

## Chemical characterization of volatile organic compounds on animal farms

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**ABSTRACT:** More than one hundred volatile organic substances were identified by gas chromatography and mass spectrometry (GC/MS) in the indoor and outdoor air, stable and farm road dust and farm soil samples from two pig and cattle farms in the South Moravian Region. Volatile fatty acids (acetic, propanoic, butanoic and pentanoic acids) and their esters dominated along with aldehydes (butanal, pentanal and hexanal) and 4-methylphenol in the indoor and outdoor air samples. Road dust and soil samples contained mainly volatile aromatic compounds (toluene, benzene, ethylbenzene, styrene and xylenes), aliphatic hydrocarbons (largely *n*-alkanes), dichloromethane and carbon disulphide. The health risks associated with particular volatile compounds detected in the indoor and outdoor samples from the farms need to be assessed.

**Keywords:** VOCs; SPME; GC/MS; pigs; cattle

Volatile organic compounds (VOCs) are non-methane organic compounds containing one or more carbon atoms that have high vapour pressures and therefore evaporate readily to the atmosphere (Pankow, 1987; U.S. EPA, 1992). VOC emissions result from natural and anthropogenic (man-made) sources. Natural sources of VOCs include vegetation, forest fires, and animals (Lemieux et al., 2004; Buzcu and Fraser, 2006). Although natural sources of VOC emissions are more overall (Guenther et al., 1995), there are anthropogenic sources in populated and industrialized areas that are another contributor to air quality. The major anthropogenic sources of VOCs are vehicles, the use of solvents and solvent containing products, and industrial and agricultural sources (Fenger, 1999; Schiffman et al., 2001; Klemp et al., 2002; Folsom Murphy and Allen, 2005).

Key symptoms associated with exposure to some VOCs with adverse effects for humans and animals include conjunctive irritation, nose and throat discomfort, headache, allergic skin reaction, nausea,

emesis, epistaxis, fatigue and dizziness (Jones, 1999). The potency of organic chemicals to cause health effects varies greatly from those that are highly toxic, to those with no known health effect (Eljarrat and Barcelo, 2003). As with other pollutants (such as persistent, bioaccumulative and toxic substances /PBTs/), the extent and nature of the health effect will depend on many factors including time and intensity of exposure. Eye and respiratory tract irritation, headaches, and memory impairment are among the immediate symptoms that some people have soon after exposure to some volatile organics (Guo et al., 2004). At present, little is known about what health effects occur from the levels of organics usually found in the indoor and outdoor atmosphere. Many organic compounds are known to cause cancer in animals; some are suspected human carcinogens (IARC, 1987, 1999a,b).

Animal production results in conversion of feeds into valuable products such as meat and milk as well as into unavoidable and less desirable waste products (Mackie et al., 1998). Over 168 chemical

compounds have been identified in the air of pig buildings (Tamminga, 1992). These compounds are not only responsible for unpleasant odours but also they affect the comfort, health and production efficiency of animals as well as the comfort and health of human workers (Tamminga, 1992). An overview of studies of VOCs emitted from animal (dairy and pig) facilities (Hartung and Phillips, 1994; Zahn et al., 1997; Schiffman et al., 2001) indicates that hundreds of substances can be present. A total of 331 different VOCs and fixed gases from pig facilities were identified by GC/MS in North Carolina (Schiffman et al., 2001). The compounds identified were diverse, and included many acids, alcohols, aldehydes, amides, amines, aromatics, esters, ethers, halogenated hydrocarbons, hydrocarbons, ketones, nitriles, other nitrogen-containing compounds, phenols, sulphur-containing compounds, steroids and other compounds.

Odours from pig production facilities are associated with the storage and decomposition of manure. Manure odours are a complex mixture of volatile fatty acids, alcohols, aromatic compounds, amides and sulphides produced during digestion and subsequent manure storage (O'Neill and Phillips, 1992; Hartung and Phillips, 1994). Microorganisms mediate the odour compound production during the incomplete anaerobic fermentation of substances in manures (Mackie et al., 1998). However, aromatic compounds (3-methylindole) and volatile fatty acids were most closely correlated with pig odour (Zahn et al., 1997, 2001; Powers et al., 1999).

Miller and Varel (2001, 2002, 2003) studied differences in the odour formation processes between cattle and pig manure. They found that odours from pig production were more unpleasant than odours from cattle production. Manure storage, handling, and treatment practices are very different between these facilities and are likely to account for some of the differences in perceived odour. Volatile fatty acids (mainly acetic, propanoic and butanoic acids) and alcohols (ethanol and propanol) were the dominant compounds released from pig and cattle farms.

More than 100 compounds, including various paraffins, olefins, aromatics, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols and sulphides were identified at five pig facilities in the eastern part of North Carolina (Blunden et al., 2005). Among total measured VOCs, oxygenated hydrocarbons, i.e. ethanol, methanol, acetaldehyde and acetone (ranged from 37 to 73% of the total)

emitted from the pig barns at various sites typically dominated.

Filipy et al. (2006) identified a total of 113 compounds at a lactating cow open stall and from a slurry wastewater lagoon. These compounds included alcohols, aldehydes, ketones, esters, ethers, aromatic hydrocarbons, halogenated hydrocarbons, terpenes, other hydrocarbons, amines, other nitrogen-containing compounds, and sulphur-containing compounds. Emission rates of some volatile compounds were reported in their paper.

Solid-phase microextraction (SPME) technology is a recent advance in sample preparation for trace analysis. In this solvent-free extraction technique, developed in 1990 by Arthur and Pawliszyn, the analytes are adsorbed directly from a gaseous or aqueous phase onto a fused silica fibre coated with a polymeric phase. Hence sampling, extraction and concentration are accomplished in a single step. Collected analytes are then thermally desorbed directly to the gas chromatographic column and analyzed by mass spectrometry (Chai and Pawliszyn, 1995; Koziel et al., 1999; Namiesnik et al., 2000).

Headspace solid-phase microextraction (HS-SPME) can be used for the analysis of volatile organic compounds in the solid samples. This method uses a solvent-free sample preparation technique in which a fused silica fibre coated with polymeric organic liquids is introduced into the headspace above the sample closed in a glass vial. The volatilized organic analytes are extracted and concentrated in the coating and then transferred to the GC/MS (Zhang and Pawliszyn, 1993; Llompert et al., 1999; Ezquerro et al., 2004). Cai et al. (2006) firstly characterized VOCs and odorants associated with pig barn particulate matter using SPME and GC/MS.

The present study was focused on the analysis and chemical characterization of volatile organic compounds in the indoor and outdoor (ambient) environment of two selected pig and cattle farms. Indoor and outdoor air samples were analyzed by a home-made device suitable for dynamic sampling of analytes on SPME fibres followed by GC/MS analysis. Volatile organic compounds in stable dust, farm road dust and farm soil samples were analyzed by headspace solid-phase microextraction.

These results systematically extended our earlier studies dealing with the detection of semivolatile organic compounds in pig and dairy facilities (Raszyk et al., 1998; Ciganek et al., 1999, 2000, 2002 and 2006).

## MATERIAL AND METHODS

### Chemicals and materials

All standards of volatile organic compounds [benzene, toluene, ethylbenzene, xylenes, *n*-alkanes and EPA 524.2 VOC Mix (60 compounds in methanol)] were purchased from SUPELCO (Bellefonte, PA, USA). The concentration of each standard in methanol was 10 ng/ml.

SPME fibres [three types with different sorbent polarity – Polydimethylsiloxane (polymer film thickness 100 µm), Carboxen (70 µm) and Carbowax/Divinylbenzene (65 µm)] were also purchased from SUPELCO (Bellefonte, PA, USA).

The AirCheck 2000 pump used for air sample collection was from SKC (Eighty Four, PA, USA).

### Gaseous and solid sample collection

A home-made device (Figure 1) proper for a dynamic sampling was designed for simultaneous collection of air samples on the three types of SPME fibres with different sorbent polarity. Sampling time was 30 min for indoor and 60 min for outdoor air with flow rate of sampled air 1 000 ml/min. The collection of indoor and outdoor air samples was started on one farm at the same time. SPME fibres with collected air samples were sealed with Teflon plug and shipped to the laboratory in a box cooled to about 6°C. Air samples were analyzed on the same day when they were collected. The content of analytes was normalized to 1 l of sampled air.

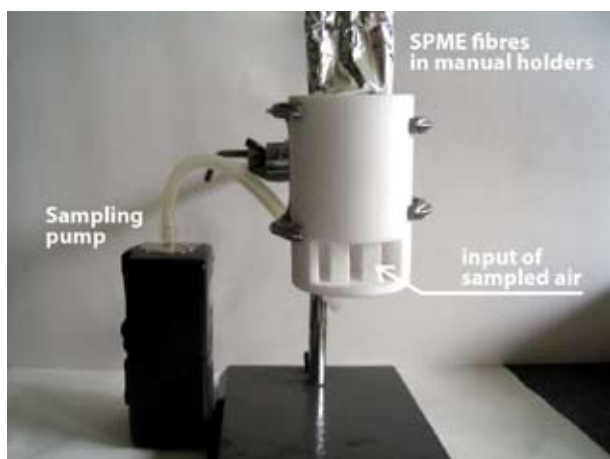


Figure 1. Home-made device for simultaneous dynamic sampling of air by three different SPME fibres

Three types of solid specimens were sampled directly to the head-space glass vials of 60 ml volume. Stable dust (SD) samples from the selected stables, farm road dust (RD) and farm soil (S) samples from the outdoor surroundings of the farms at about 10 m from the selected stables were collected. Solid samples were shipped to the laboratory in the same way as SPME fibres. No manipulations with these samples were done before their HS-SPME analysis. All samples were analyzed next day.

Solid and air samples were collected on two pig (P1, P2) and two cattle farms (C1, C2) in the South Moravian Region of Czech Republic.

### HS-SPME

The extraction of solid samples using HS-SPME was accomplished by placing the fibre in the head-space above the sample in a 60-ml headspace glass vial. Extraction temperature was 50°C; the extraction procedure consisted of 10 min temperature equilibration of a sample to 50°C in the headspace vial followed by 20 min extraction successively with three types of SPME fibres, which were used for air sampling. Each SPME fibre was then analyzed by GC/MS.

### GC/MS analysis

The GC/MS separation of volatile organic compounds was performed in a DB VRX fused silica capillary column (60 m × 0.25 mm I.D., 1.4 µm – J. and W. Scientific, Folsom, CA, USA). An ion trap mass spectrometer (Saturn 2100, Varian, Walnut Creek, CA, USA) was used for the detection and identification of the analytes. The mass spectrometer was operated in an electron ionization (EI) mode at the electron ionization energy of 70 eV. The identification of analytes was done by retention time and by a comparison of the mass spectra of identified substances with mass spectral library (NIST 1998, Gaithersburg, MD, USA). SPME fibre desorption time and temperature were 10 min and 260°C, respectively.

The mass spectrometer used can operate as a selective detector in a selected ion monitoring mode and/or as a universal detector of organic matter, when it measures in a scan mode and detects all in-

tensities of molecular and fragment ions of analytes. The sum of intensities of these ions interpreted as the total ion current can be used for evaluation of differences in the individual compound distribution in analyzed samples.

## RESULTS AND DISCUSSION

### Optimization of analytical method

A dynamic sampling method with three types of SPME fibres with different sorbent polarity was used for simultaneous VOC collection from indoor and outdoor air samples. Sorption selectivity expressed as relative amounts of three selected classes of compounds (oxygenated and aromatic compounds and *n*-alkanes) on the three types of SPME fibres (CAR-Carboxen, CW+DVB-Carbowax/Divinylbenzene and PDMS-Polydimethylsiloxane) is summarized in Figure 2. Different SPME fibres were found to have different sorption selectivity for analyzed compounds. Volatile aromatic and oxygenated compounds (benzene, toluene, xylenes, acetone, acetic, propanoic and butanoic acids) were mainly adsorbed by Carboxen, polycyclic aromatic compounds and low volatile organic compounds

were collected predominantly by Carbowax/Divinylbenzene and low volatile *n*-alkanes by Polydimethylsiloxane SPME fibre. Abundances of individual substances collected on SMPE fibres were calculated as the sum of their abundances on the three individual SPME fibres used in this study. The identical procedure was used for HS-SPME determination of VOCs in solid samples. A typical SPME GC/MS chromatogram of air sample from the pig stable (P1) is shown in Figure 3.

### Occurrence of volatile organic compounds on selected pig and cattle farms

More than one hundred abundant volatile organic substances were identified in the indoor and outdoor air, stable and road dust and soil samples from the two selected pig and cattle farms. Identified classes of volatile compounds with higher abundances are listed in Table 1. Acetic acid, butanoic acid, *p*-cresol, propanoic and pentanoic acids, phenol and hexanal prevailed in the indoor air of pig farms, acetic, butanoic, propanoic acids, *p*-cresol, phenol and methyl esters of carboxylic acids mentioned above dominated on cattle farms. Similar compounds dominated in the outdoor air. Acetic and propanoic acids, *p*-cresol,

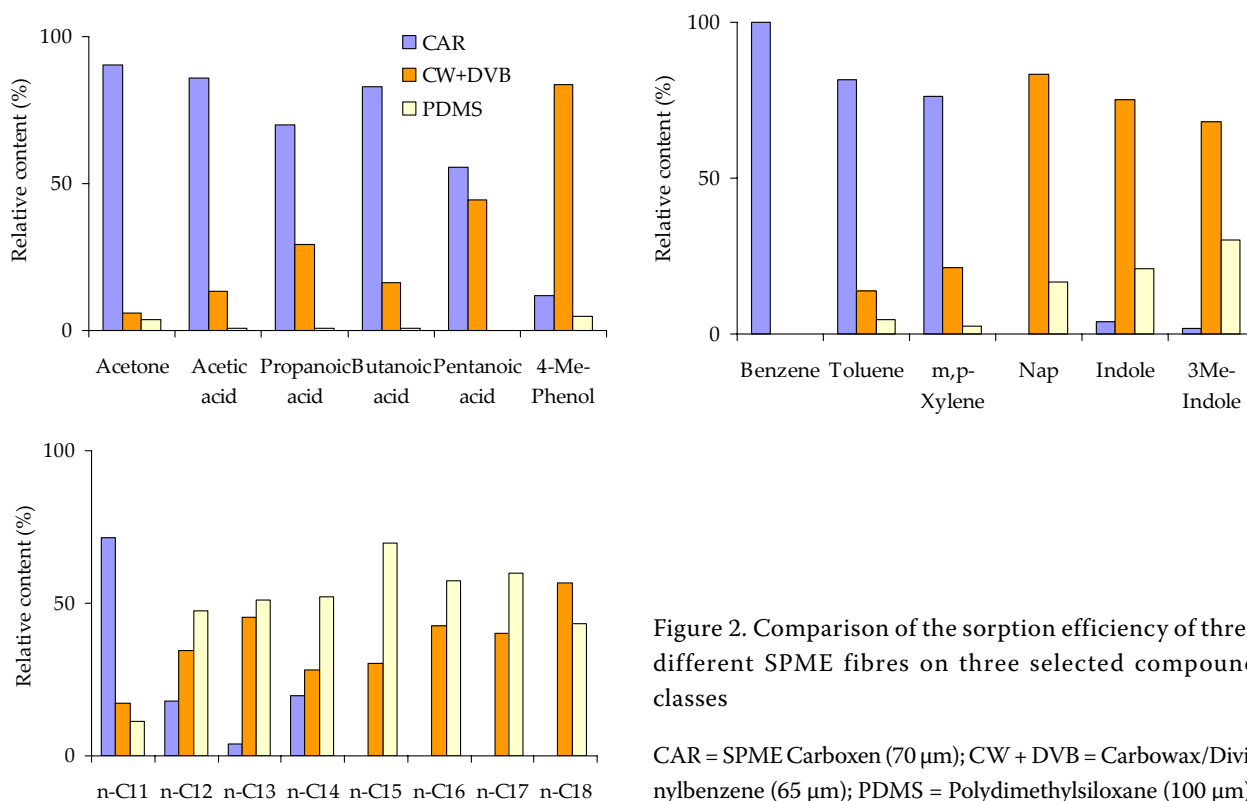


Figure 2. Comparison of the sorption efficiency of three different SPME fibres on three selected compound classes

CAR = SPME Carboxen (70  $\mu$ m); CW + DVB = Carbowax/Divinylbenzene (65  $\mu$ m); PDMS = Polydimethylsiloxane (100  $\mu$ m)

Table 1. List of abundant volatile organic compounds identified in the indoor and outdoor parts of animal farms

Oxygenated compounds		Aromatic hydrocarbons	
Alcohols and ketones	ethanol	BTEX	benzene
	acetone		toluene
	6-heptene-2,4-diol		ethylbenzene
	ethyl Acetate		<i>m,p</i> -xylene
	3-hexen-1-ol		<i>o</i> -xylene
	2-hexanol		styrene
	3-methyl-4-nonanone		iso-propylbenzene
	5-hepten-2-one		<i>n</i> -propylbenzene
Phenols	3-nonen-1-ol	Alkylbenzenes	1-ethyl-3-methylbenzene
	phenol		1-ethyl-4-methylbenzene
	2-methylphenol		1,3,5-trimethylbenzene
Aldehydes	4-methylphenol ( <i>p</i> -cresol)		1-ethyl-2-methylbenzene
	hexanal		<i>t</i> -butylbenzene
	heptanal		1,2,4-trimethylbenzene
	octanal		<i>sec</i> -butylbenzene
Carboxylic acids	acetic acid		<i>iso</i> -butylbenzene
	acetic acid methyl ester		<i>p</i> -IsoPropyl-Toluene
	propanoic acid ethyl ester		1,2,3-trimethylbenzene
	propanoic acid		1,3-diethylbenzene
	3-methylbutanoic acid		1,4-diethylbenzene
	propanoic acid propyl ester		<i>n</i> -butylbenzene
	butanoic acid		1,4-dimethyl-2-ethylbenzene
	3-methylpentanoic acid		1,3-dimethyl-4-ethylbenzene
	2-methylpentanoic acid		1,2-dimethyl-2-ethylbenzene
	butanoic acid propyl ester		1,2,4,5-tetramethylbenzene
	pentanoic acid		1,2,3,5-tetramethylbenzene
	hexanoic acid methyl ester		1,2,3,4-tetramethylbenzene
	hexanoic acid ethyl ester		1,2,3,4-tetrahydronaphthalene
	ethyl benzoate		naphthalene
	hexanoic acid propyl ester		1-methylnaphthalene
Nitrogen-containing compounds	1,2-propanediamine	Polycyclic aromatic hydrocarbons	2-methylnaphthalene
	1-methylamine		biphenyl
	cyclobutylamine		methylbiphenyl
	<i>N,N</i> -dimethylformamide		1H-indene
	aniline		3-methyl-1H-indole
	benzonitrile		methylcyclohexane
Sulphur-containing compounds	carbon disulphide	Hydrocarbons	<i>n</i> -heptane
	dimethylsulphide		<i>n</i> -octane
	dimethyldisulphide		<i>n</i> -nonane
Chlorinated compounds	methylene chloride		<i>n</i> -decane
	chloroform		<i>n</i> -undecane
	trichloroethylene		<i>n</i> -dodecane
	tetrachloroethylene		<i>n</i> -tridecane
	chlorobenzene		<i>n</i> -tetradecane
			<i>n</i> -pentadecane
			<i>n</i> -hexadecane

## Chromatogram Plot

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 Scan Range: 1 - 8089 Time Range: 0.00 - 36.48 min. Date: 13.7.2005 15:46

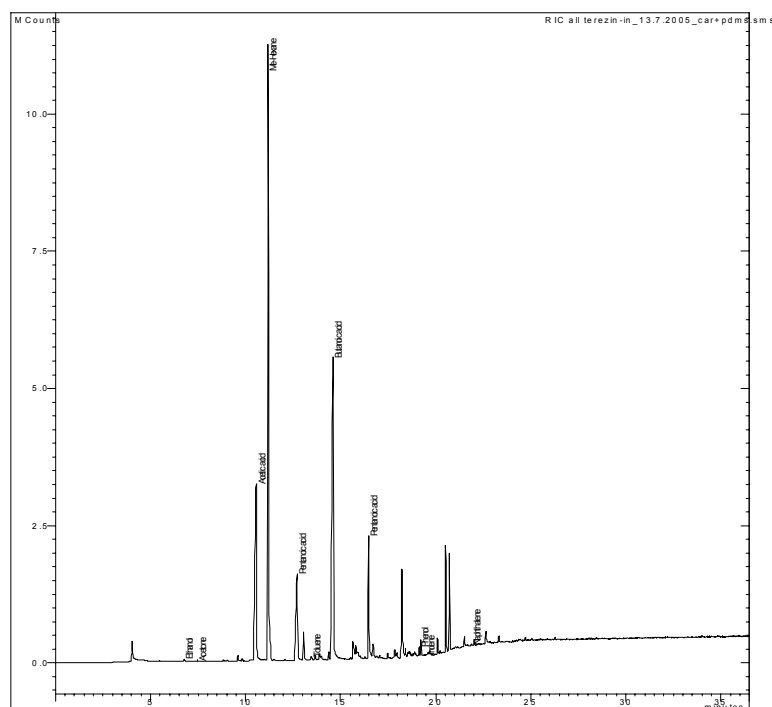


Figure 3. Typical SPME GC/MS chromatogram of VOC analysis of indoor air from a pig stable (P1)

pentanoic and butanoic acids dominated in the stable dust likewise in air samples. Toluene, ethylbenzene, benzene, xylenes and *n*-alkanes, compounds mainly emitted from vehicles, were dominant in road dust and soil samples.

The abundance ratios of selected compound classes and/or individual compounds can be used for

Table 2. Abundance ratios of selected compound classes for the indoor and outdoor air

Compounds	In/Out ratios			
	P1	P2	C1	C2
N-Compounds <sup>1</sup>	2.0	2.4	4.3	2.6
O-Compounds <sup>2</sup>	128.0	30.3	8.4	10.3
Cl-Compounds <sup>3</sup>	1.6	2.1	2.3	2.4
BTEX <sup>4</sup>	2.0	1.5	0.3	3.6
Alkylbenzenes	0.3	1.5	0.4	0.6
Alkanes	0.6	2.7	0.7	3.2
PAHs	3.2	3.7	6.0	0.9

P1 and P2 = pig farm No. 1 and 2; C1 and C2 = cattle farm No. 1 and 2

<sup>1</sup>nitrogen-containing compounds; <sup>2</sup>oxygen-containing compounds; <sup>3</sup>halogenated compounds; <sup>4</sup>benzene, toluene, ethylbenzene and xylenes

determination of compounds which are mainly emitted from indoor or outdoor sources. Compounds emitted from indoor sources will have the In/Out ratio > 1. In/Out ratios of selected compound classes are summarized in Table 2. Oxygenated compounds with higher values of this ratio were mainly emitted from indoor sources on pig farms. Alkylbenzenes, alkanes and PAHs were mainly emitted from outdoor sources. Some substances were identified only in the indoor air of pig and cattle stables (maleic acid, propanoic acid, pentadecanoic acid, *p*-cresol, 1-methylamine), 3-methylindole was detected only on pig farms. The highest In/Out ratios were found for acetic acid on the pig farms – 230 (P1) and 102 (P2).

### Distribution of VOCs in the indoor and outdoor air

The results of chemical analyses showed significant differences in the total VOC abundances between the indoor and outdoor air samples of two pig (P1, P2) and two cattle (C1, C2) farms (Figure 4). The highest abundances were always found in the indoor air samples. Total VOC abundances were 9.6 (farm P1), 6.1 (farm P2), 1.5 (farm C1) and 4.2 (farm C2) times higher in the indoor air samples in

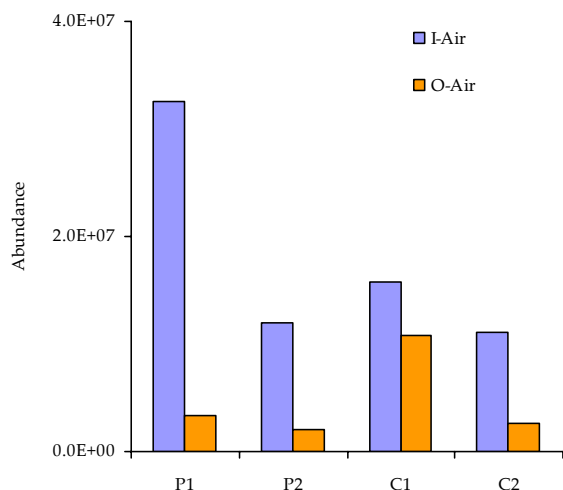


Figure 4. Differences in VOC distribution between the indoor and outdoor (ambient) air on the pig and cattle farms

I-Air (O-Air) = indoor (outdoor) air of two pig (P1, P2) and two cattle (C1, C2) farms

comparison with the outdoor air samples on two pig and cattle houses, respectively.

Chemical analysis of selected classes of organic compounds showed a different distribution of these

compounds in the indoor and outdoor air expressed as their relative contents (Figure 5). Oxygenated organic compounds (mainly volatile fatty acids) dominated in the indoor air of all farms except one cattle farm (C1). The dominance of volatile aromatic compounds (BTEX) in the outdoor air of a cattle farm (C1) was caused by the emissions from tractors used for distribution of feedstuffs around the farm.

### Distribution of VOCs in the solid samples

Figure 6 shows differences in the total VOC abundances among the indoor stable dust (SD) and outdoor road dust (RD) and soil (S) samples. It was found that stable dust, similarly like indoor air, contained the highest total amount of VOCs. These abundances were from 3.1 to 44.3 and from 13.6 to 76.6 times higher in stable dust compared with road dust and soil, respectively. The highest total VOC abundances were found in the stable dust (SD) and road dust (RD) on the cattle farm C2. Total VOC abundances were similar for soil samples on all pig and cattle farms under study.

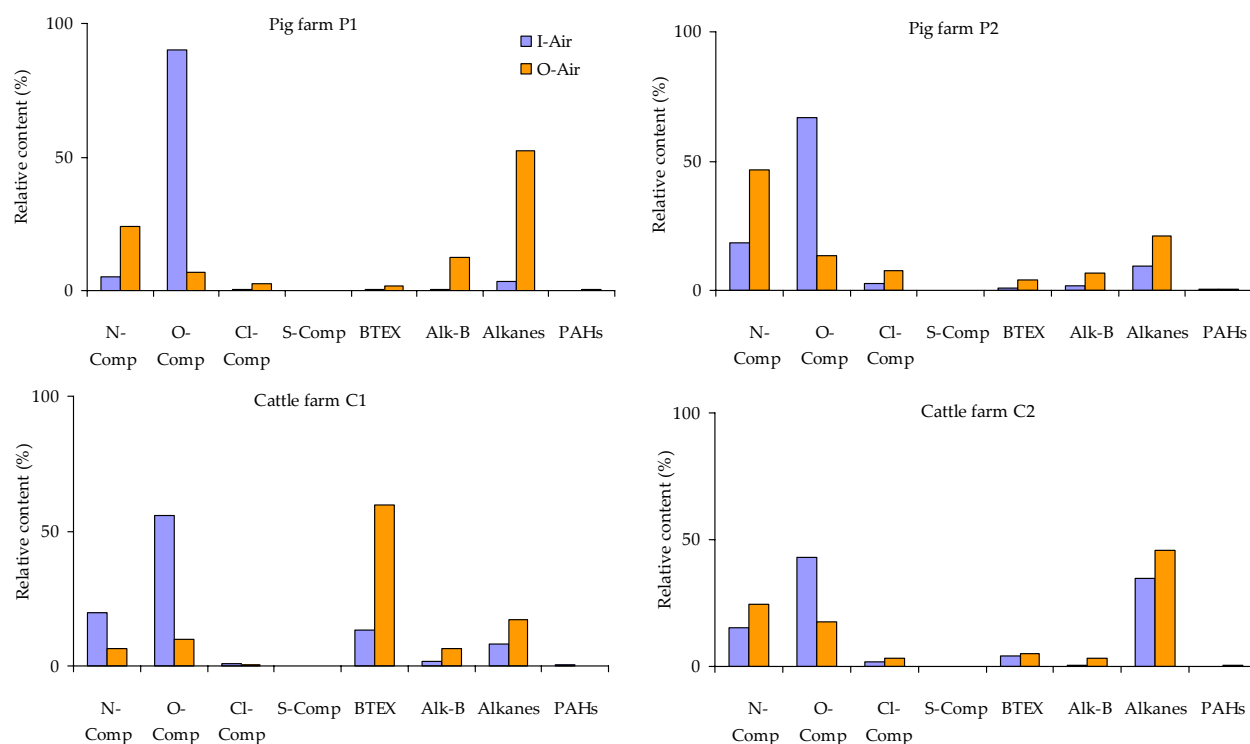


Figure 5. Relative content (%) of VOC classes in the indoor and outdoor air

I-Air (O-Air) = indoor (outdoor) air of two pig (P1, P2) and two cattle (C1, C2) farms;

N-Comp = nitrogen-containing compounds; O-Comp = oxygen-containing compounds; Cl-Comp = halogenated compounds;

S-Comp = sulphur-containing compounds; BTEX = benzene, toluene, ethylbenzene and xylenes; Alk-B = alkylated benzenes

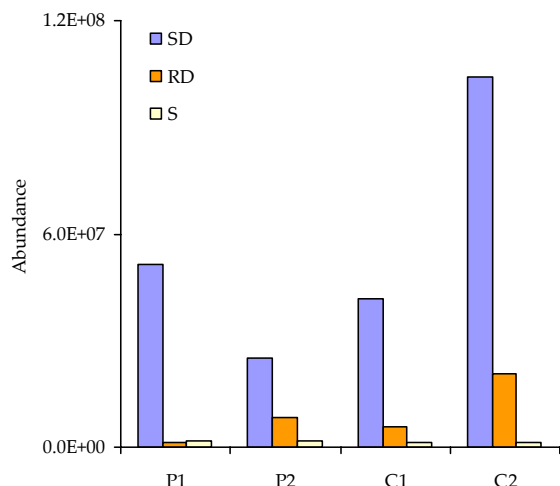


Figure 6. Differences in VOC content between solid samples from animal farms

SD = stable dust; RD = road dust; S = soil of samples from pig (P1, P2) and cattle (C1, C2) farms

Relative contents (percentages of selected classes of organic compounds) were used for characterization of differences in the distribution of substances in the indoor air (I-Air) and stable dust (SD) samples (Figure 7) and outdoor air (O-Air), road dust (RD) and soil samples (S) (Figure 8). Oxygenated compounds (O-Comp) prevailed in the indoor air and stable dust

on both pig farms. Volatile aromatic compounds (BTEX), chlorinated compounds (Cl-Comp), nitrogen-containing compounds (N-Comp) and alkanes were other classes prevalent on the cattle farms.

Different distribution of selected substances was found in the outdoor air, road dust and soil samples. A high relative content of nitrogen-containing compounds was found in all samples due to high abundances of 1,2-propanediamine and dimethylformamide, mainly in soil and road dust on the pig (P1) and cattle (C1) farms. Alkanes and volatile aromatic compounds, substances mainly emitted from vehicles and transported around for a long time, were other contaminants found in the outdoor samples of the farms. The relative content of these compound classes in the outdoor farm samples was occasional due to time and concentration differences.

It was found that oxygenated organic compounds, acetic acid and 4-methylphenol with the greatest abundances were largely distributed in the indoor environment.

### Statistical evaluation of analytical data

Pearson's correlation coefficient ( $R$ ) and two tailed  $t$ -test were used for statistical evaluation of the

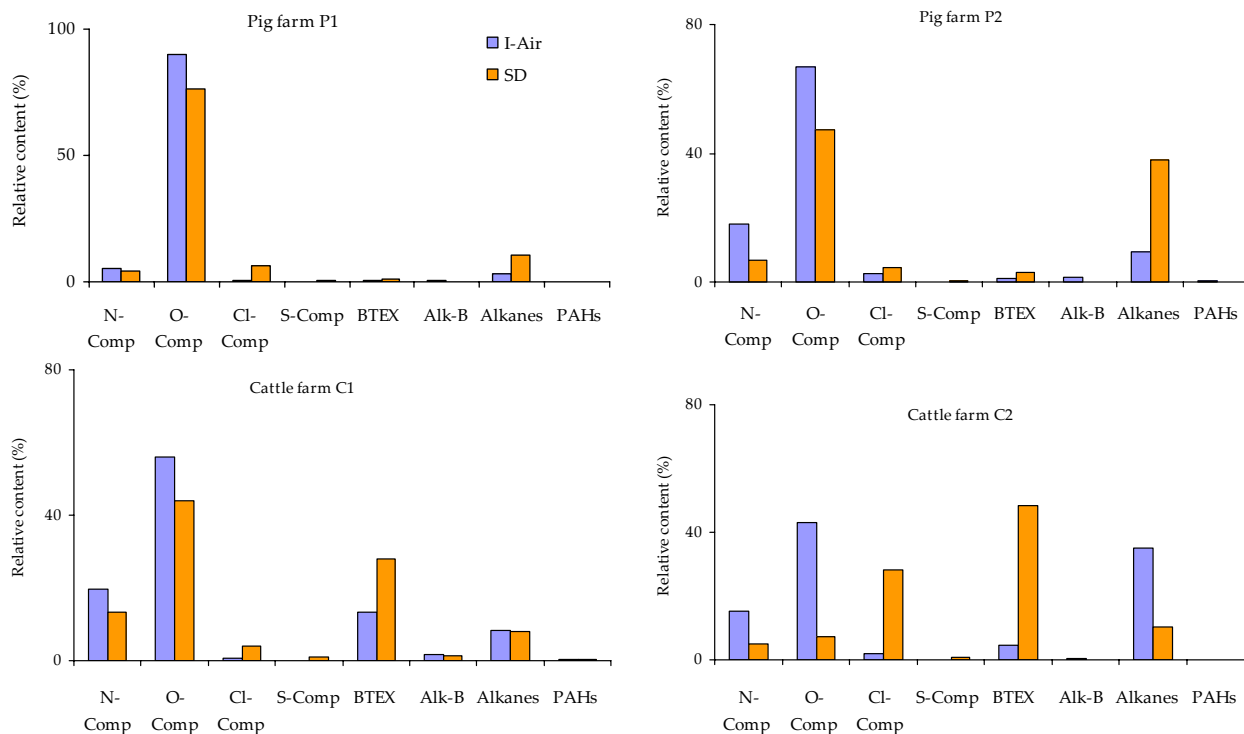


Figure 7. Relative content (%) of VOC classes in the indoor samples of pig and cattle farms

I-Air = indoor air; SD = stable dust of two pig (P1, P2) and two cattle (C1, C2) farms; x-axis abbreviations see Figure 5



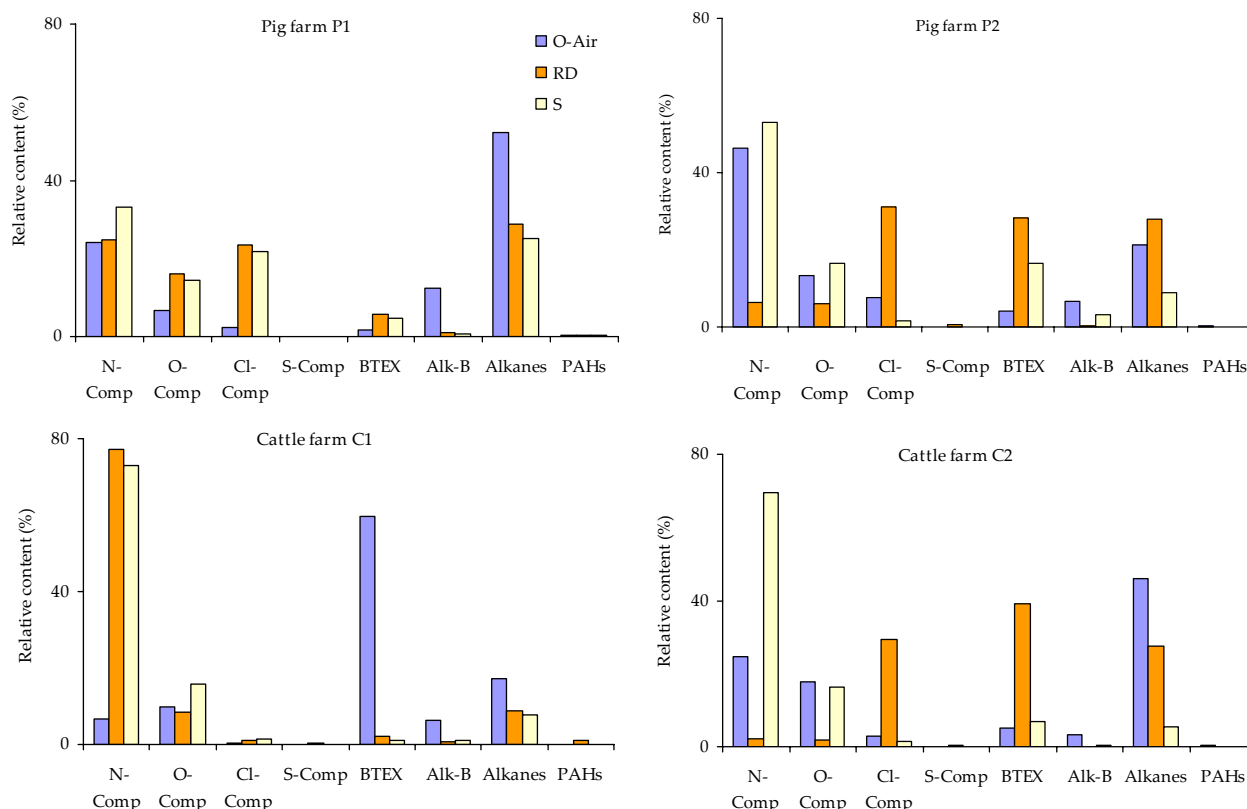


Figure 8. Relative content (%) of VOC classes in the outdoor samples

O-Air = outdoor air; RD = road dust; S = soil of two pig (P1, P2) and two cattle (C1, C2) farms; x-axis abbreviations see Figure 5

distribution of individual compounds among selected sample types on the animal farms under study (Table 3).

Correlations were tested between two samples from the indoor pig and cattle houses (stable dust vs. indoor air) and three outdoor samples (road dust vs. outdoor air, soil vs. outdoor air and soil vs. road dust). All tested pairs showed positive correlations, which means that if the abundance of a compound in one sample type from the tested pair increased, its abundance in the other type also rose.

The highest correlation was found for soil and road dust from outdoors of cattle farm C1 (0.994). Soil-road dust (0.978) and stable dust-indoor air (0.953) from pig farm P1 and soil-outdoor air (0.923) from pig farm P1 were other samples with a higher correlation. No correlation was determined for stable dust-indoor air, road dust-outdoor air and soil-road dust from cattle farm C2. Low or medium correlations were detected for the other samples (values between 0.1 and 0.7).

The results of evaluation of statistical significances between individual abundances of analyzed compounds are summarized in the last two col-

umns of Table 3. Significant statistical differences were found between stable dust-indoor air and soil-road dust from pig farm P1; stable dust-indoor air, soil-outdoor air and soil-road dust from pig farm P2; stable dust-indoor air and soil-outdoor air from cattle farm C1 and soil-road dust from cattle farm C2. No significant statistical differences were found for all road dust-outdoor air samples and soil-outdoor air samples except for cattle farm C1.

## CONCLUSIONS

Two analytical methods for the determination of volatile organic compounds in the air (SPME GC/MS) and solid samples (HS-SPME GC/MS) were developed. These simple methods were used for chemical characterization of VOCs in the indoor and outdoor parts of animal farms. More than one hundred abundant organic compounds were identified by GC/MS in the indoor and outdoor air, stable and farm road dust and farm soil samples.

It was found that oxygenated organic compounds, acetic acid and 4-methylphenol with the greatest

Table 3. Statistical evaluation of analytical data

Location	Sample type	R
P1	SD vs. I-Air	0.953*
	RD vs. O-Air	0.343
	S vs. O-Air	0.308
	S vs. RD	0.979*
P2	SD vs. I-Air	0.614**
	RD vs. O-Air	0.218
	S vs. O-Air	0.927*
	S vs. RD	0.269*
C1	SD vs. I-Air	0.648**
	RD vs. O-Air	0.140
	S vs. O-Air	0.134*
	S vs. RD	0.994
C2	SD vs. I-Air	0.019
	RD vs. O-Air	0.055
	S vs. O-Air	0.422
	S vs. RD	0.087*

R = Pearson's correlation coefficient; I-Air = indoor air; O-Air = outdoor air; RD = road dust; SD = stable dust; S = soil

\* $P < 0.05$ , \*\* $P < 0.001$

relative abundances were largely distributed in the indoor environment. Volatile aromatic compounds (BTEX) and alkanes prevailed in the outdoor samples of pig and cattle farms. Stable dust contained mainly volatile fatty acids (acetic, propanoic and butanoic acids); road dust and soil largely contained toluene, alkanes and compounds emitted from vehicles and long-term atmospheric transport. Toxicity and hazard identification of volatile compounds should be characterized in future studies.

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