit a wide range of VOCs. Even though all of the
248 filters inside the TEOMs were at 50 °C during sampling, 8% of compounds had b.p. < 50 °C. Thus,
249 it is likely that more compounds with b.p. < 50 °C could be observed if PM sampling were
250 conducted at ambient temperature.

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251 Vapor pressure and solubility are the two key parameters which can influence the state of
252 compounds in the headspace. Organics with low v.p. and high solubility are more likely to have a
253 higher adsorptive character onto solids than those with a high v.p. and low sol. [50]. The
254 distributions of b.p. and v.p. are given in Figures 3c and 3d. The range of v.p. varied widely from
255 0.0044 mmHg to 1.56E+4 mmHg. About 48% of compounds had v.p. > 0.52 mmHg and 64%
256 were very soluble in water with solubility ranging between 500 to 5E+05 mg/L. The octanol-water
257 partitioning coefficient (log K_{ow}) ranged from -1.41 to 5.52 (Figure 3d). About 78% of volatiles
258 had a log K_{ow} < 3 and only 10% had log K_{ow} > 3.

259 VOCs in the atmosphere participate in degradation/transformation reactions [51,52,53,54].
260 The hydroxyl (OH·) radical is the key reactive species in the troposphere, reacting with all VOCs
261 except the CFCs and those halons not containing H atoms [51,52,54]. An average 24 hr
262 OH· concentration is 1.0× 10⁶ molecule/cm³ [55,56]. The value of τ for each compound was
263 calculated using the following equation:

264

$$265 \quad \tau = 1 / (k \times [\text{OH}\cdot])$$

266

267 where each k is a rate constants (at 298 K, cm³/molecule/sec) found in the Environmental Science-
268 Interactive PhysProp Database Demo (SRI, 2005) [57]. The distribution of τ is given in Figure 3f.
269 Although the TEOM filters had been exposed in air for 24 hr, there were 29 compounds detected
270 in swine barn dust with τ < 24 hr. About 58% of the compounds had the τ < 24 hr and 36% had τ >
271 24 hr.

272

273 *3.4. Measured PM concentrations in swine finishing barn*

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274

275 A total of seven sets of swing barn PM samples were collected with collocated TEOMs
276 including 7 TSP, 7 PM-10, 6 PM-1, and 1 PM-2.5. Mean measured concentrations of PM-1, PM-
277 10 and TSP are displayed in Table 3. As can be seen, there are 2 PM-1, 4 PM-10 and 5 TSP
278 concentrations available due to the malfunction of the sampling setup. The average measured
279 concentrations of PM-1, PM-10 and TSP were 5.8, 226 and 858 $\mu\text{g}/\text{m}^3$, respectively. The mass of
280 PM on each filter (M) was calculated by the following equation:

281

$$282 \quad M = Q_{\text{air}} \times C \times t$$

283

284 where: Q_{air} = air flow rate set at 3 mL/min; C = mean measured concentration over the sampling
285 period (t). The total surface area (TSA) for PM-1, PM-10 and TSP was estimated based on the
286 particle size and particle count (count/mL) reported for swine PM by Chen et al. [58] and is shown
287 in Table 3. The PM-1 and PM-10 fractions account for 0.35% and 21.94% of the total PM mass.
288 However, the TSA represented by PM-1 and PM-10 are about 0.86 and 81% of the TSA of TSP.
289 Nilsson et al. [9] reported about 80% of the PM (based on particle count) in a swine barn was
290 small and ranged from 0.5-2.5 μm . However, these particles accounted for only 10% of the total
291 mass. Das et al. [15] calculated the TSA of swine PM to be in the 0.5-2.5 μm range and found
292 particles is about 19% of the TSA of all PM to be in the 0-10 μm range.

293

294 *3.5. Comparison of the adsorption capability of characteristic compounds between difference size*
295 *particles on swine barn*

296

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297 The mean peak area counts of selected 24 compounds detected in PM-1, PM-10 and TSP
298 by the mean of single ion integration were used to compare the adsorption capacity between the
299 different-size PM (Figure 4a). The selected compounds are those that significantly contribute to
300 the characteristic malodor of swine barn, which include H₂S, methyl mercaptan, trimethylamine,
301 acetone, diacetyl, 7 aldehydes, 7 volatile fatty acids, phenol, 4-methyl phenol, 4-ethyl phenol,
302 indole, and skatole. Figure 4a shows that TSP adsorbed much more of those characteristic
303 compounds than PM-10 and PM-1. However, when the peak area counts were normalized by the
304 total PM mass and the TSA for different size particles, respectively, the values (area count/ mass
305 and peak area count/TSA) show a significant difference (Figures 4b and 4c). Figure 4b displays
306 that the relative amounts of most of those characteristic compounds adsorbed to PM-1 are greater
307 than those on PM-10 and TSP except hexanal. Similarly, PM-10 also shows higher adsorption
308 capability than TSP. Figure 4c shows that the relative amount of organics adsorbed to mm² of PM-
309 1 TSA > that on PM-10 and TSP, respectively. This is likely due to smaller PM having greater
310 surface area /volume ratio, and thus offering a relatively large surface area for VOCs adsorption
311 [59]. The result is that smaller PM adsorbed more VOCs per mass than larger PM. Figure 4d
312 shows the peak area count normalized by the M and by TSA of different size. The results for all
313 characteristic compounds suggest that the apparent adsorption capability (normalized by M and
314 TSA) of PM-1 is higher than PM-10 and TSP, respectively.

315 The results are consistent with Das et al. [15] who reported significantly higher amounts of
316 H₂S, octanal and nonanal in small size PM (5 to 20 μm) compared to medium (20-40 μm) and
317 large (40 to 75 μm) swine PM. Odabasi et al. [23] quantitatively analyzed several aromatic,
318 oxygenated and halogenated VOCs in atmospheric PM and investigated the distribution of
319 particle-phase VOCs between fine (< 2.5 μm) and coarse (2.5 μm-10 μm) fractions. They also

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320 found that VOCs were mostly associated with fine PM (< 2.5 µm). The presence of hazardous
321 VOCs in fine PM is important in terms of human and animal health since they have the ability to
322 penetrate through the respiratory tracks.

323

324 *3.6. Effects of SPME extraction time on odor of swine barn PM*

325

326 Odor is the property of a chemical compound or mixture of compounds above a certain
327 concentration to activate the sense of smell and thus initiate an odor sensation [60]. The odor
328 generated in animal production facilities originates from feed, enteric rumination, urine, feces and
329 manure [8]. O'Neill & Phillips [61] classified four main chemical groups of odor-causing VOCs in
330 livestock operations: sulfurous compounds, phenols and indoles, volatile fatty acids (VFA),
331 ammonia and volatile amines. In this study, odor carried by swine barn PM was investigated with
332 the sniff port on the GC-MS system and Aromatrax software. Each odor analysis resulted in an
333 aromagram. The aromagram was generated by the panelist sniffing and monitoring the odor
334 impression of the separated compounds eluting from the chromatographic column. The width of
335 each peak in aromagram reflected the start and end time for the individual odor responses, and the
336 peak height was related to the perceived intensity of these responses. The effects of HS-SPME
337 extraction time on aromagrams, peak areas associated with characteristic odors, and the numbers
338 of odor and aroma events were evaluated.

339 Aromagrams of VOCs extracted from TSP filters at different SPME sampling times are
340 presented in Figure 5. This time series was adopted for the purpose of focusing on the key odorants
341 defining the characteristic swine odor in swine barn PM [62]. Figure 5 shows aromagrams
342 generated by increasing sampling time: 10 sec, 1 min, 3 hr and 24 hr. Longer sampling time

Cai, L., J.A. Koziel, Y.C. Lo, S.J. Hoff. Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and GC-MS-Olfactometry. Journal of Chromatography A. 2005, in press.*

343 resulted in a significant increase in the total number of detected odor events and the increase in
344 odor intensity. For example, for the SPME sampling time of only 10 sec, eight characteristic odors
345 were still faintly detectable (Figure 5a), such as onion (methyl mercaptan), buttery (diacetyl),
346 grassy (hexanal), mushroom (tentatively identified as 1-octene-3-one), body odor (isovaleric acid),
347 phenolic (phenol) and barnyard (p-cresol) (Figure 5a). With longer sampling time (3 hr and 24 hr),
348 indole and skatole presented with significant individual odor response (i.e., distinct 'barnyard') as
349 shown in Figures 5c and 5d. Based on these analyses, the list of key malodorants associated with
350 swine PM could be proposed including: methyl mercaptan, isovaleric acid, p-cresol, indole and
351 skatole. The list of key odorants was very similar to the key odorants in swine manure [63]. There
352 appeared to be a rise in individual odor response for most odorants relative to those with short
353 sampling time, especially for some odorants of lower volatility, such as indole and skatole. The
354 reason for this is possibly associated with the nature of SPME sampling. The compounds of lower
355 volatility need longer time to reach equilibrium and transfer from gas phase to SPME coating [64].

356

357 *3.7. Characterization of odor and comparison of odor intensities between PM-1, PM-10 and TSP*

358

359 Comparison of the mean total odor (defined as the sum of all odor peak areas on an
360 aromagram), total odor/M, total odor/TSA and total odor/M/TSA between PM-1, PM-10 and TSP
361 is shown in Figure 6. TSP carried much more total odor than PM-1 and PM-10. When total odor
362 was normalized with the PM mass and the total surface area, the relative odor intensity of PM-1
363 was higher than that of PM-10 and TSP, respectively. This relationship was consistent with the
364 VOC distributions discussed earlier in this paper. Seven odorants (and 11 VOCs) that were most
365 frequently encountered were selected to compare the odor intensity between PM-1, PM-10 and

Cai, L., J.A. Koziel, Y.C. Lo, S.J. Hoff. Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and GC-MS-Olfactometry. Journal of Chromatography A. 2005, in press.*

366 TSP. The list of most frequently detected compounds in swine barn PM includes H₂S (sewer),
367 hexanal (grassy), acetic acid (acid), 1-octanol (earthy), butanoic acid and isovaleric acid (body
368 odor), phenol, p-cresol and 4-ethyl phenol (medicinal and barnyard) and indole and skatole
369 (barnyard). Normalization of the odor intensity to PM mass and TSA resulted in distributions
370 similar to those for VOCs and key odorants: PM-1 had much greater potential to be a carrier of
371 odor than PM-10 and TSP, respectively, for all odorants except H₂S. This could be due to the
372 relatively low affinity of H₂S to the Carboxen/PDMS fiber and low concentrations of H₂S
373 adsorbed by PM-1 below its published odor detection threshold of approximately 10 ppb [45].

374 The results of this study are consistent with earlier publications considering the
375 methodologies used two to four decades ago. Previous studies have shown that the 5-20 μm
376 diameter particle size range is mainly responsible for transporting swine odor [13]. Day et al. [10]
377 reported that most of the odor of swine houses was carried on PM, and Eby and Wilson [65]
378 reported that most of the odor of poultry houses can be eliminated by removing airborne dust.
379 Hammond et al. [11] also observed that all of the odors were removed from an air stream by using
380 a 0.8 μm filter, and they found that gaseous odors adsorbed to the particle filter consisted of half of
381 the total odor. Moreover, butyric acid and p-cresol concentration were 4×10⁷ times greater on PM
382 than in ambient air. Particles can amplify odors by the concentration of the odorants on the
383 particles and by efficient deposition of the particles on the olfactory organ. Donham et al. [3]
384 reported that predominant components of the swine house PM were associated with PM > 5 μm
385 and fecal material with PM between 1-2 μm diameter.

386

387 **4. Conclusions**

388

389 The following conclusions were drawn from this study:

390

391 (1) HS-SPME coupled with GC-MS-Olfactometry is a useful and effective analytical tool for
392 identifying VOCs and odor associated with swine barn PM. The most effective SPME fiber
393 for HS-SPME is the Carboxen/PDMS.

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

401 (3) The 50 compounds detected in swine barn PM were characterized by a wide range of
402 physicochemical parameters including carbon number, b.p., v.p., sol., log Kow and
403 atmospheric lifetime. Sixty percent of compounds were within the C5-C8 range, 68% had
404 b.p. between 80 and 230 °C, 48% had v.p. > 0.52 mmHg, 64% were very soluble in water
405 (500 to 5E+05 mg/L), 78% had a log Kow < 3, and 58% had τ_{OH} < 24 hr.

406 (4) Key malodorants associated with swine barn PM include methyl mercaptan, isovaleric acid,
407 4-methyl-phenol, indole and skatole. Twenty-four odorous compounds were selected for
408 comparing the adsorption capacity between PM-1, PM-10 and TSP including H₂S, methyl
409 mercaptan, trimethylamine, acetone, diacetyl, 7 aldehydes, 7 volatile fatty acids, phenol, 4-
410 methyl- and 4-ethyl phenol, indole, and skatole. TSP adsorbed a much more absolute amount
411 of those compounds and odors than PM-10 and PM-1, respectively. However, when absolute

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412 amounts of compounds and odors were normalized by the PM mass and the total surface area,
413 the values (area count/M/TSA) of those compounds showed significant difference. PM-1 had
414 an apparent greater capacity (normalized by M and TSA) for characteristic VOCs and odors
415 relative to PM-10 and TSP. Lastly, additional research is warranted to study desorption of
416 VOCs and odor from PM as a function of equilibrium time and air temperature.

417

418 **Acknowledgements**

419 The authors would like to thank Iowa State University for funding this research, and the
420 collaborating swine producer for hosting the collection of swine barn PM.

421

422 **Abbreviations**

423	b.p.	=	boiling point
424	CAFOs:	=	concentrated animal feeding operations
425	DVB	=	divinylbenzene
426	GC-MS-O	=	gas chromatography-mass-olfactometry
427	HAPs	=	hazardous air pollutants
428	M	=	mass of particulate matter
429	MMD	=	mass median diameter
430	ODT	=	odor detection threshold
431	PDMS	=	polydimethylsiloxane
432	PM	=	particulate matter
433	PM-1	=	particulate matter with mean aerodynamic diameter of 1 μm or less
434	PM-2.5	=	particulate matter with mean aerodynamic diameter of 2.5 μm or less

Cai, L., J.A. Koziel, Y.C. Lo, S.J. Hoff. Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and GC-MS-Olfactometry. Journal of Chromatography A. 2005, in press.*

435	PM-10	=	particulate matter with mean aerodynamic diameter of 10 μm or less
436	ppt	=	parts per trillion
437	ppm	=	parts per million
438	PTFE	=	polytetrafluoroethylene
439	SPME	=	solid-phase microextraction
440	TEOM	=	tapered element oscillating microbalance
441	TSA	=	total surface area
442	TSP	=	total suspended particulate
443	VFAs	=	volatile fatty acids
444	VOCs	=	volatile organic compounds
445	v.p.	=	vapor pressure
446	sol.	=	water solubility
447	τ	=	atmospheric lifetime

448 **References:**

- 449 [1] National Research Council. Air Emissions from Animal Feeding Operations, Current
450 Knowledge, Future Needs. The National Academies Press, Washington, DC, 2003.
- 451 [2] J.F. Robertson, Pig J. 33 (1994) 113.
- 452 [3] K.J. Donham, L.J. Scallon, W. Pependorf, M.W. Treuhaft, R.C. Roberts. Am. Ind. Hyg.
453 Assoc. J. 47 (1986) 404.
- 454 [4] J.A. Dosman, B.L. Gragam, D. Hall, P. Bhasin, F. Froh, J. Occp. Med. 29 (1987) 39.
- 455 [5] M. Iversen, H. Takai, ZBL. Arbeitsmed 40 (1990) 236.
- 456 [6] T.F. Hatch, P. Gross, Pulmonary Deposition and Retention of Inhaled Aerosols. Academic
457 Press, New York, 1964.

- Cai, L., J.A. Koziel*, Y.C. Lo, S.J. Hoff. *Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and GC-MS-Olfactometry. Journal of Chromatography A. 2005, in press.*
- 458 [7] C.M. Wathes, C.D.R. Jones, A.J.F. Webster, *Veterinary Record*, 10 Dec. 1983, p. 554.
- 459 [8] A.J. Herber, M. Stroik, J.M. Faubion, L.H. Willard, *Trans. ASAE*, 31 (1988) 882.
- 460 [9] C. Nilsson, Department of farm buildings, Swedish University of Agriculture Sciences, Lund,
461 Sweden, Report 25, 1982.
- 462 [10] D.L. Day, E.L. Hensen, S. Anderson, *Trans. ASAE*. 8 (1965) 118.
- 463 [11] E.G. Hammond, C. Fedler, R.J. Smith, *Agric. Environ.* 6 (1981) 395.
- 464 [12] E.G. Hammond, C. Fedler, G. Junk, *Trans. ASAE*. 22 (1979) 1186.
- 465 [13] L.F. Honey, J.B. McQuitty, *Can. J. Agric. Eng.* 21 (1979) 9.
- 466 [14] S.J. Hoff, D.S. Bundy, X.W. Li, *Proceedings of the International Symposium Ammonia and*
467 *Odour Control from Animal Production Facilities*, Vinkeloord, The Netherlands, 1997, p. 101.
- 468 [15] K.G. Das, J.R. Kastner, S. M. Hassan, *ASAE/CSAE Annual International Meeting*,
469 Paper number: 04-4125, 2004.
- 470 [16] J. Hartung, *Environ. Tech. Lett.* 6 (1985) 21.
- 471 [17] Takai, H., P.J. Dahl, M. Maahn, *Proceedings for AgEng. Katholieke Universiteit Leuven*,
472 Leuven, Belgium, 2004, p. 8.
- 473 [18] E.B. Razote, R.G. Maghirang, L. M. Seitz, J. J. Jeon, *Trans. ASAE* 47 (2004) 1231.
- 474 [19] L.L. Oehrl, K.M. Keener, R.W. Bottcher, R.D. Munilla, K.M. Connelly, *Appl. Eng.*
475 *Agric.* 17 (2001) 659.
- 476 [20] E. Razote, I. Jeon, R. Maghirang, *J. Environ. Sci. Health B* 37 (2002) 365.
- 477 [21] J.M. Vaz, *Talanta*, 60 (2003) 687.
- 478 [22] O. Khanal, D. Shooter, *Atmos. Environ.* 38 (2004) 6917.
- 479 [23] M. Odabasi, O. Ongan, E. Cetin, *Atmos. Environ.* 39 (2005) 3763.
- 480 [24] A. Nilsson, V. L agesson, C.G. Bornehag, J. Sundell, C. Tagesson, *Environ. Int.* 2005, in

Cai, L., J.A. Koziel, Y.C. Lo, S.J. Hoff. Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and GC-MS-Olfactometry. Journal of Chromatography A. 2005, in press.*

481 press.

482 [25] P.H. Fischer, G. Hoek, H. van Reeuwijk, D.J. Briggs, E. Lebret, J.H. van Wijnen, S. Kingham,

483 P.E. Elliott, Atmos. Environ. 34 (2000) 3713.

484 [26] J. Pawliszyn (Editor), Applications of Solid Phase Microextraction, The Royal Society

485 of Chemistry, Hertfordshire, UK, 1999.

486 [27] J.A. Zahn, J.L. Hatfield, Y.S. Do, A. A. DiSpirito, D.A. Laird, R.L. Pfeiffer, J. Environ.

487 Qual. 26 (1997) 1687.

488 [28] S. Yo, Chemosphere 38 (1999) 823.

489 [29] W. Powers, T. van Kempen, D. Bundy, A. Sutton, S. Hoff, in Air Pollution from Agricultural

490 Operations: Proc. 2nd International Conference, St. Joseph, Mich.: ASAE. 2000, p. 163.

491 [30] A. Gralapp, W. Powers, D. Bundy. Trans. ASAE 44 (2001) 1283.

492 [31] H. Kim–Yang, S. Davies, R.D. von Bernuth, E.A. Kline, ASAE. St. Joseph, Mich: ASAE.

493 Paper No. 014037, 2001.

494 [32] S.J. Hoff, B.C. Zelle, M.A. Huebner, A.K. Gralapp, D.S. Bundy, L.D. Jacobson, A.J.

495 Heber, J. Ni, J.A. Koziel, J. Sweeten, Y. Zhang, D.B. Beasley, Proceedings of the 2005

496 AWMA Annual Meeting and Exhibition, Minneapolis, MN, Paper No. 648, 2005.

497 [33] V. Mani, in: J. Pawliszyn (Editor), Applications of Solid Phase Microextraction,

498 Royal Society of Chemistry, Cambridge, UK, 1999, p. 57.

499 [34] T. Gorecki., In: J. Pawliszyn (Editor), Applications of Solid Phase Microextraction,

500 Royal Society of Chemistry, Cambridge, 1999, p. 92.

501 [35] R.E. Shirey, V. Mani, R. Mindrup, Am. Environ. Lab. 10 (1998) 21.

502 [36] P. Popp, A. Paschke, Chromatographia, 46 (1997) 419.

503 [37] R.E. Shirey, J. Chromatogr. Sci. 38 (2000) 109.

Cai, L., J.A. Koziel, Y.C. Lo, S.J. Hoff. Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and GC-MS-Olfactometry. Journal of Chromatography A. 2005, in press.*

- 504 [38] E. Woolfenden, J. Air Waste Manage Assoc. 47 (1997) 20.
- 505 [39] M. Jia, J.A. Koziel, J. Pawliszyn. Field Anal. Chem. Technol. 4 (2000) 73.
- 506 [40] J.A. Koziel, M. Jia, J. Pawliszyn, Anal. Chem. 72 (2000) 5178.
- 507 [41] B. Zabiegala, E. Przyk, A. Przyjazny, J. Namiesnik, Chem. Anal. (Warsaw) 45 (2000) 11.
- 508 [42] R. I., Mackie, P.G. Stroot, V.H. Varel, J. Anim. Sci. 76 (1998) 1331.
- 509 [43] J. Martinez, G. Le Bozec, Cahiers Agricultures, 9 (2000) 181.
- 510 [44] M. Devos, J. Rouault, P. Laffort, Standardized Olfactory Power Law Exponents. Editions
511 Universitaires de Dijon, France, 2002.
- 512 [45] M. Devos, F. Patte, J. Roualt, P. Laffort, L.J. Van Gemert, Standardized
513 Human Olfactory Thresholds. IRL Press at Oxford Press, NY, New York, 1990.
- 514 [46] Odor Thresholds for Chemicals with Established Occupational Health Standards.
515 American Industrial Hygiene Association. Fairfax, VA, 1989.
- 516 [47] M. Rychlik, P. Schieberle, W. Grosch, Compilation of Odor Thresholds, Odor
517 Qualities and Retention Indices of Key Food Odorants. Germany, 1998.
- 518 [48] E.J. Amoore, E. Hautala, J. Appl. Toxicol. 3 (1983) 272.
- 519 [49] De Nevers, Noel, Air Pollution Control Engineering. McGraw-Hill Education –
520 Europe, 1995.
- 521 [50] K. Verscherene, Handbook of Environmental Data of Organic Chemicals. Wiley,
522 New York, 2001
- 523 [51] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 2, 1994, p. 1
- 524 [52] R. Atkinson, J. Phys. Chem. Ref. Data 26 (1997) 215.
- 525 [53] R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson, R.F. Kerr, M.J. Rossi, J.
526 Troe, J. Phys. Chem. Ref. Data 28, 1999, p. 391.

Cai, L., J.A. Koziel*, Y.C. Lo, S.J. Hoff. *Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and GC-MS-Olfactometry. Journal of Chromatography A. 2005, in press.*

- 527 [54] W.B. DeMore, S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard,
528 A.R. Ravishankara, C.E. Kolb, M.J. Molina, Chemical Kinetics and Photochemical Data for
529 use in Stratospheric Modeling, Evaluation No.12, NASA Panel for data Evaluation. Jet
530 Propulsion Laboratory Publication 97-4, Pasadena, CA, 1997.
- 531 [55] R.G. Prinn, R.F. Weiss, B.R. Miller, J. Huang, F.N. Alyea, D.M. Cunnold, P.J. Fraser,
532 D.E. Hartley, P.G. Simmonds, Science 269 (1995) 187.
- 533 [56] R. Hein, P.J. Crutzen, M. Heimann, Global Biogeochem. Cycles 11 (1997) 43.
- 534 [57] Syracuse Research Corporation, Interactive PhysProp Database Demo.
535 <http://www.syrres.com/esc/physdemo.htm>. Accessed on July 30, 2005.
- 536 [58] Y.C. Chen, Y.H. Zhang, E.M. Barber, ASHRAE Trans. 101 (1995) 1169.
- 537 [59] Y.T. Chyi, R.R. Dague, Wat. Env. Fed. Proceeding of the 65th Annual Conference and
538 Exposition, 1992, p. 191.
- 539 [60] G. Winneke, Ann. N.Y. Acad. Sci. 641 (1992) 261.
- 540 [61] D.H. O'Neill, V.R. Phillips, J. Agri. Eng. Res. 53 (1992) 23.
- 541 [62] D. Wright, L. Nielsen, D. Eaton, F. Kuhrt, J.A. Koziel, J.P. Spinhirne, D.B. Parker,
542 J. Agri. Food Chem. 2005, in press. (DOI: 10.1021/jf050763b)
- 543 [63] J.A. Koziel, M. Jia, J. Pawliszyn, Anal. Chem. 72 (2000) 5178.
- 544 [64] J.A. Koziel, C.M. Lo, D. Wright, S. Trabue, B. Kerr, Proceedings of the 2005
545 AWMA Annual Meeting and Exhibition, Minneapolis, MN, Paper No. 996, 2005.
- 546 [65] H.J. Eby, G.B. Wilson, Proceedings of the Cornell University Conference on Agricultural
547 Waste Management, 1969, p. 303.
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549

FIGURE CAPTIONS

550 **Figure 1** Comparison of extraction efficiency of selected odorous gases associated with PM-
551 1 fraction of swine dust for the Carboxen/PDMS, Carbowax/DVB and PDMS
552 SPME fibers. Extraction conditions: extraction temperature = 25 °C, extraction
553 time = 3 hr. Number in parentheses is the single ion of each compound used for peak area
554 count integration.

555 **Figure 2** Effect of time on HS-SPME extraction of 8 compounds from swine barn PM (TSP)
556 at 25 °C with Carboxen/PDMS fiber 85 µm. Extraction time = 10 sec, 30 sec, 1 min,
557 10 min, 30 min, 1 hr, 3 hr, and 24 hr.

558 **Figure 3 (a-f)** Distribution of carbon number, b.p., v.p (at 25 °C), solubility (at 25 °C),
559 log K_{ow} , and τ for 50 compounds found in swine barn PM.

560 **Figure 4** Comparison of peak area count (Part A), peak area count/ M_{PM} (Part B), peak area
561 count/TSA (part C), and area count/ M_{PM} /TSA (Part D) of selected VOCs in swine barn
562 TSP, PM-10, and PM-1. Error bars show the plus standard deviation of the mean. Number in
563 parentheses is the single ion of each compound used for peak area count integration.

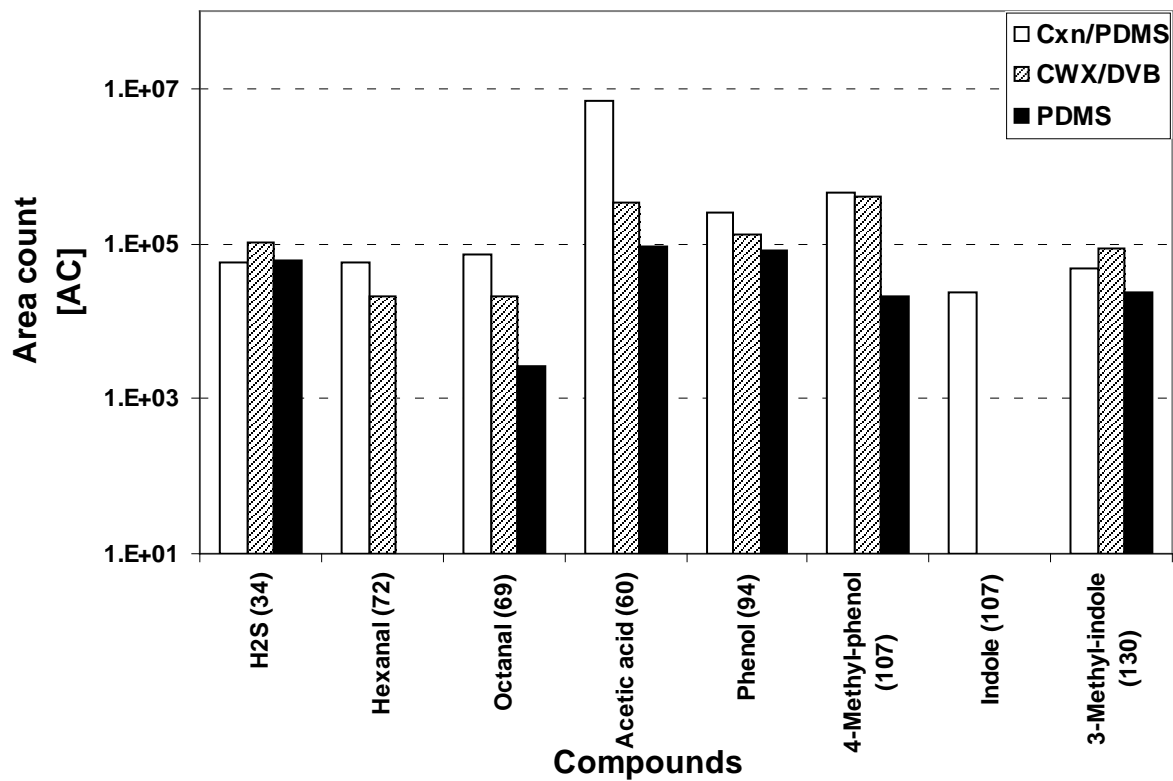
564 **Figure 5** Effects of SPME extraction time on aromagrams of swine barn PM (TSP) - a. 10 sec;
565 b. 1 min; c. 3 hr; d. 24 hr.

566 **Figure 6** Characterization of odor for swine barn dust at PM-1, PM-10 and TSP.

567 **Figure 7** Comparison of characteristic odor distribution between swine barn PM-1, PM-10 and
568 TSP.

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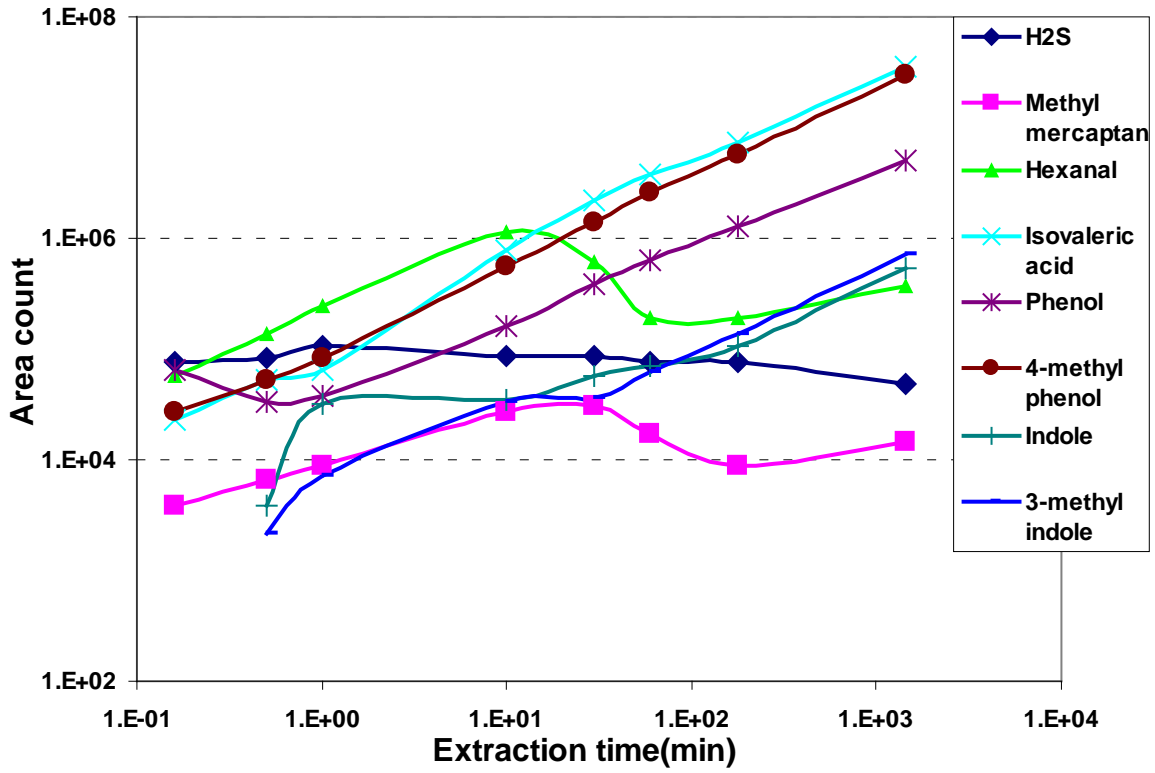
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Figure 1 (Lingshuang Cai et al.)

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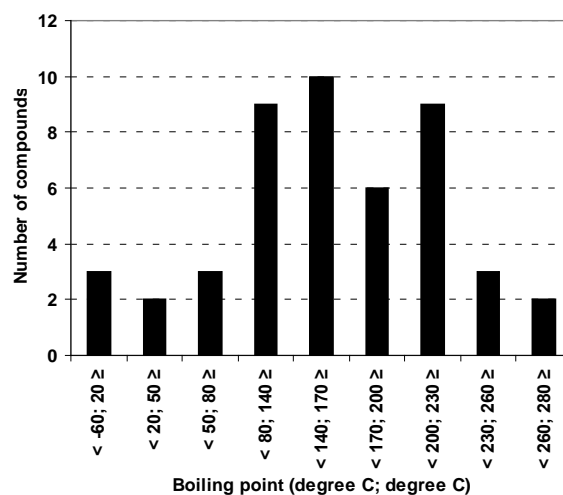
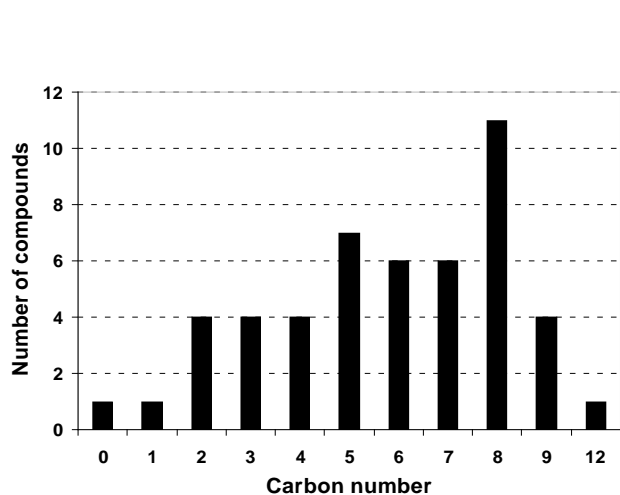
Figure 2 (Lingshuang Cai et al.)

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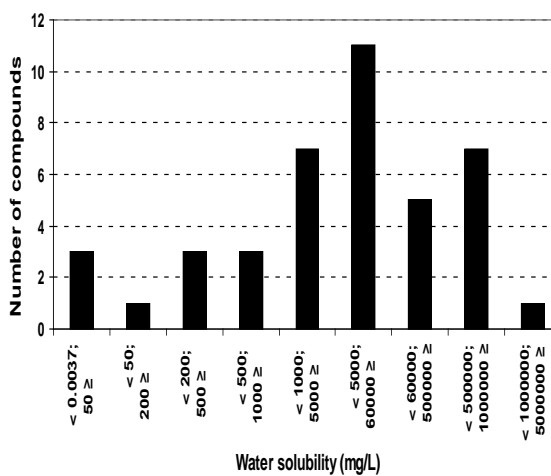
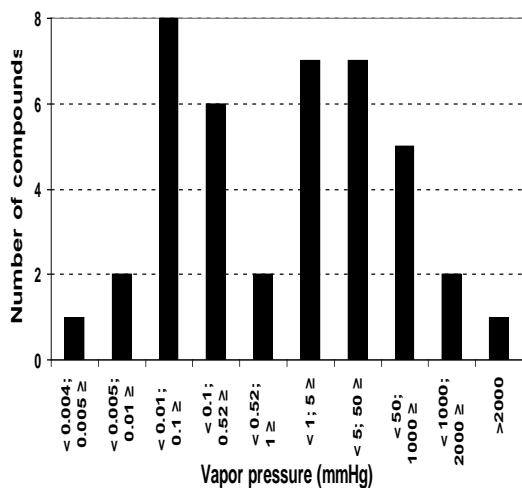
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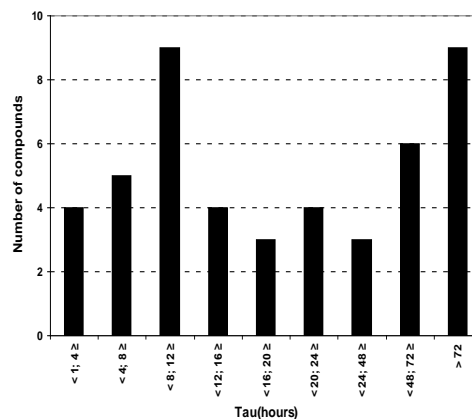
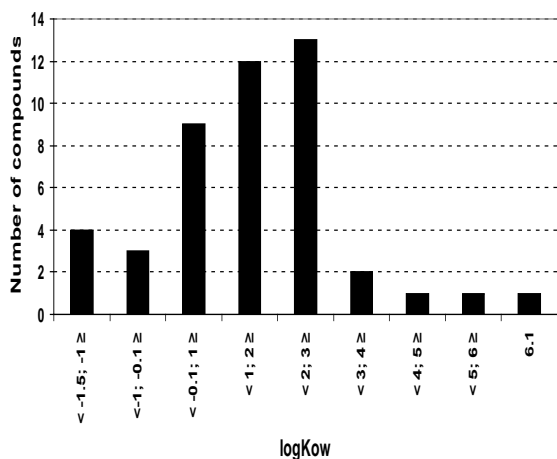


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Figure 3 (Lingshuang Cai et al.)

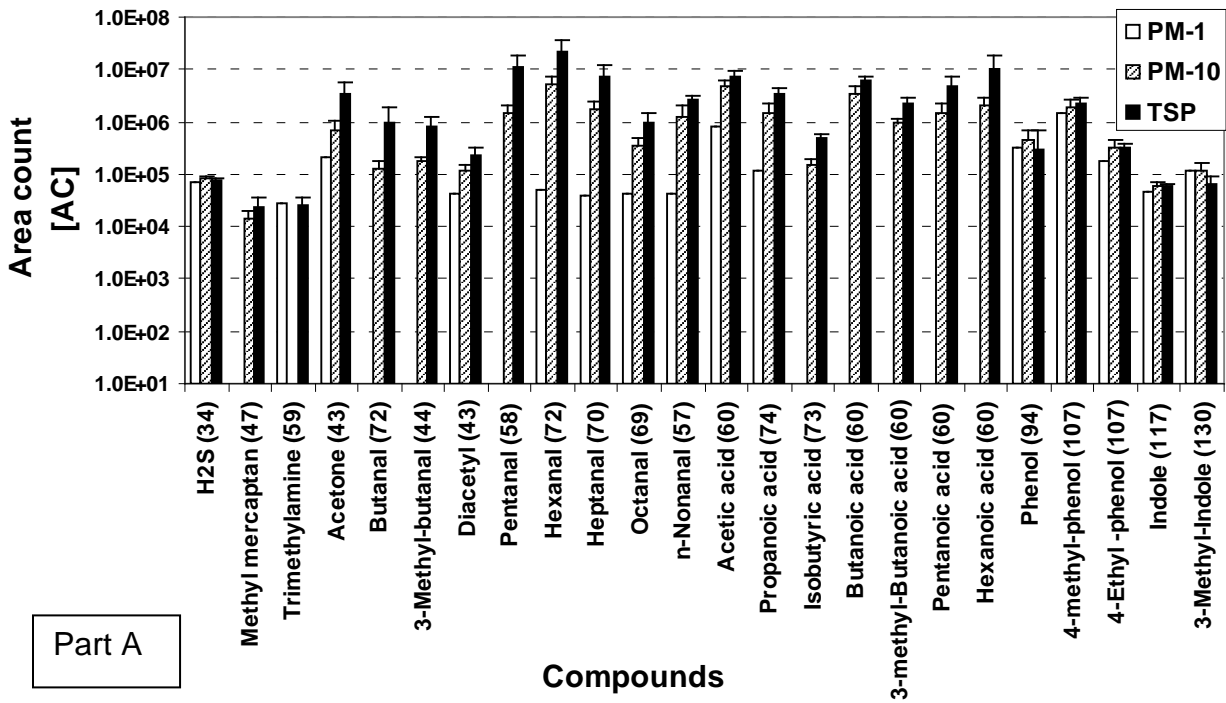
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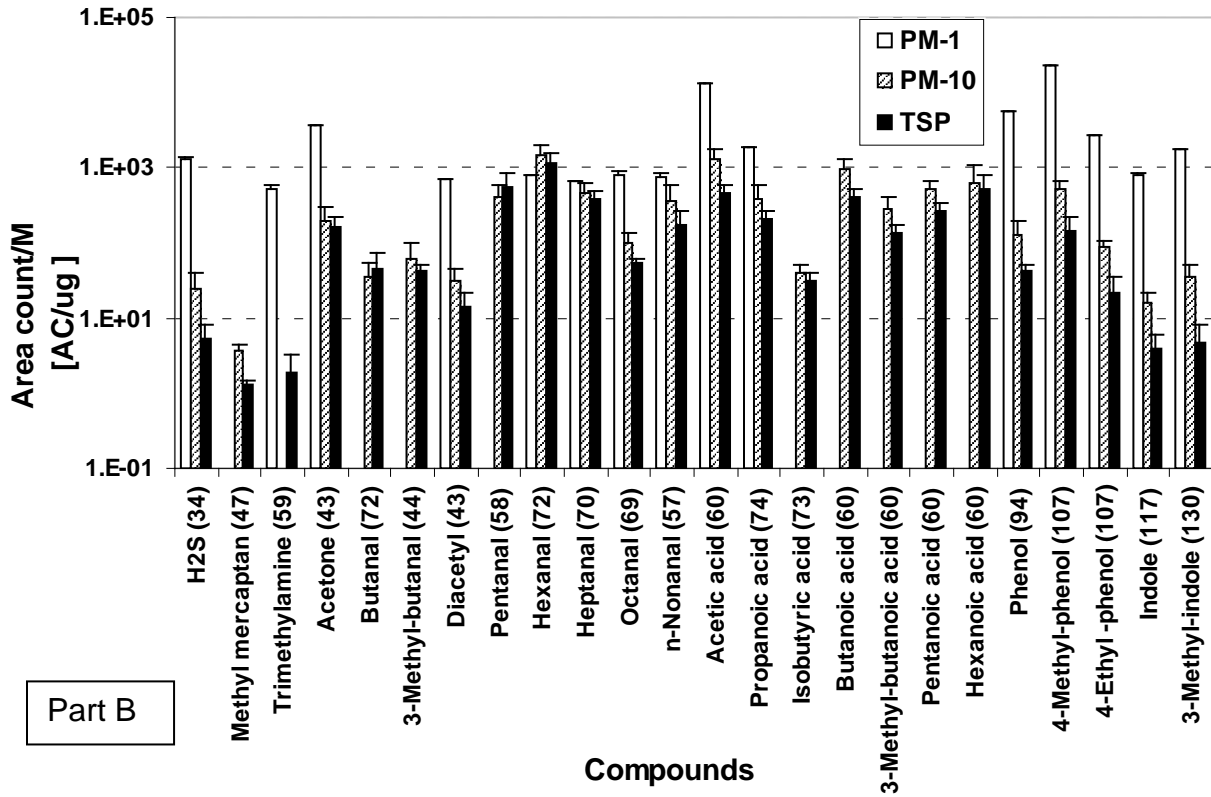
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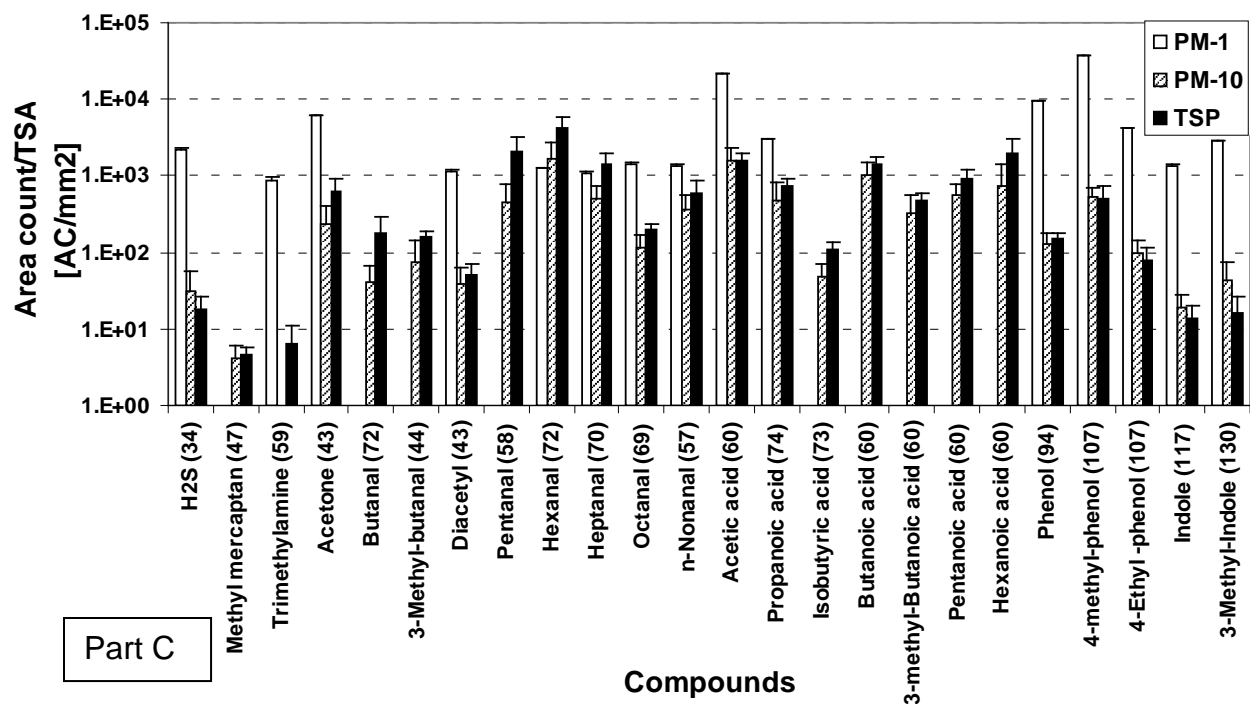
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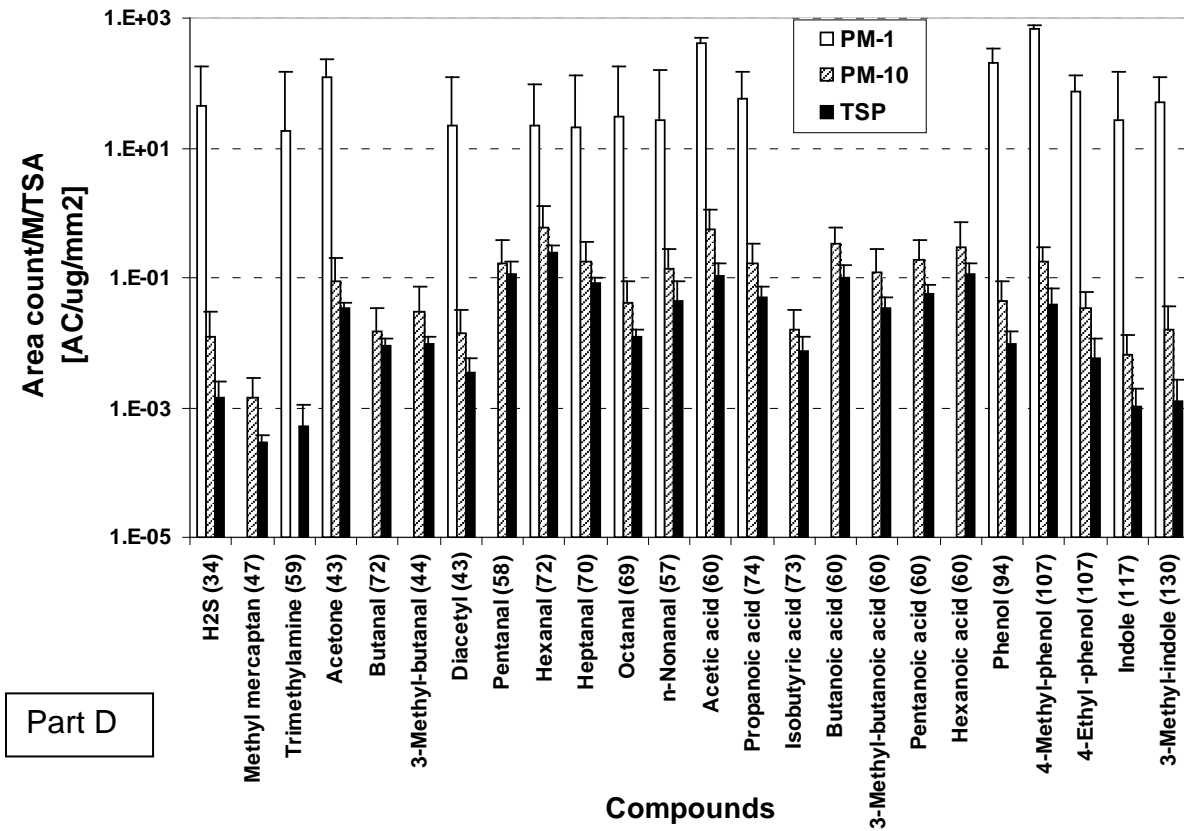
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Figure 4 (Lingshuang Cai et al.)

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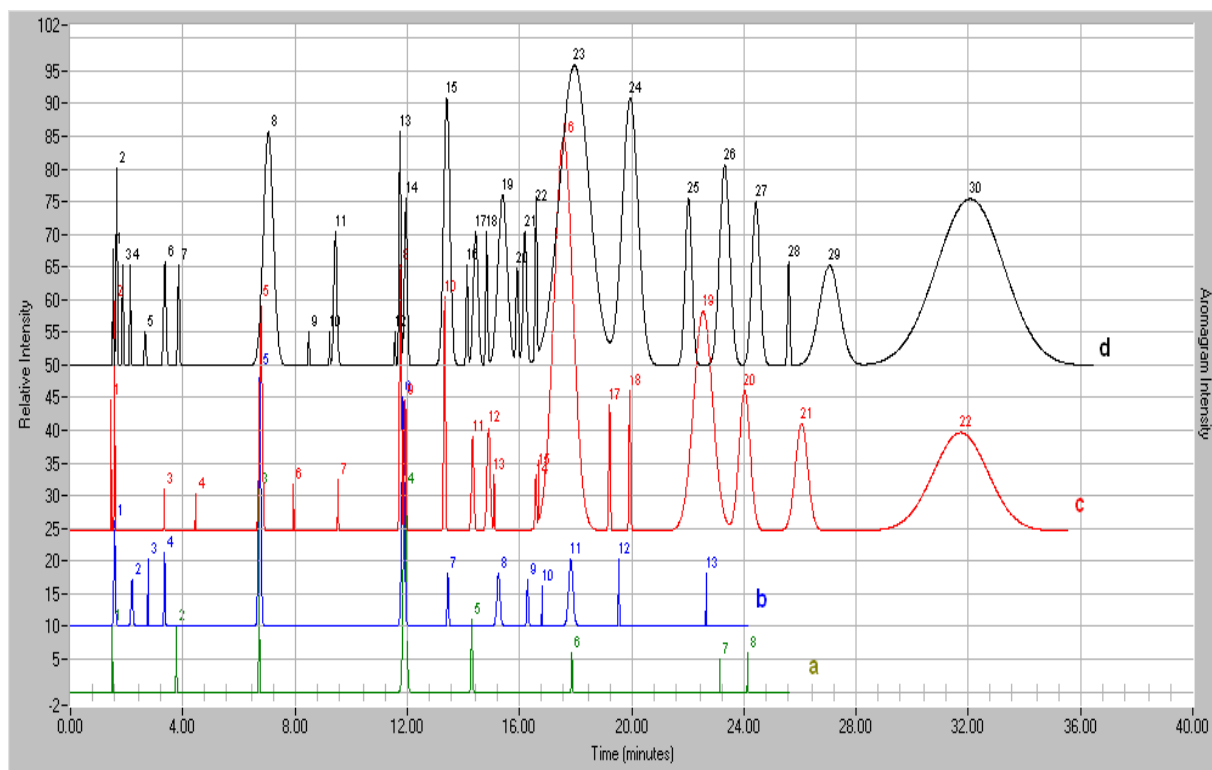
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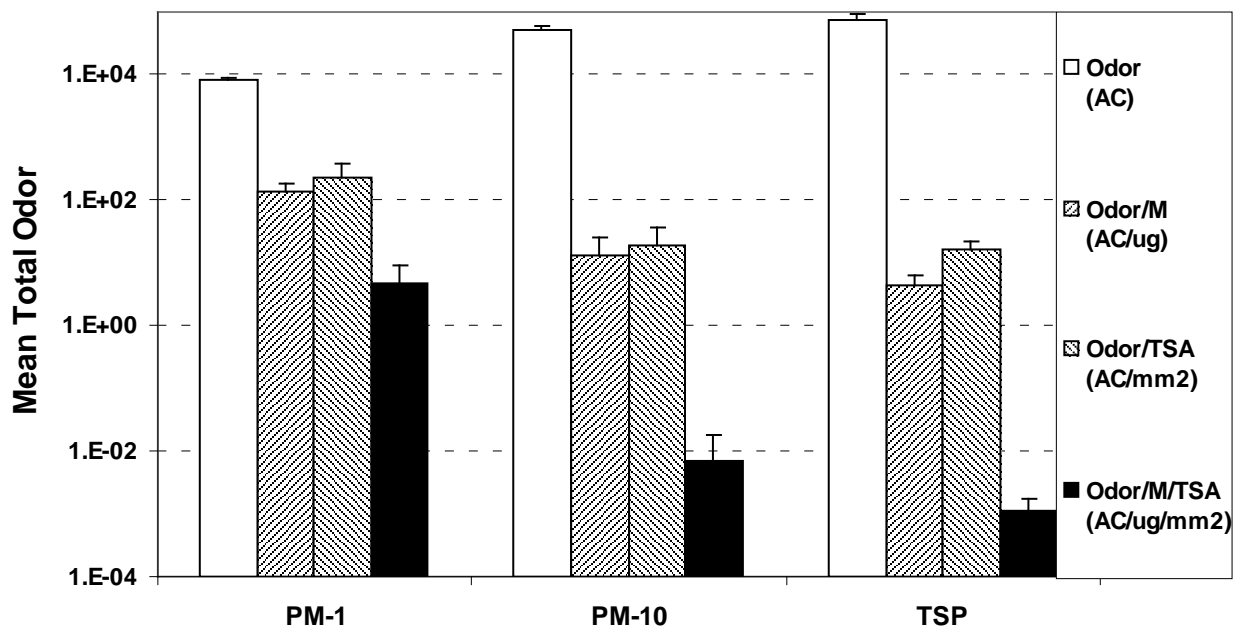
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Figure 5 (Lingshuang Cai et al.)

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Swine Barn Dust Size

Note: AC = peak area count TSA = estimated total surface area

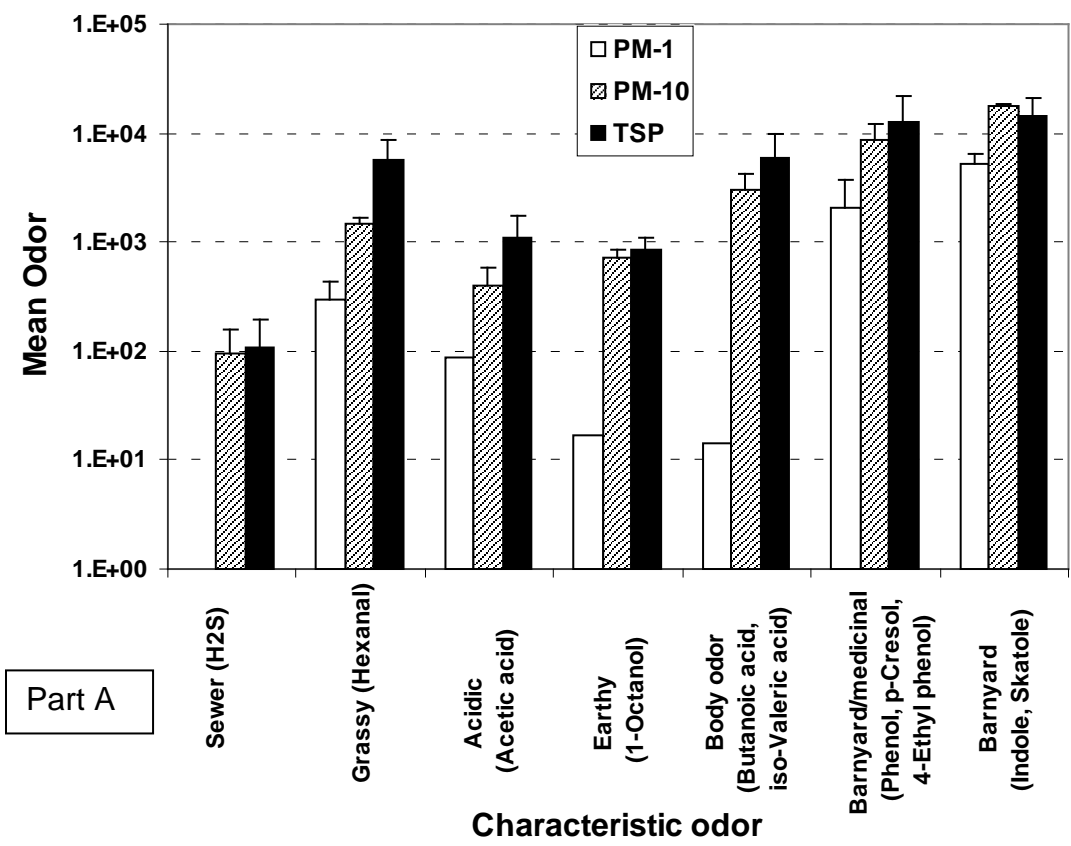
Error bar = standard deviation

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Figure 6 (Lingshuang Cai et al.)

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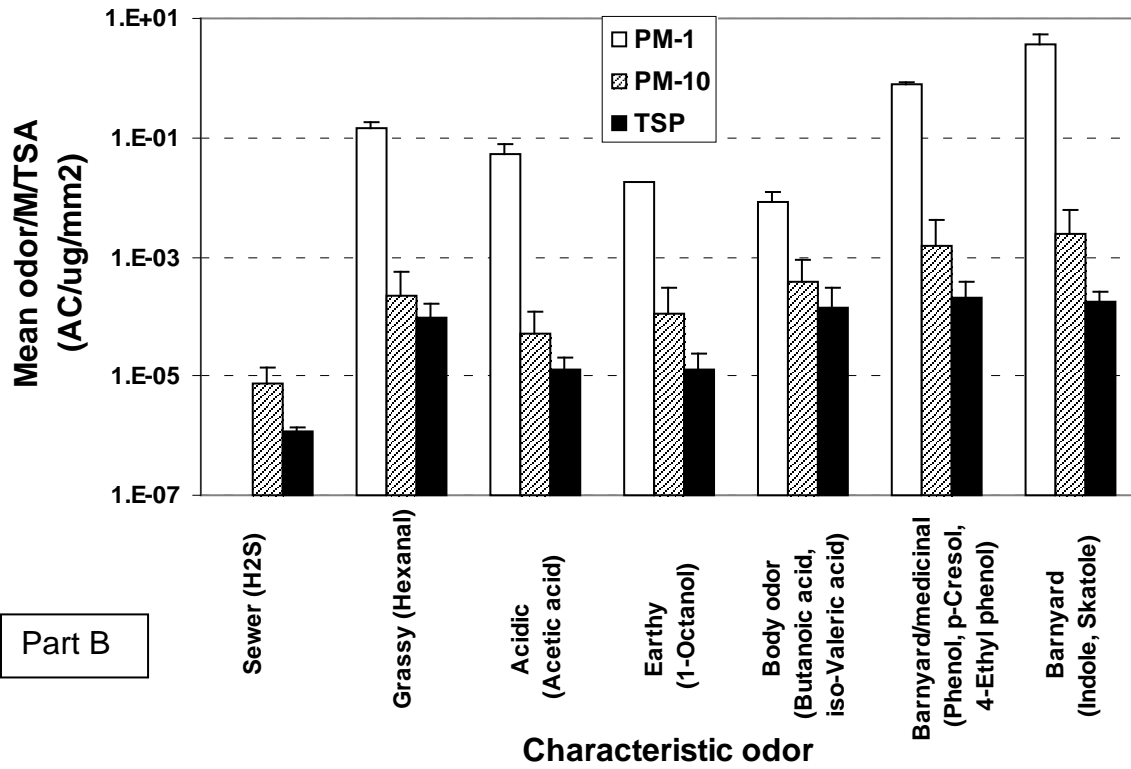


Figure 7 (Lingshuang Cai et al.)

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660 Table 1 Comparison of sampling and analytical methods used to characterize VOCs in swine barn
661 dust, ambient and indoor air particles

Ref. #	PM Sampling	Sample Preparation	Analyses	Odor Analysis	Location/type of PM; number of gases reported (n)
This work	TEOM filters TSP, PM-10, PM-2.5, and PM-1	SPME (Cxn/PDMS), extraction temperature = 25 °C and time = 3 hrs	GC-MS-O	Sniff port on GC-MS-O	Swine barn PM, (50)
[18]	Glass-fiber filter	1. Solvent extraction; 2. SPME; extraction temp. = 80 °C and time = 30 min; 3. Purge and Trap Tenax trap, thermal desorption	GC-MS	None	swine barn PM (84)
[19]	PM scraped and weighed into glass headspace vials	Solvent extraction	GC-FID	None	Swine barn PM, (14)
[16]	PM harvested from Aluminum-foil-covered sedimentation plate	Solvent extraction	GC-FID	None	Swine barn PM, (11)
[12]	Glass electrostatic precipitator	Solvent extraction	GC-FID	None	Swine barn PM (35)
[11]	Empty 20-L bottle	Solvent extraction	GC-FID, MS	Smelled through Millipore filter	Swine barn PM (19)
[15]	Dust sample bags	Solvent extraction	GC-MS, GC-S-detector	None	Hog growing operations (7)
[21]	Teflon-coated glass fiber PM-10 filter	SPME 100 µm PDMS sampling temp = 50 °C and time= 20 min,	GC-MS	None	Atmospheric urban PAHs (14)
[22]	Quartz filter PM-10	SPME 100µm PDMS, each vial heated at 100 C for 30 min and then left at room temp. for 7 min prior to 10 min extraction,	GC-MS	None	Atmospheric urban PM (72)
[23]	Glass fiber filter PM-1, PM-2.5	Thermal desorption	GC-MS	None	Atmospheric PM (31)
[24]	Filter	Thermal desorption in a glass tube followed by SPME.	GC-UV	None	Indoor PM (28)
[25]	2 µm pore size PM-10 and PM-2.5 PTFE filters	Solvent extraction:	GC- MS	None	Outdoor and indoor air PM (14)

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664 Table 2. Frequency of occurrence of the compounds identified on different size particulate matters
665 and relevant references.

No	RT (min)	Compound s Name	CAS	References ^a						PM-1 ^b	PM-2.5 ^c	PM-10 ^d	TSP ^e	Odor Threshold (ppm) Summary ^f	Odor
				i	ii	iii	iv	v	vi						
1	1.16	H ₂ S	7783-06-4						Y	6	1	7	7	0.0178 ² , 0.0045(r) ³ , 0.0081 ⁵	sewer, fecal
2	1.38	Pentane	109-66-0							2	0	0	5	31.623 ² , 119-1147 ³ , 400 ⁵	
3	1.48	Methyl mercaptan	74-93-1							0	0	7	7	0.00105 ² , 0.00054 ³ , 0.0016 ⁵	Sewer
4	1.55	1, 1-Dichloro-1-fluoroethane	1717-00-6							6	1	7	7		
5	1.56	Trimethylamine	75-50-3							6	1	0	7	0.00240 ² , 0.00011-0.87 ³ , 0.001034 ⁴ , 0.00044 ⁵	
6	1.83	3-Pentanamine	616-24-0							0	0	0	3		
7	1.91	Acetone	67-64-1	Y			Y			6	1	7	7	14.454 ² , 62 ³ , 13 ⁵	aldehydic
8	2.45	Heptane	142-82-5	Y						0	0	6	7	9.772 ² , 230 ³ , 150 ⁵	
9	2.53	Butanal	123-72-8				Y			0	1	7	7	0.00891 ² , 0.00523-0.0654 ⁴	aldehydic
10	3.21	3-Methyl-butanal	590-86-3	Y						0	0	6	7	0.00224 ² , 0.000852-0.001703 ⁴	aldehydic
11	3.70	Diacetyl	431-03-8							4	1	7	7	0.00437 ² , 0.00142-0.00739 ⁴	buttery
12	4.21	Pentanal	110-62-3	Y			Y			0	0	7	7	0.00603 ² , 0.0006-8.2 ³ , 0.00965-0.0111 ⁴ , 0.028 ⁵	
13	6.61	Hexanal	66-25-1	Y			Y	Y	Y	6	1	7	7	0.0138 ² , 0.00732-0.0129 ⁴	grassy
14	8.33	Ethanone, 1-(1-cyclohexen-1-yl)	932-66-1							0	0	4	7		
15	9.06	2-Heptanone	110-43-0							0	0	7	7	0.141 ² , 0.18-0.19 ³ , 0.278 ⁴ , 0.35 ⁵	unknown
16	9.21	Heptanal	111-71-7	Y				Y	Y	0	1	7	7	0.00479 ² , 0.0535 ⁴	sweet, estery
17	10.15	Styrene	100-42-5							6	1	7	7	0.145 ² , 0.14 ³ , 0.32 ⁵	
18	10.56	2-Heptanone, 6-methyl-	928-68-7							0	0	2	4		
19	10.86	Formamide, N,N-dimethyl-	68-12-2							0	0	2	5	100 ² , 0.47-100 ³ , 2.20 ⁵	
20	10.98	Furan, 2-pentyl-	3777-69-3	Y						0	0	7	7	0.0158 ² , 0.0478 ⁴	
21	11.51	1-Hexanol	111-27-3	Y						0	0	6	7	0.0437 ²	
22	11.78	Octanal	124-13-0	Y					Y	5	1	7	7	0.00135 ² , 0.00111-0.00259 ⁴	aldehydic
23	12.01	Dodecane	112-40-3							6	0	3	2	2.042 ²	
24	12.55	Ethanol, 2-butoxy-	111-76-2							6	1	7	7	0.339 ² , 0.10 ³ , 0.10 ⁵	
25	13.1	Acetic acid	64-19-7	Y	Y	Y	Y			6	1	7	7	0.145 ² , 0.07 ³ , 0.0245 ⁴ , 0.48 ⁵	acidic
26	13.65	3-Octen-2-one	1669-44-9	Y						1	1	7	7		
27	14.16	n-Nonanal	124-19-6	Y				Y	Y	5	1	7	7	0.00224 ² , 0.000774-0.00208 ⁴	earthy, aldehydic
28	14.53	2-Ethylhexanol	104-76-7	Y						6	1	7	7	0.245 ²	
29	14.81	Propanoic acid	79-09-4	Y	Y	Y	Y			4	1	7	7	0.0355 ² , 0.033(r) ³ , 0.16 ⁵	acidic
30	15.40	Isobutyric acid	79-31-2		Y	Y				0	0	3	3	0.0195 ²	buttery, acidic
31	15.80	1-Octanol	111-87-5	Y						0	0	7	7	0.00575 ²	earthy, moldy
32	16.46	Butanoic acid	107-92-6	Y	Y	Y	Y			0	0	7	7	0.00389 ²	acidic, fatty acid
33	17.20	3-Methyl-butanoic acid	503-74-2	Y	Y	Y				0	0	7	7	0.00246 ² , 0.000359 ⁴	body odor, acidic
34	18.13	gamma-Hexalactone	695-06-7							1	0	6	7		
35	18.38	Pentanoic acid	109-52-4	Y	Y	Y	Y			0	0	7	7	0.00479 ²	acidic
36	18.78	Acetamide	60-35-5							0	0	1	0	60.256 ²	
37	18.81	2, 4-Nonadienal	5910-87-2	Y			Y	Y		0	0	4	6	0.000035 ² , 0.0000708 ⁴	herbaceous
38	20.16	Hexanoic acid	142-62-1		Y		Y			0	0	6	7	0.0126 ²	
39	20.71	Benzenemethanol	100-51-6							6	1	7	5		
40	21.11	Dimethyl sulfone	67-71-0							1	1	6	7		

Cai, L., J.A. Koziel*, Y.C. Lo, S.J. Hoff. Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and GC-MS-Olfactometry. *Journal of Chromatography A*. 2005, in press.

41	21.86	Heptanoic acid	111-14-8		Y		Y			0	0	0	1	0.0275 ²	acidic
42	22.66	Phenol	108-95-2	Y	Y	Y		Y		6	1	7	7	0.1096 ² , 0.06 ³ , 0.04 ⁵	medicinal, phenolic, smoky
43	23.7	2, 6-Di-tert-butyl-4-ethylphenol	4130-42-1							6	1	7	7		
44	23.78	4-Methyl-phenol	106-44-5	Y	Y	Y	Y	Y		6	1	7	7	0.00186 ² , 6.793E-5 - 2.264E-4 ⁴	medicinal, phenolic, barnyard
45	24.56	2-Piperdinone	675-20-7							0	0	0	1		medicinal, phenolic, barnyard
46	25.13	4-Ethyl -phenol	123-07-9	Y		Y	Y	Y		6	1	7	7		
47	25.95	2'-Aminoacetophenone	551-93-9							0	0	0	1		
48	28.81	Indole	120-72-9	Y	Y	Y				6	1	7	7	0.000032 ²	barnyard, medicinal, phenolic
49	29.50	3-Methyl-Indole	83-34-1	Y	Y	Y		Y		6	1	7	7	0.000562 ²	barnyard, medicinal, phenolic
50	31.00	5-Acethyl-2-methylpyridine	42972-46-3							0	0	1	0		

666 a. i. Razote et al. [18], ii. Oehrl et al [19], iii. Hartung et al [16], iv. Hammond et al. [12], v.
667 Hammond et al.[11] , vi. Das et al. [15]
668 b. Out of 6 c. out of 1 d. out of 7 e. out of 7
669 g.¹ Devos et al. [44], ² Devos et al. [45], ³ Odor Thresholds for Chemicals with Established
670 Occupational Health Standards [46], ⁴ Rychlik et al. [47], ⁵ Amoores et al [48].
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696 Table 3. Measured concentrations, mass and total surface area of PM-1, PM-10 and TSP.

Date (start)	PM-1				PM-10				TSP			
	Duration (hr)	C ($\mu\text{g}/\text{m}^3$)	Mass (μg)	TSA (mm^2)	Duration (hr)	C ($\mu\text{g}/\text{m}^3$)	Mass (μg)	TSA (mm^2)	Duration (hr)	C ($\mu\text{g}/\text{m}^3$)	Mass (μg)	TSA (mm^2)
11/08/04	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	68.0	755	9230	2890
11/11/04	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	97.5	794	13900	4140
11/18/04	94.5	4.8	81.6	60.8	95.0	253	4330	3390	94.5	824	14000	4010
11/22/04	n/a	n/a	n/a	n/a	143	239	6180	5120	143	1,050	27100	6090
11/29/04	35.2	6.8	43.0	22.6	35.2	296	1870	1260	n/a	n/a	n/a	n/a
12/06/04	n/a	n/a	n/a	n/a	166	115	3430	5920	166	868	25900	7050
AVG		5.8	62.3	41.7		226	3950	3920		858	18000	4840

697 n/a= not available.

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