RESEARCH REPORT
ENVIRONMENT

Title: Quantifying Volatile Organic Compound Interaction With Particulate Matter For The Development Of Odor Transport Models – **NPB# 01-088**

Investigator: KC Das

Institution: The University of Georgia

Co-Investigators: S Hassan, JR Kastner, G. Van Wicklen, Rick Jones

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ABSTRACT

A method of extracting the organics adsorbed to dust particles was developed and tested with dust collected from two commercial hog growing operations. Five aldehydes, one alkane, and hydrogen sulfide were consistently measured in dust samples. Dust samples collected were separated into three sizes, small (5 to 20 µ), medium (20 to 40 µ) and large (40 to 75 µ) and analyzed individually. The key results and conclusions from this work are as follows:

1. As much as 85 to 90% of the total mass of dust samples are in the range of 20 to 75 µ size (sampling range = 5 to 75 µ).
2. When a combined analysis including all sizes were conducted to quantify differences based on location of sampling, only three compounds, heptanal, nonanal, and decanal showed differences based on sampling location.
3. Significantly higher hydrogen sulfide, octanal, and nonanal were found in small (5 to 20 µ) size particles when compared to medium and larger samples. All other compounds tested showed no difference based on size of particles.
4. One location (B) showed a greater amount of differences based on when the samples were obtained (warmer weather v. cooler weather). In this case warmer weather tended to have significantly higher concentration of compounds.
5. At location A, only two (decanal and n-octane) of the seven compounds tested showed differences based on when the dust samples were obtained (summer v. winter). In this case the cooler weather conditions resulted in greater amount of compound adsorbed.

INTRODUCTION

The Odor problem: Odors are produced through the biological decomposition of organics such as manure and feed. Release of odors into the atmosphere and their transport has resulted in significant concern to operators in swine farms and neighbors around farms. In some cases, community discontent with true and potential odor has been sufficient to generate lawsuits, close farming operations and prevent large lucrative businesses from establishing in certain states. Although odors have been studied for years, simple and reliable methods to quantify odors in an air stream are not available. An understanding of odor's interaction with dust would aid in the design of simple collection systems used to prevent odor transport. Quantifying this dust-odor interaction was the purpose of this project.

There are two general odor measuring techniques, (1) gas chromatography and (2) olfactometric methods using human panels. Gas chromatography is compound specific, but many methods do not account for VOC adsorption nor correlate an associated "odor" with the identified compound. Similarly, gas samples (30L) typically collected in Tedlar bags, are transported, pre-filtered and then administered to human odor panels and used in a dynamic olfactometric apparatus to rate the odor. The disadvantages of this method are high cost (over $200 per sample), the long response time, the subjective nature of the analysis, large variations in results, pre-filtration underestimates "odor" levels, and the fact that the method is not quantitative. Since olfactometric methods are neither quantitative (i.e., concentration), nor descriptive (type of VOCs), use of these data in transport models can lead to erroneous conclusions.

Transport models using odor threshold data must assume that the odor travels as a uniform plume, which predicts much longer transport distances than measured experimentally (Zahn et al., 1997). Recent experimental data indicate the chemical composition of the odor plume changes significantly with distance (Zahn et al., 1997). Moreover, any control and management strategies that are implemented will be selective for certain VOCs or particulate sizes (e.g., a biofilter or wet scrubber). These strategies can only be evaluated and designed using methods that measure VOC/particulate concentration and composition.

LITERATURE REVIEW

As much as 80% of the dust (based on numbers) in a swine house is small, ranging 0.5-2.5 μm (Nilsson, 1982). However, based on mass the small particles account for only 10% of the total mass. Simple calculations yield that total surface area represented by particles in the 0.5-2.5 μm range is about 19% of the total surface area of all particles in the 0-10.0 μm range. In addition the density of the 0.5-2.5 μm particles is eight times that of the 2.5-10.0 μm range particles, suggesting very different sources, adsorption capacities and transport properties. Heber et al. (1988) performed microscopic evaluation of particles in the size range of <2.7 to 30.5 μm range and found particles consisting of epithelial cells, undigested feed, starch, grain meal, trichomes, corn silk, hyphae, spores, pollen, insect parts and mineral ash. They attributed these to seven potential sources, namely, (1) feed, (2) fecal matter, (3) dander, (4) mold, (5) mineral ash, (6) pollen, and (7) insect parts. Their results show that particles <2.0 μm are

generally fecal matter, the 5.4 to 16.0 μm range predominantly grain meal, and the 10.8-15.3 μm predominantly starch. Skin and hair were present in the 7.0-15.3 μm range. This clearly suggests that particles of different sizes are from different sources and will behave in different manner as to their adsorption capability for different odorous gases.

Earlier studies have indicated that particles greater than 4.0 μm, ranging 5-20 μm primarily contribute to dust-borne odors (Robertson and Frieben, 1984; Carpenter, 1986; Honey and McQuitty, 1979; Burnett, 1969). Donham et al. (1986) quantified the adsorption capability of dust to ammonia and found that we can expect 3.9 mg(NH_3)/g(dust). Hammond et al. (1979) reported that all of the odors were removed from an air stream if a dust filter of 0.8 μm was used to remove all particles. In another work, Hammond et al. (1981) observed that gaseous odors were adsorbed to the particle filter and this typically constituted about half of the total odors. Moreover, butyric acid and p-cresol concentrations were reportedly 4 x 10^7 times greater on particulate matter than in ambient air. In general they concluded that about half of the odors in a gas stream were attributed to gaseous odors and the remaining to dust-borne odors. However, this result was not quantitatively evaluated. These studies suggest that a large fraction of odors adsorb to particles in the larger size range and likely have different affinities to odorous compounds.

The types of compounds adsorbed on dust, when extracted with ether followed by GC analysis, have been found to consist of **acids, phenols, and carbonyls** (Hammond et al., 1981). Day et al. (1965) utilized methanol as an extractant and found several compounds similar to the work of Hammond et al. (1979). Hammond et al. (1979, 1981) and Zahn (1997) indicate the difficulty of identifying sulfur compounds and it is likely that these are lost in a chemical reaction during the extraction procedure or inadequately adsorbed if tubes are used. Sulfur compounds such as methanethiol are known to be extremely odorous and significantly contribute to overall odors. Hence a better method that accounts for these sulfur compounds is required.

OBJECTIVES

The overall objective in this project was to develop a method to quantify the VOC concentration and composition adsorbed to particulate matter emanating from swine farms. The specific objectives were:

1. Develop a simple, sensitive and reliable method to quantify odorous compounds adsorbed to dust collected from a swine house.
2. Determine the particle size distribution for particulate matter in the swine house.
3. Quantify the odorous gaseous compounds adsorbed to dust sampled from different farms during different seasons and report them based on size of particulates.
4. Determine the emission factors for the odorous VOCs and particulate matter.

MATERIALS AND METHODS

Collection of Dust Samples

Dust samples were collected from two different farms (location A and B) between Feb and July of 2002. A model 500x vacuum sampler containing dust sample bags (0.05 μ allergy dust bags, DACI reference Lab, Asthma & Allergy Ctr. Rm. 1A20, 5501 Hopkins

Bay View Cir., Baltimore MD. 21224) were used to obtain a large sample (typically 3-5 g) from within the growing houses.

Dust samples were brought back to the laboratory and a total weight was recorded before sieving using a sonic sifter (cut size 90 µ). An ATM Sonic Sifter Model L3P (ATM Corp., Milwaukee, WI) was used with five size cuts to separate the dust into fractions between 5 and 90 µ (Figure 1). Typically the amount of sample in the size below 5 µ and above 75 µ were too small to use, and were therefore discarded. The sizes used in this work were small (5 to 20 µ), medium (20 to 40 µ) and large (40 to 75 µ). Individual sample size weights were recorded before sending the dust samples for analytical extraction.

Analytical Methodology

Extraction of Particle Adsorbed VOC's

About 1 g of the dust sample was accurately weighed and transferred into a 125 ml-serum bottle and combined with 20 ml of pesticide residue grade acetone. The bottle was sealed with a 20 mm aluminum foil / silicone septa with the aluminum surface facing the bottle contents. The seal was secured in place with aluminum crumbles and the bottle was placed in an ultrasonic bath for 30 minutes. The bottle was centrifuged at 3000 rpm for 20 minutes and the acetone extract was transferred into a 50 ml-conical flask. The extract was concentrated down to about 1 ml by immersing in a warm water bath under a stream of nitrogen. One ml aliquot of methanol was added and evaporation of acetone on the water bath under nitrogen was continued. The alcohol addition and evaporation was repeated for 2 additional times. Care was taken to avoid dryness of the samples. The extract (~ 1 ml) was quantitatively transferred to 2 ml measuring flasks and made up to volume with methanol.

Analysis of Aldehydes and n.Octane Content

The compound concentration in the extract was determined using a gas chromatography mass spectrometric procedure. A Hewlett Packard gas chromatograph model 5890 series II supplied with an HP 5971A mass spectrometer and an HP 7873 automatic sampler was used. The injector temperature was 250°C while that of the mass spectrometer was 280°C. The initial temperature of the oven was 50°C for 1 minute then increased to 160°C at a rate of 6°C/minute and finally increased at a 20°C/minute to 220°C and kept at that temperature for an additional 1 minute. Helium was used as the carrier gas at constant flow; the initial pressure of the inlet was 3.9 psi. The column used was an HP DB-5 MS; its length was 30 meters and its diameter was 0.32 mm. The mass spectrometer was in the selective ion monitoring mode and the solvent delay was 4 minutes.

Analysis of Hydrogen Sulfide content

Hydrogen sulfide was determined using a Hewlett Packard 5890 series II gas chromatograph connected to a Sulfur Chemiluminescence detector (Sievers Model 355). The inlet temperature of the GC was 200°C and helium was the carrier gas. An SPB1-Sulfur column (Supelco, Inc) 30 m long, 0.32 mm X 4 mm was used for separation. The oven program starting temperature was 60°C for 2.5 minutes then increased at a rate of 15°C/minute till 120°C and stayed for 2 minutes. The pressure of

the sulfur detector controller was 150-275 Torr, the burner temperature was 800°C, hydrogen flow rate was 100 ml/min and airflow rate was 40 ml/min.

RESULTS AND DISCUSSION

Two locations were selected for this study while samples were collected over periods covering summer and winter times. Table 1 shows the month and location where selected samples were collected and its corresponding weight distribution. Some of the sampling times include additional samples, which were used only for gas analysis and not for weight distribution. Location A was found to have a significantly greater weight fraction of medium size samples compared to location B where medium and large sizes were evenly represented (Figure 1). It should be noted that these distribution are weight based and do not indicate the number of samples. Small size samples, although contributing to only 10.6 and 14.3 % of the total weight, significantly outnumber large particles because of their size

Six aldehydes, one alkane, and one sulfur-compound were consistently seen in most of the dust samples collected. Analysis of the concentration of individual gases in the entire set of dust samples based only on location from which they were collected revealed that there were significant differences between locations only in heptanal, nonanal, and n-octane (Table 2). All other compounds were found to be within statistical variability and the location of sample did not show any differences in the amount adsorbed to the dust. Hydrogen sulfide was an order of magnitude higher than aldehydes and was 432.4 (Location A) and 278.9 mg/kg (Location B). Highest aldehyde concentration was nonanal at location B (18.8 µg/kg).

From the earlier analysis discussed above, we decided to look at differences in location of sampling and season based on the individual sizes (small, medium, and large). Significant differences were found in octanal, nonanal and hydrogen sulfide (Table 3). In the case of hydrogen sulfide significantly higher ($\alpha = 0.05$) amount of compound was adsorbed to the small, and there was no difference between that in medium and large size dust. Similar results were seen in the two aldehydes but with larger differences ($\alpha = 0.01$).

Analysis of the seasonal impact (Winter v. Summer) showed that at location A, there were no differences in the amount of hydrogen sulfide in dust collected in winter or in summer (Table 4). Decanal and n-octane were the only aldehydes that showed any difference between the seasons. In both cases, the winter months showed higher amounts of compounds. The possible reason fro this is the longer residence time of dust within the houses resulting from lower aeration during winter months. For these analyses, February through March was considered winter months and compared to samples obtained in July, which was considered the summer month. Samples collected in June were not used in this analysis.

At location B greater differences between the dust samples were found, especially in the small and medium size ranges. Although both locations were of identical operation, the key difference was that in Location B there was a more frequent cleaning of dust within the house (approx. twice a week) compared to Location A. In the small size samples, hexanal, heptanal, octanal, and nonanal were significantly ($\alpha = 0.01$) different

based on when the samples were collected (May v. July) (Table 5). Unlike location A, in all cases here, the warmer months had greater amounts of aldehydes and hydrogen sulfide. Differences were found in the samples of large size only for hydrogen sulfide and n-octane, all of the aldehydes were statistically similar and independent of the season of sampling.

FUTURE WORK

The method developed here has potential for evaluation of dust-odor impact of hog houses on the environment and neighbors. Future work can refine our understanding by collecting additional data from different operations. Potential remediation options can be evaluated using dispersion modeling and implementation of technologies like windbreak walls, wet fitters, or dry fitters.

Figure 1. Sonic sifter apparatus used for separating the collected dust samples into small (5 to 20 µ), medium (20 to 40 µ) and large (40 to 75 µ) sizes.

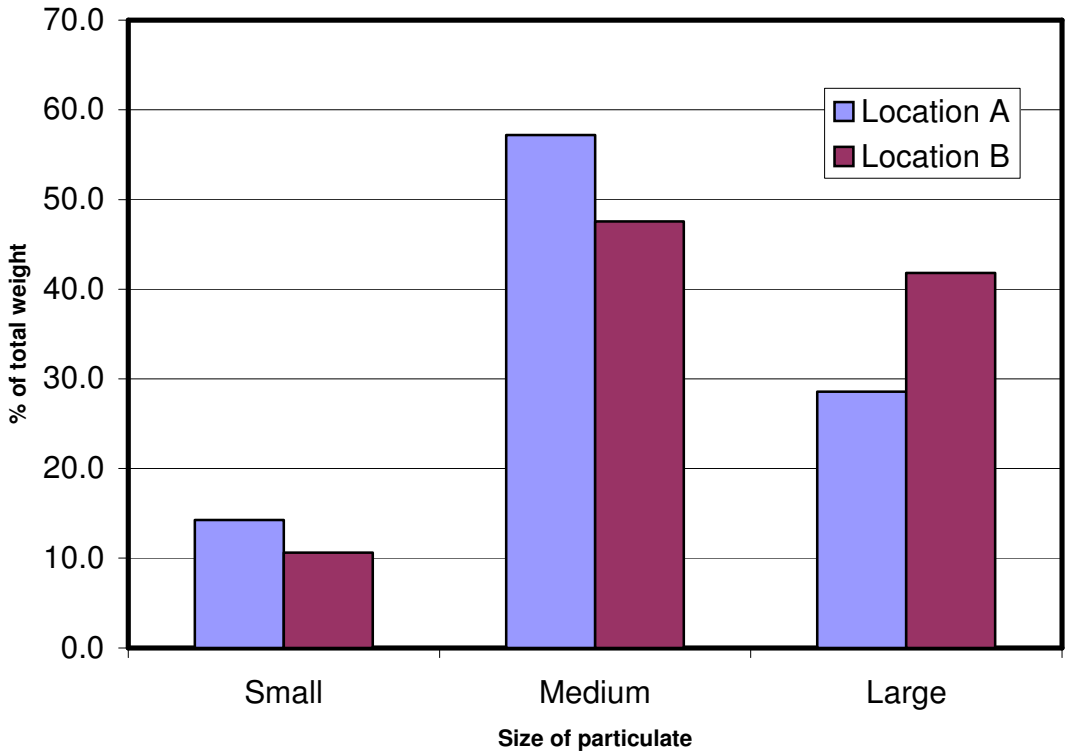

Figure 2. Average weight distribution of dust samples collected from two different farming operations (locations A and B).

Table 1. Weight distribution of selected samples obtained from two different farming operations.

		Weights of samples (g)			% Distribution		
Month	Location	5-20	20-40	40-75	Small	Medium	Large
Feb	A	1.068	7.506	2.771	9.4	66.2	24.4
Mar	A	1.308	6.258	2.074	13.6	64.9	21.5
Mar	A	8.053	1.345	1.403	74.6	12.5	13.0
Mar	A	0.28	8.256	11.262	1.4	41.7	56.9
Mar	A	0.482	6.887	3.642	4.4	62.5	33.1
Mar	A	1.712	7.172	1.884	15.9	66.6	17.5
Mar	A	2.538	6.342	2.95	21.5	53.6	24.9
Mar	A	1.706	6.452	2.257	16.4	61.9	21.7
June	A	0.381	4.595	2.514	5.1	61.3	33.6
June	A	0.577	7.643	2.827	5.2	69.2	25.6
July	A	0.978	4.153	1.708	14.3	60.7	25.0
July	A	0.73	4.148	1.928	10.7	60.9	28.3
July	A	0.485	7.246	4.15	4.1	61.0	34.9
July	A	0.364	6.817	4.693	3.1	57.4	39.5
				AVG	**14.3**	**57.2**	**28.6**
				STDs	18.4	14.5	10.8
May	B	2.613	7.413	6.166	16.1	45.8	38.1
May	B	0.539	2.076	1.688	12.5	48.2	39.2
May	B	1.166	3.668	2.368	16.2	50.9	32.9
May	B	0.871	3.38	2.475	12.9	50.3	36.8
May	B	1.451	4.174	2.573	17.7	50.9	31.4
May	B	1.466	5.392	3.358	14.4	52.8	32.9
May	B	1.688	5.565	3.141	16.2	53.5	30.2
May	B	2.189	6.843	5.199	15.4	48.1	36.5
June	B	1.262	5.534	4.983	10.7	47.0	42.3
June	B	1.64	6.455	5.681	11.9	46.9	41.2
July	B	0.018	2.136	3.501	0.3	37.8	61.9
July	B	0.083	2.529	2.747	1.5	47.2	51.3
July	B	0.087	3.023	3.337	1.3	46.9	51.8
July	B	0.037	1.439	2.138	1.0	39.8	59.2
				AVG	**10.6**	**47.6**	**41.8**
				STDs	6.5	4.4	10.3

Table 2. Concentration of extracted aldehydes, octane, and hydrogen sulfide in dust samples obtained from two different farms (Location A and B).

Compound	Concentration of adsorbed compound to dust particulate of defined size		Significance difference[1]
	Location A	Location B	
Hexanal, µg/kg	15.72	17.90	
Heptanal,µg/kg	4.44	9.92	**
Octanal, µg/kg	1.88	2.07	
Nonanal, µg/kg	9.05	18.80	**
Decanal, µg/kg	4.26	8.98	*
n- Octane, µg/kg	1.44	1.75	
H_2S, mg/kg	432.4	278.9	

[1]* indicates significant difference at α = 0.05
** indicates significant difference at α = 0.01 based on ANOVA.

Table 3. Concentration of extracted aldehydes, octane, and hydrogen sulfide in dust samples compared based on the size of the dust sample.

Compound	Concentration of adsorbed compound to dust particulate of defined size			Significance difference[1]
	Large 40 to 75 µ	Medium 20 to 40 µ	Small 5 to 20 µ	
Hexanal, µg/kg	15.16	16.75	18.69	
Heptanal,µg/kg	5.91	6.40	9.98	
Octanal, µg/kg	1.39 a [2]	1.47 a	3.11 b	**
Nonanal, µg/kg	11.23 a	11.41 a	20.17 b	**
Decanal, µg/kg	5.06	5.90	8.54	
n- Octane, µg/kg	1.32	1.45	2.09	
H_2S, mg/kg	274.6 a	253.9 a	539.2 b	*

[1]* indicates significant difference at α = 0.05
** indicates significant difference at α = 0.01 based on ANOVA.
[2] Numbers in columns followed by different alphabet are significantly different from each other based on Fisher LSD multiple comparison.

Table 4. Concentration of extracted aldehydes, octane, and hydrogen sulfide in dust samples collected from location A and compared based on the season when sample was collected (summer or winter).

Compound	Concentration of adsorbed compound to dust particulate of defined size		Significance difference[1]
	Summer	Winter	
Size Small, 5 to 20 µ			
Hexanal, µg/kg	11.30	14.66	
Heptanal,µg/kg	3.83	6.92	
Octanal, µg/kg	1.81	3.63	
Nonanal, µg/kg	11.69	14.42	
Decanal, µg/kg	4.66	21.23	
n- Octane, µg/kg	0.37	2.7	*
H_2S, mg/kg	493.2	477.8	
Size Medium, 20 to 40 µ			
Hexanal, µg/kg	11.78	23.27	
Heptanal,µg/kg	2.20	5.90	
Octanal, µg/kg	0.95	1.88	
Nonanal, µg/kg	6.29	8.29	
Decanal, µg/kg	3.14	10.96	*
n- Octane, µg/kg	0.25	2.73	**
H_2S, mg/kg	360.2	403.8	
Size Large, 40 to 75 µ			
Hexanal, µg/kg	15.18	20.18	
Heptanal,µg/kg	1.69	5.46	
Octanal, µg/kg	1.01	2.14	
Nonanal, µg/kg	5.00	9.00	
Decanal, µg/kg	1.81	13.82	*
n- Octane, µg/kg	0.21	2.09	*
H_2S, mg/kg	383.8	456.8	

[1]* indicates significant difference at α = 0.05
** indicates significant difference at α = 0.01 based on ANOVA.

Table 5. Concentration of extracted aldehydes, octane, and hydrogen sulfide in dust samples collected from location B and compared based on the season when sample was collected (May or July).

Compound	Concentration of adsorbed compound to dust particulate of defined size		Significance difference[1]
	May	July	
Size Small, 5 to 20 µ			
Hexanal, µg/kg	5.05	44.07	**
Heptanal,µg/kg	5.18	14.52	**
Octanal, µg/kg	1.01	4.61	**
Nonanal, µg/kg	10.47	45.93	**
Decanal, µg/kg	1.52	1.87	
n- Octane, µg/kg	0.70	0.79	
H_2S, mg/kg	55.56	1753.2	**
Size Medium, 20 to 40 µ			
Hexanal, µg/kg	4.61	24.82	*
Heptanal,µg/kg	4.18	9.8	*
Octanal, µg/kg	0.86	1.38	
Nonanal, µg/kg	9.28	21.97	*
Decanal, µg/kg	1.59	1.9	
n- Octane, µg/kg	0.56	0.82	
H_2S, mg/kg	25.81	205.03	**
Size Large, 40 to 75 µ			
Hexanal, µg/kg	5.18	24.71	
Heptanal,µg/kg	4.25	5.16	
Octanal, µg/kg	0.81	0.94	
Nonanal, µg/kg	11.36	11.37	
Decanal, µg/kg	1.67	1.87	
n- Octane, µg/kg	0.26	0.92	**
H_2S, mg/kg	31.26	160.37	**

[1]* indicates significant difference at α = 0.05
** indicates significant difference at α = 0.01 based on ANOVA.

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