Comparison of odorants in room-air and in headspace of sediment dust collected in swine buildings

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Abstract

This paper presents preliminary results from a study aimed at comparing odorants in room-air and odorants in static headspace of sediment dust samples collected in swine buildings. The study included the samples collected during winter and summer surveys at four different swine farms, each equipped with gestation, farrowing, rearing, and finishing buildings.

The room-air odorants in different swine buildings were sampled using solid-phase microextraction (SPME) fibres and their relative concentrations were analyzed using gas chromatography and mass spectrometry (GC/MS). On each sampling occasion, two SPME samples were taken and a sediment dust sample was collected from the surfaces of fixtures in the room. About 5 g of the sediment dust sample was packed in a ∅ 38 mm stainless steel pipe, whose headspace was connected with a closed air circulation pipe. In a climate chamber, the whole setup was kept at 30 °C for 30 min to achieve the equilibrium stage, then, the dust-headspace odorants were sampled using SPME. Then, their relative concentrations were analyzed by GC/MS. The odorants included in the present study are: trimethyl amine (TMA), dimethyl sulphide (DMS), butanoic acid (BA), 3-methyl-butanoic acid (3MBA), 4-methyl-pentanoic acid (4MPA), benzyl alcohol (BAL), indole (IND), and 3-methyl-indole (3MIND). These 8 odorants are called technical key odorants (TKOs).

As overall, TKO concentrations in room-air and headspaces are significantly correlated; but a relatively large spreading was also observed. Further study on interaction between TKOs in room air and dust particles is recommended.

Keywords: odour, swine building, dust headspace, SPME

Introduction

More than 300 different odorous compounds have been identified in livestock buildings (Tanaka H. 1988, Schiffman S. S. et al. 2001). Tanaka H. (1988) reported that ammonia, sulphides, volatile fatty acids, amines, indoles, phenols, ketones, aldehydes and mercaptans are compounds/compound groups of special importance in connection with offensive odours from animal husbandry. Many of these odorants are generated in slurry under anaerobic conditions. The profile of the odorant concentrations in room air is affected by different conditions, such as feeding, management of livestock manure, hygiene and ventilation methods, and the rate of air exchange (Jacobson L. D. et al. 2000, Janni K. et al. 2001). Hartung J. (1985) showed that dust from swine confinement buildings contains VFA, phenols, indoles and scatole. The airborne dust originated from manure contains these compounds. The dust particles interact with the surrounding air and may exchange the odorous compounds by means of ad-, ab- and desorption processes. Hammond E. G. et al. (1981) estimated that the concentration of butyric acid and p-cresol will be about 4×10^7 greater in a dust particle than in an equal volume of air. Reynolds S. J. et al. (1998) estimated that a significant proportion (15 - 23%) of airborne ammonia in enclosed livestock facilities is associated with particles. Takai H. et al. (2002) reported that ammonia contents in inhalable dust collected in dairy, poultry and farrowing houses ranged from 1-6 µg per mg of dust, i.e. 1,000 to 6,000 ppm on a weight basis, while about 7 µg NH_3 per mg of dust, i.e. 7,000 ppm, was found in respirable dust.

Ammonia, hydrogen sulphide and other odorous compounds in the respirable fraction of inhaled dust particles may reach the lower parts of the respiratory tract, i.e. the bronchi and the alveoli, and irritate the organs. If this hypothesis is true, the chemical compounds absorbed in dust particles plays an important role in the development of respiratory diseases in farmers' lungs. The deposition of dust particles in the nose may result in high local concentrations of odours at and in the mucosa in the *regio olfactoria*, which will affect the perception of odour.

To understand the synergistic effects of gases and aerosols on farmers' health and malodour problems improved knowledge on relation between odorant concentrations in dust particles and in room air is desired.

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The present study is aimed at comparing the odorants in the room-air and in the headspace of the sediment dust samples collected in swine buildings.

Method and materials

The study have included samples collected during winter and summer surveys at four different swine farms, each equipped with gestation, farrowing, rearing, and finishing buildings. Two surveys were carried out in the winter of 2003–2004 and two in the summer of 2004.

The odorants included in the present study are: trimethyl amine (TMA), dimethyl sulfide (DMS), butanoic acid (BA), 3-methyl-butanoic acid (3MBA), 4-methyl-pentanoic acid (4MPA), benzyl alcohol (BAL), indole (IND), and 3-methyl-indole (3MIND). These 8 odorants are called technical key odorants (TKOs) and were selected based on the results from earlier study (Takai H. et al. 2007), who applied principal variable analysis to identify TKOs. The study showed that these 8 TKOs could explain more than 90% of the variation found in a data set of 18 room-air odorants. The physical properties and odor threshold levels of TKOs found in the literatures are shown in table 1.

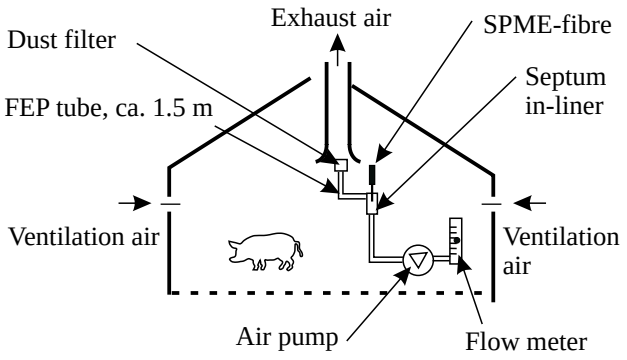

Figure 1:
Odorant sampling in a swine building by means of SPME

About 5 g of the sediment dust sample was packed in a ∅ 38 mm stainless steel pipe, of which the headspace air was circulated in a closed system consisting of FEP tubes, a septum in-liner and a stainless steel air pump (AFC 123 personal air sampler; BGI Inc., USA). In a climate chamber, the setup was kept at 30°C for 30 min to achieve the equilibrium stage, then, the dust-headspace odorants were sampled by using SPME, figure 2. Then, their relative concentrations were analyzed by GC/MS.

Table 1:
Physical properties and odor threshold levels of the technical key odorants (TKOs) included in the present study (Syracuse Research Corporation's, 2007)

Name	CAS #	Mol weight m	Solubility H_2O (25°C)	Boiling point	Vapor Pressure (25°C)	Henry's constant k_h	Dis-sociation constant	Odour threshold[2)]
		g mol^{-1}	g l^{-1}	(°C)	mm Hg	atm l mol^{-1}	pK_a	µg m^{-3}
Trimethyl amine (TMA)[1)]	75-50-3	59.11	890.0	2.8	1.61E+03	1.04E-01	9.80	5.9
Dimethyl sulphide (DMS)	75-18-3	62.13	22.0	37.3	5.02E+02	1.61E+00		5.9
n-Butyric acid (BA)	107-92-6	88.11	60.0	164.1	1.65E+00	5.35E-04	4.83	14.5
3-Methyl butanoic acid (3MBA)	503-74-2	102.10	40.7	176.5	4.40E-01	8.33E-04	4.77	10.5
4-Methyl pentanoic acid (4MPA)	646-07-1	116.16	5.3	200.5	4.45E-01	1.70E-03	4.84 15.40	75.9 24,500.0
Benzyl alcohol (BAL)	100-51-6	108.14	42.9	205.3	9.40E-02	3.37E-04	0	0
Indole (IND)	120-72-9	117.20	3.6	253.0	1.22E-02	5.28E-04	-2.40	0.2
3-Methyl-1H-indole (3MIND)	83-34-1	131.10	0.5	265.0	5.55E-03	2.13E-03	-3.40	3.1

[1)] As a solution in water ~50%
[2)] Schiffmann S. S. et al. (2001)

The room-air odorants in different swine buildings were sampled using solid-phase microextraction (SPME) fibres (figure 1), and their relative concentrations were analyzed using gas chromatography and mass spectrometry (GC/MS). On each sampling occasion, two SPME samples were collected in parallel and a sediment dust sample was collected from the surfaces of fixtures in the room. The sediment dust samples were kept in airtight blue cap glass bottles (100 ml) with PTFE sealing in a freezer at -15°C until analysis within about 120 days.

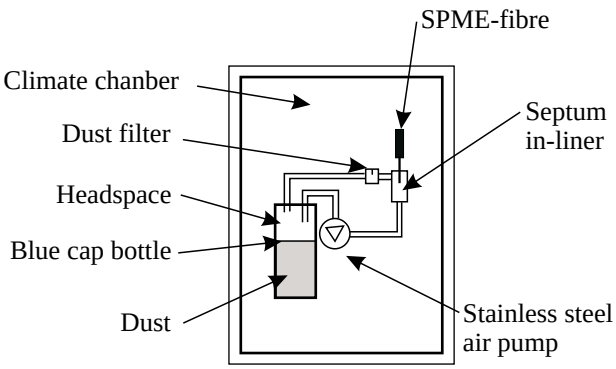

Figure 2:
Sampling of odorants of dust headspace air at different temperatures

Solid-phase microextraction for determining the relative odorant concentrations:

SPME is a qualitative analysis technique. To conduct *quantitative* analysis, a calibration method would have to be developed, which was not possible in the present study. It was assumed that the amount of molecules of an odorant sampled using SPME would indicate its relative concentration. This assumption apparently works for comparing odors composed of similar chemical compositions, e.g., odors in and from swine buildings. To improve the comparability of the relative odorant concentrations in different swine buildings, a standard procedure for SPME sampling was used, as follows. SPME fibers coated with 50/30 µm Divinylbenzene/Carboxen/Polydimethylsiloxane (Supelco, Bellefonte, Pennsylvania, USA**)** were inserted into a Polytetrafluorethylene (PTFE) septum injector (Omnifit, Cambridge, England), which was inserted between a dust filter (25 mm of 0.2-µm PTFE membrane syringe filter, Whatman, Brentford, Middlesex, UK) and an air pump with a suction sampling rate of 0.001 m^3 min^{-1} (fig. 1). The septum injector ensured that all SPME fibers used in the surveys were exposed to the air samples under the same air flow conditions. The sampling period was 10 min, equivalent to a sampled air volume of 0.01 m^3. This sampling period was chosen on the basis of pre-surveys indicating that an SPME fiber has a much greater absorption capacity than the amount of odorant molecules that can be absorbed in swine buildings within the applied sampling period.

The amounts of different odorant molecules sampled by means of SPME were analyzed using a Varian 3800 gas chromatograph (GC) coupled to a Varian Saturn 2000 ion trap mass spectrometer (MS) (Varian; Palo Alto, CA., USA). The GC was equipped with a special SPME liner (Varian) and a Varian VF-1ms Factor Four non-polar capillary column (60 m × 0.32 mm × 1.0 µm). Helium Alphagaz 2 (Air Liquide Danmark, Ballerup, Denmark) was used as carrier gas at 2.5 mL min^{-1} (constant pressure at 1×10^5 N m^{-2}). The SPME fiber was inserted directly into the injector for five min at 250°C. The oven temperature program was as follows: 4 min at 40°C , a ramp to 150°C at 5°C/min, followed by a ramp to 220°C at 10°C/min, and 7 min at 220°C. The MS was used in the electron impact mode at 70 eV and with a scanning range of 30–150 m/z. The temperatures were as follows: ion trap, 175°C; manifold, 110°C; and transfer line, 170°C.

It was estimated that the detection limit (DL) of the applied GC/MS analysis was approximately 500 counts. In the case of a count less than 500, a dummy value of DL/2 = 250 (which is almost zero compared to the GC/MS counts representing the concentrations typically found in the samples) was inserted to allow log transformation before further statistical analysis. Log transformation was performed mainly because the distributions of the original data were skewed, with long tails to the right.

Results and discussions

Technical parameters, which assumed to have influence on odour and dust emissions in the swine buildings, were determined at the sampling occasions. The maximum, minimum and average values of the technical parameters are shown in table 2a and 2b. The final datasets subjected to the statistical analyses were derived from 6, 14, 11 and 13 averaged values of duplicate measurements of room-air odorant and from the corresponding 6, 14, 11 and 13 measurements of odorants in the headspace of the sediment dust samples collected in gestation, farrowing, rearing and finishing buildings, respectively. The reason for the small observation number for gestation building is that the surfaces in the building were often too wet to be able to collect a satisfactory amount of sediment dust. Table 3 shows the number of observations, where the TKO concentrations were higher than DL. As seen in the table, DMS concentrations have often been lower than DL especially in the gestation and farrowing buildings. Only 6 out of 44 measurements on DMS in dust headspaces showed higher concentrations than DL. All 6 measurements on 4MPA in room-air of gestation buildings were lower than DL. While 4MPA was observed more frequently in the room-air of the other buildings types . Dust headspaces for gestation, farrowing and rearing buildings often showed 4MPA concentration lower than DL, whereas, the 4MPA was more common compound in the dust headspaces of finishing buildings.

Table 2a:
Ranges and averages of some technical parameters determined in connection with sampling of odorants in the swine house

	Gestation			Farrowing		
	Max.	Min.	Ave.	Max.	Min.	Ave.
Room:						
Rom volume, m^3	1122	468	734	870	92	644
No. of pens, $room^{-1}$	180	78	121	75	16	55
Area of slatted floor, %	100	50	67	33	33	33
Animals:						
Body weight, kg pig^{-1}	250	150	192	250	200	225
Heat production, W $animal^{-1}$	490	393	434	473	426	449
Stocking density:						
No. of animals, $room^{-1}$	189	68	114	75	16	49
Do., m^{-2}	0.4	0.3	0.4	0.4	0.1	0.2
Boddy weight, kg m^{-3}	42.1	20.5	29.3	43.5	10.0	18.8
Do., kg m^{-2}	105.2	51.3	72.7	100.0	28.7	47.2
Indoor climate:						
Ventilation rate, $m^3\ h^{-1}\ hpu^{-1}$	247	86	154	336	76	229
Do, $m^3\ h^{-1}\ room^{-1}$	11810	2869	7234	10095	965	5030
Air exchange rate, h^{-1}	14	6	10	16	2	8
Temperature	24	18	21	27	18	23
Relative humidity	76	61	69	73	47	63
NH_3 concentration, ppm	18	6	12	14	3	6
CO_2 concentration, ppm	2500	1100	1733	2800	900	1371
Room cleanliness:						
1-5: Dry floor - Wet floor	4	2	2.7	3	1	1.5
1-5: Not dusty - Very dusty	3	1	2.0	4	1	2.5

Table 2b:
Ranges and average of some technical parameters determined in connection with sampling of odorants in the swine houses

	Rearing			Finishing		
	Max.	Min.	Ave.	Max.	Min.	Ave.
Room:						
Rom volume, m^3	427	104	224	1008	330	703
No. of pens, $room^{-1}$	8	5	7	28	9	16
Area of slatted floor, %	100	33	51	100	100	100
Animals:						
Body weight, kg pig^{-1}	30	12	20	80	50	68
Heat production, W $animal^{-1}$	130	73	101	217	174	202
Stocking density:						
No. of animals, $room^{-1}$	300	125	187	560	75	267
Do., m^{-2}	3.8	1.1	2.4	1.5	0.4	1.1
Boddy weight, kg m^{-3}	46.2	6.6	21.0	38.7	8.2	25.1
Do., kg m^{-2}	92.3	16.4	49.8	109.1	32.8	75.8
Indoor climate:						
Ventilation rate, $m^3\ h^{-1}\ hpu^{-1}$	1233	76	299	529	59	203
Do, $m^3\ h^{-1}\ room^{-1}$	14314	1190	4876	57036	2055	12139
Air exchange rate, h^{-1}	95	5	28	66	4	17
Temperature	24	19	22	26	17	21
Relative humidity	77	51	65	83	52	67
NH_3 concentration, ppm	8	1	3	24	6	14
CO_2 concentration, ppm	2800	500	1545	3500	700	1638
Room cleanliness:						
1-5: Dry floor - Wet floor	4	1	2.5	4	1	2.3
1-5: Not dusty - Very dusty	3	1	2.5	4	2	2.8

Figure 3 shows the correlation between odorant concentrations in room-air and dust headspace. The trend line in the figure shows the overall trend of the 8 odorants. Although the overall correlation is significant some of TKOs show relatively large spreading. To explore a possible effect of building type on the interaction between room-air and dust particles, correlation coefficients between relative TKO concentrations in the room-air and in the dust headspaces were determined for different building types. The results are shown in table 4. None of the correlation coefficients for the gestation building were significant. One reason for this might be the small number of observations, n=6. Farrowing buildings showed that TMA, BA and 3MBA concentrations in room-air and dust headspace were significantly correlated. TMA, DMS, BA and 3MBA concentrations in rearing buildings were significantly correlated. While in the finishing buildings, 5 TKOs, i.e. TMA, BA, 3MBA, IND and 3MIND concentrations in room-air and dust headspace were significantly correlated.

Conclusions

- Relative concentrations of 8 TKOs in room-air and dust headspaces samples from gestation, farrowing, rearing and finishing buildings have been determined and their correlations are studied.
- As overall, TKO concentrations in room-air and headspaces were significantly correlated; but relatively large spreading was observed.
- Further study on the interaction between TKOs in room-air and dust particles is recommended.

Table 3:
Number of TKO concentration data higher than detection limit for room-air and dust head spaces for different building types.

Type of buildings	No. of observations	Trimethyle-amine (TMA)	Dimethyl-sulfide (DMS)	Butanoic-acid (BA)	3-methyl-butanoic-acid (3MBA)	4-methyl-pentanoic-acid (4MPA)	Benzyl-alcohol (BAL)	Indole (IND)	3-methyl-indole (3MIND)
	Room-air								
Gestation	6	6	2	6	4	0	5	6	6
Farrowing	14	12	2	14	14	7	12	14	14
Rearing	11	10	6	11	11	10	10	11	11
Finishing	13	12	8	13	13	7	12	13	13
	Dust headspace								
Gestation	6	6	1	6	5	2	6	6	6
Farrowing	14	14	1	14	14	3	13	14	14
Rearing	11	11	2	11	11	6	10	11	11
Finishing	12	13	2	13	13	11	12	13	13

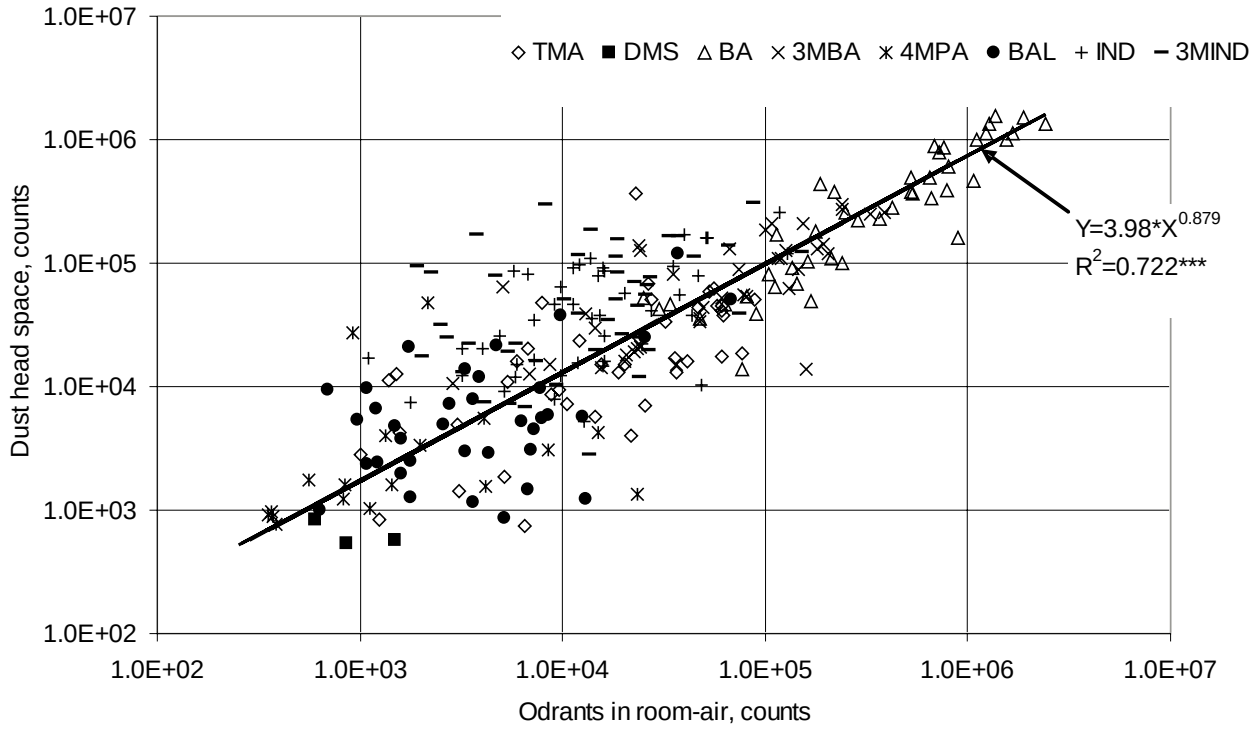

Figure 3:
Correlation between relative odorant concentrations in room-air (X-axis) and dust headspace (Y-axis)

Table 4:
Correlation coefficients between relative odorant concentrations (GC/MS counts) in the room air and in the dust headspace

Type of buildings		Trimethyle-amine (TMA)	Dimethyl-sulfide (DMS)	Butanoic-acid (BA)	3-methyl-butanoic-acid (3MBA)	4-methyl-pentanoic-acid (4MPA)	Benzyl-alcohol (BAL)	Indole (IND)	3-methyl-indole (3MIND
Gestation	r	0.580	-0.299	-0.103	-0.327	-	0.190	0.586	0.450
	P-value	0.132	0.473	0.809	0.430	-	0.653	0.127	0.263
Farrowing	r	0.681	-0.104	0.815	0.681	0.124	0.374	0.141	-0.030
	P-value	0.004	0.701	0.000	0.004	0.648	0.154	0.601	0.912
Rearing	r	0.611	0.678	0.874	0.739	0.397	0.538	0.511	0.305
	P-value	0.027	0.011	0.000	0.004	0.180	0.058	0.074	0.310
Finishing	r	0.663	-0.226	0.788	0.650	0.266	0.231	0.531	0.558
	P-value	0.007	0.418	0.000	0.009	0.338	0.407	0.042	0.031

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References

Hammond E.G., Fedler C., Smith R. J. (1981). Analysis of particle-borne swine house odors. Agriculture and environment, 6 (1981): 395-401.

Hartung J. (1985). Gas chromatographic analysis of volatile fatty acid and phenolic/indolic compounds in pig house dust after ethanolic extraction. Environmental Technology Letters, Vol. 6, 1985: 21-30.

Jacobson L. D., Huiqing G., Schmidt D. R., Nicolai R. E., Zhu J., Janni K. (2000). Development of an odour rating system to estimate setback distances from animal feedlots: odour for feedlots setback Estimation Tool (OFFSET): Dept. of Biosystems and Agricultural Engineering, College of Agricultural, Food and Environmental Sciences, Univ. of Minnesota: 27 pp.

Janni K., Jacobson L., Schmidt D., B. Koehler (2001). Livestock and Poultry odour Workshop. The department of Biosystems and Agricultural Engineering extension odour Team, University of Minnesota: 186 pp.

Reynolds S. J., Chao D. Y., Thorne P. S., Subramanian P., Waldron P. F., Selim M., Whitten P. S., Popendorf W. J. (1998). Field comparison of methods for evaluation of vapor/particle phase distribution of ammonia in livestock buildings. J. Agr. Safety and Health 4(2): 81-93.

Schiffman S. S., Bennett J. L., Raymer J. H. (2001). Quantification of odours and odorants from swine operation in North Carolina. Agricultural and Forest Meteorology 108, Elsevier: 213-240.

Syracuse Research Corporation's (SRC) (2007). Interactive PhysProp Database Demo, http://www.syrres.com/esc/physdemo.htm , Corporate Headquarters, 7502 Round Pond Road, North Syracuse, New York 13212-2510

Takai H., Nekomoto K., Dahl P., Okamoto E., Morita S., Hoshiba S. (2002). Ammonia contents in and desorption from dusts collected in livestock buildings. CIGR e-journal: http://baen.tamu.edu/cigr/volume4.html

Takai H., Dahl P. J., Tøgersen F. Aa., Johnsen J. O., Maahn M., Søgaard H. T. (2007). Regression analyses of the effects of technical parameters on the relative concentrations of principal variable-selected odorants in swine buildings. Submitted for publication in the Transaction of ASABE.

Tanaka H. (1988). Characteristics of odours from animal Industry (in Japanese). Journal of Agricultural Machinery Association 51-4: 99-104