

## Volatile organic compound emission and other trace gases from selected animal buildings

Ngwa Martin Ngwabie<sup>1,2</sup>, Gunnar W. Schade<sup>2,3</sup>, Thomas G. Custer<sup>2,4</sup>, Stefan Linke<sup>5</sup> and Torsten Hinz<sup>5</sup>

### Abstract

Using chemical ionization mass spectrometry and photoacoustic spectroscopy, we analysed the evolution of volatile organic compounds (VOCs) and other trace gases during an approximately one-week measurement period each in a pigsty and a sheep shed at the Federal Agricultural Research Centre (FAL) in Mariensee, Germany. When activities in the sheep shed were most intense during feeding hours and manure removal, concentration surges of VOCs were observed, which strongly correlated with methane and ammonia levels. Immediately after this disturbance, especially the manure removal, which lasted for about 30 minutes, the short-term concentration spikes decayed exponentially as a result of dilution of the shed air with relatively clean air from outside the shed. Emission factors were modelled from the daily surge and decay profiles in the shed and were further used to estimate emission rates for Germany. Concentrations measured at an exhaust flue of a pigsty section were much smoother than in the sheep shed. For both sheds, correlations of VOC mixing ratios with methane or ammonia were used to calculate shed, respectively per animal emission factors, and to estimate nationwide release rates for a number of VOCs. VOC emissions from both sheds were dominated by alcohols, ethanol from the sheep, methanol from the pigs. Ethanol and other fermentation products have known sources in the fodder and the excrements. New is the finding that also high amounts of methanol are released, the source of which is not entirely clear. Total annual VOC emissions from the animal husbandry sector in Germany are likely around 150 Tg carbon, less than previously estimated and of a much different composition.

*Keywords: Volatile Organic Compounds (VOC), emissions, animal sheds, sheep, pigs, excrements*

### Zusammenfassung

#### Volatile Organische Komponenten und andere Spurengase in ausgewählten Tierställen

In dieser Arbeit werden die jeweils rund eine Woche dauernden Spurengasmessungen in einem Schafstall und am Abzug einer Schweinestallabteilung der FAL in Mariensee beschrieben. Mittels photoakustischer Spektroskopie wurden Ammoniak, Methan, Kohlenstoffdioxid, Distickstoffmonoxid und Wasserdampf, mittels chemischer Ionisations-Massenspektrometrie die Konzentrationen von über 40 volatilen organischen Komponenten (VOK) im 2- oder 3-Minuten Zyklus bestimmt. Die Konzentrationen im Schafstall stiegen besonders während der regelmässigen Abfuhr der Exkreme (30 min) unter dem Spaltenboden zeitgleich mit der Fütterung stark an. Spitzenwerte für verschiedene VOK stiegen dann bis in den  $\mu\text{mol pro mol}$ -Bereich, und waren mit parallelen Anstiegen von Ammoniak und Methan korreliert. Die nur kurzzeitig sehr hohen Konzentrationen wurden im Anschluss über die normale Stallventilation mit Frischluft von aussen verdünnt, was zu einer exponentiellen Abnahme führte. Eine Bilanzanalyse mittels Modellierung des dieses Konzentrationsabfalls wurden dazu benutzt, VOK-Emissionsfaktoren pro Stall bzw. Tier zu berechnen. Anders als im Schafstall zeigte der Konzentrationsverlauf am Abzug des Schweinestalls wesentlich moderatere Veränderungen, In beiden Fällen jedoch wurden die Korrelationen zu Ammoniak und Methan dazu verwendet, Gesamtemissionen zu bestimmen. In beiden Stallungen dominierten Alkohole die VOK-Emissionen, im Schafstall Ethanol, im Schweinestall Methanol. Die VOK-Quellen liegen in der Futterfermentation und Exkrementzerersetzung. Die Fermentationsprodukte Ethanol, Acetaldehyd, und Essigsäure waren stets präsent. Neu sind insbesondere die Messungen hoher Konzentrationen Methanols, dessen Ursprung noch etwas unklar ist. Auf Deutschland hochgerechnete Gesamtemissionen von VOK pro Jahr liegen wahrscheinlich um 150 Tg Kohlenstoff, etwas weniger als zuvor berechnet und in deutlich anderer Zusammensetzung.

*Schlüsselwörter: Volatile Organische Komponenten (VOK), Emissionen, Tierstall, Schaf, Schwein, Exkreme*

<sup>1</sup> Department of Agricultural Biosystems and Technology, Swedish University of Agricultural Sciences, Alnarp, Sweden

<sup>2</sup> Institute of Environmental Physics, University of Bremen, 28334 Bremen/Germany

<sup>3</sup> Department of Atmospheric Sciences, Texas A&M University, College Station, TX, USA; Email: schade@ariel.met.tamu.edu

<sup>4</sup> Max Planck Institute for Chemistry, Department of Atmospheric Chemistry, Joh.-Joachim-Becher-Weg 27, 55020 Mainz/Germany

<sup>5</sup> Federal Agricultural Research Center (FAL), Institute of Technology and Biosystems Engineering, Bundesallee 50, 38116 Braunschweig/Germany

## 1 Introduction

Agriculture is a source of trace gases and particles emitted into the atmosphere with possible effects on global atmospheric chemistry, a source of odour and particulate matter pollution (Gustafsson and Wachenfelt, 2006; Hobbs et al., 1997; Hobbs et al., 1998; McGinn et al., 2003; Rabaud et al., 2002; 2003; Schiffman et al., 2001), and impact on human and animal health (Zhang et al., 1998). Livestock management has been identified as a source of methane, ammonia and nitrous oxide (Berges and Crutzen, 1996). Although many Volatile are also produced, there is limited information on the factors affecting their release and the subsequent effects on the environment. To begin addressing these issues, more comprehensive studies of aerial pollutants from livestock husbandry are necessary. Mitigation strategies through better animal management practices are more effective if planning is done with up-to-date information on the types and magnitudes of odorous VOC emissions. Previous work has identified numerous VOC species contributing to odour problems inside various animal buildings (Filipy et al., 2006; Rabaud et al., 2002; Hobbs et al., 2004; Schiffman et al., 2001) and in ambient air (Rabaud et al., 2003; Hobbs et al., 1997; Hobbs et al., 1998;). However, based on the analytical techniques used, it is unclear whether the identified species represent the bulk of VOC carbon or just a small fraction. Recently, chemical ionisation mass spectrometry has been used to quantify VOCs in cow sheds (Shaw et al., 2007; Ngwabie et al., 2007), and short-chain alcohols were identified as the dominant contributors to VOC emissions alongside many VOCs previously found.

This article reports on measurements carried out by the University of Bremen and the Federal Agricultural Research Centre in Germany. Recently we have calculated flux values for a number of VOCs from dairy cows in Germany (Ngwabie et al., 2007) and this contribution is a follow-up from the dairy cow report. Alongside the mixing ratio measurements of ammonia, methane, nitrous oxide and carbon dioxide, this paper identifies major VOCs emitted from sheep and pig buildings. We also present the estimated mass release rates of some VOCs from these buildings.

## 2 Materials and methods

VOCs were measured with a commercial proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik, Innsbruck, Austria), full details of which are given elsewhere (de Gouw et al., 2003; Lindinger et al., 1998). The instrument was operated in a similar way as within the cowshed (Ngwabie et al., 2007), with measured VOC mixing ratios reported with an accuracy of 30 %, or better when a calibration gas was available. The concentrations

of methane, nitrous oxide, ammonia and carbon dioxide were monitored in 2-minute intervals with a photo-acoustic spectrometer (Brüel and Kjaer model, 1302), operated the same way as inside the cowshed. Factory calibration of the instrument was left unchanged for the experiments reported here.

### 2.1 Experimental sites

Measurements were carried out in a sheep shed and a pigsty at a FAL branch in Mariensee near Neustadt-Hannover, Germany, during the winter months when all animals spend their time indoors.

Data was collected from a pigsty from 21<sup>st</sup> to 28<sup>th</sup> of January 2005. Hygiene regulations did not permit entry into the pigsty, and the measurement setup was therefore deployed in a nearby building with a heated sampling line hooked up to the exhaust of a flue. The normally intermittent exhaust was changed to a constant low flow midway through the weeklong sampling period. The pigsty had a mixture of weaner and finishing pigs on a slated floor system. Liquid manure collected beneath the floor was channelled to a storage tank outside the pigsty. The solid manure under the floor was pushed out once to twice a week. Feeding times during sampling were between 7:30 and 8:30 in the morning and between 13:00 and 13:30 in the afternoon.

Measurements in the sheep shed (dimensions 23 m × 15 m × 4 m [LWH]) were carried out from 1<sup>st</sup> to 7<sup>th</sup> February 2005. This shed housed 120 sheep subdivided into 72 ewes, 18 rams and 30 lambs. It had a two double stall setting with the sheep free to move about. Each row was further subdivided into 5 compartments to prevent overcrowding. The floor was slatted with the manure collected in a pit beneath. Twice a day at about 08:00 h and 14:00 h the manure was mechanically removed and dumped in a heap outside the shed. Passive ventilation was provided through four flues in the roof and via opening of windows.

### 2.2 Measurements

The PTR-MS and the photo-acoustic spectrometer were set up as shown in Figure 1. Air was sucked at a constant 12 L min<sup>-1</sup> through 20 m long sampling lines from inside or outside of the animal shed (0.635 mm ID Teflon PFA) to the PTR-MS and photo-acoustic monitoring devices using a membrane pump. The source of the sample air was chosen through switching a three-way, PFA solenoid valve controlled by the PTR-MS computer.

#### Sheep shed

Air from inside the shed was sampled from a central location at a height of 2 m. The air at this location should generally be well-mixed and a good representative of the shed as

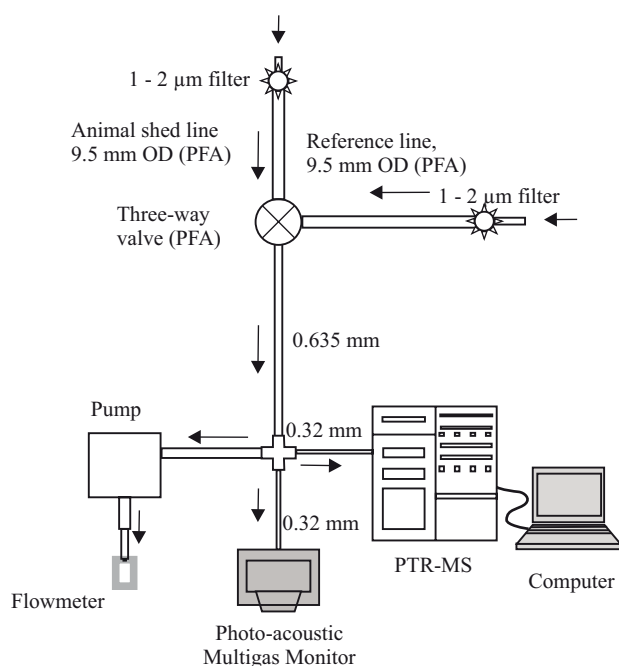


Figure 1:  
Experimental set-up for monitoring gaseous emissions in animal housing

a whole. To complement air measurements, a temperature sensor was placed near the centre of the shed at a height of 2 m and recorded temperatures (0.5 °C resolution) at a 120 s time interval. Reference air was sampled at a point outside a partially open shed window.

### Pigsty

The instrumental setup was installed in a neighbouring office building. The sample line ran up to the exhaust of a ventilation shaft in the roof where the air was sucked from near the edge of the exhaust hood through an externally heated Teflon PFA line. Reference air was sampled from the roof of the office building in which the instrument was housed.

Although the reference air in both cases was unavoidably influenced by emissions from the surrounding animal sheds, these sampling positions represented the closest natural source of „clean“ air that could be used for comparison with that in the sheds. Both animal shed air and outside air sampling inlets were equipped with 1 – 2 µm Teflon PTFE filters that trapped particles from the air stream prior to trace gas monitoring. The high air-flow rate ensured that sampled air spent a very short time in the tubing (~3 s) prior to chemical analysis. For all measurements, the residence time of air in the PTR-MS is estimated to be on the order of 0.3 seconds with a total measurement cycle including one measurement of each selected mass every 107 seconds. Air was exchanged in the photo-acoustic spectrometer approx-

imately every 120 seconds. Animal shed air was sampled for 30 minutes at the top of each hour while outside reference air was sampled for the last 30 minutes of each hour enabling monitoring of both shed and outside conditions proportionally.

## 3 Results and discussions

### 3.1 PTR-MS data and VOC assignment

Prior to individual mass monitoring in the pigsty and the sheep shed, initial measurements were conducted in order to determine which mass-to-charge ratios (chemicals) might be found at elevated abundances inside the animal facilities as compared to ambient air. Full mass scans ranging from 20 to 210 atomic mass units were performed and a t-test of means carried out comparing ion signals observed in animal shed air to those in ambient air using  $P < 0.05$  as a cut-off to determine whether there was an observable difference between them. Those mass-to-charge ( $m/z$ ) ratios showing significant deviation between inside and outside air were pinpointed for further measurements.

Although the PTR-MS instrument is very reliable for on-line monitoring, secondary techniques or hyphenation with gas chromatography are necessary for complete and unambiguous compound identification. In the event where such instrumentations are not available, mass to VOC assignments must be approached with some care. We have previously discussed our mass to VOC assignments (Ngwabie et al., 2007), so only a summary shall be given here. It has been shown that several ions associated with common VOCs are essentially free from interference from other VOCs when sampling air in the troposphere of rural and urban environments (de Gouw et al., 2003; Warneke et al., 2003). We assumed that the sample air from the animal housings was not significantly different from that of the urban or rural troposphere. As a more solid approach, we consulted reports that detailed other techniques for compound identification in animal housings for comparisons (Filipy et al., 2006; Hobbs et al., 1997, 1998, 2004; McGinn et al., 2003; Rabaud et al., 2002, 2003; Schiffman et al., 2001; Spinhirne et al., 2003, 2004; von Hartungen et al., 2004). In some cases, such as with  $m/z$  47, the natural  $^{13}\text{C}$  abundance of an ion at  $m/z + 1$  provided additional insight into the dominant carbon number of an ion at  $m/z$ . When available and of sufficient intensity, measured  $^{13}\text{C}$  abundances of ions were compared to those expected.

Here, we report on 17 major VOCs that were temporally associated with particular  $m/z$  values in the sheep shed according to the previously described criteria. They are listed in Table 1. The same VOCs were identified in the pigsty at different concentrations with the exception of toluene and caproic acid due to significantly lower pigsty signals

Table 1:

Trace gases identified in the sheep shed and pigsty with associated mass to charge ratios, mixing ratios and ranges observed. Legal 8-h limits in workplace environments for Germany (MAK) are included.

VOC and other gases	Sheep shed Median (Range)	Pigsty Median (Range)	MAK
<b>Data from multi-gas monitor</b>			
	----- $\mu\text{mol mol}^{-1}$ (ppm)-----		
Nitrous oxide	0.47 (0.39 – 0.60)	0.43 (0.34 – 0.50)	100
Carbon dioxide	1200 (902 – 1970)	723 (503 – 1250)	5000
Methane	71.05 (35.2 – 336)	4.69 (3.01 – 8.96)	NA
Ammonia	6.39 (0.92 – 19.6)	4.17 (1.16 – 6.92)	20
<b>Data from PTR-MS</b>			
	----- $\text{nmol mol}^{-1}$ (ppb)-----		
Methanol (m/z 33)	121.7 (8.2 – 1756.1)	45 (6 – 71.3)	200000
Acetaldehyde (m/z 45)	183.6 (46.4 – 1011.1)	5.8 (1.1 – 33.1)	50000
Ethanol (m/z 47)	6570.7 (1263.7 – 94363.8)	118.3 (98.2 – 163.9)	500000
Acetone (m/z 59)	20.6 (6.7 – 57.9)	10.1 (3.3 – 361.1)	500000
Trimethylamine (m/z 60)	14.2 (2.6 – 35.4)	7.7 (2.5 – 18)	2000
Isopropanol (m/z 41,43)	17.9 (4.1 – 140.2)	17 (1.5 – 91.9)	200000
Dimethyl sulphide (m/z 63)	1.6 (0.5 – 5.3)	2.9 (0.9 – 5.9)	NA
Methyl ethyl ketone (m/z 73)	1.4 (0.4 – 8.3)	1.1 (0.5 – 1.9)	200000
Toluene (m/z 93)	0.2 (0 – 8.8)	NA	50000
Phenol (m/z 95)	1 (0.3 – 1.8)	0.3 (0.1 – 0.5)	2000
C8 aromatic (benzaldehyde m/z 107)	0.1 (0.02 – 0.8)	0.06 (0.01 – 0.14)	100000
4-methyl phenol (m/z 109)	3.9 (0.9 – 9)	1.9 (0.8 – 3.7)	5000
<b>Volatile fatty acids</b>			
	----- $\text{nmol mol}^{-1}$ (ppb)-----		
Acetic (m/z 43, 61, 79)	14.3 (2.9 – 87.8)	44.5 (7.8 – 107.9)	10000
Propanoic (m/z 55, 75, 93)	11.4 (3 – 139.7)	6.3 (2 – 11.7)	10000
Butyric & isobutyric (m/z 71, 89, 107)	5.5 (1 – 56.2)	4.9 (1.6 – 9.7)	NA
Valeric & isovaleric (m/z 103, 121)	0.6 (0.3 – 3)	0.6 (0.2 – 41.4)	NA
Caproic (m/z 99, 117, 135)	0.6 (0.1 – 5)	NA	NA

NA: Not available

compared to ambient air.

Ion signal intensities at m/z 33, 45, 47, and 59 were associated with methanol, acetaldehyde, ethanol and acetone, respectively with mixing ratios calculated based on results of calibration gas dilution. The signal at m/z 47 was assigned to ethanol based on the  $^{13}\text{C}$  abundance of m/z 48. High mixing ratios of methanol were observed in both facilities, a dominant compound also identified inside the large FAL cowshed (Ngwabie et al., 2007). However, it was ethanol that had the highest mixing ratio in both ruminant sheds, a finding supported by measurements in California (Mitloehner et al., 2007; Shaw et al., 2007).

While ions observed at m/z 61 might be associated with acetic acid, isopropanol, n-propanol, or methyl formate (Spanel and Smith, 1997; Warneke et al., 1996), we have associated them solely to acetic acid for reasons described in our earlier publication (Ngwabie et al., 2007), further supported by the m/z 61 to m/z 62 ratio. The fragment ion at m/z 43 was similarly assumed to be a mixture of higher alcohols ( $\text{C}_3 - \text{C}_8$ ) and acetic acid (Buhr et al., 2002; von

Hartungen et al., 2004). As before, we investigated the m/z 43 to m/z 44 ratio, which in this case suggested that the acetic acid contribution to m/z 43 was negligible, instead finding a ratio  $\geq 0.036$  suggestive of higher alcohol contributions to m/z 43. The sum of the m/z 43 abundance with its fragment ion at m/z 41 was used to calculate the mixing ratio of all higher alcohols as “isopropanol”. The resulting mixing ratios of acetic acid and “isopropanol” ought to be regarded as upper limits for either animal housing.

The major odorants trimethylamine, dimethyl sulfide, Volatile Fatty Acids (VFAs), and p-cresol (4-methyl phenol), were assigned to m/z 60, 63, the series 75 ( $\text{C}_3$ ), 89 ( $\text{C}_4$ ), 103 ( $\text{C}_5$ ), and 117 ( $\text{C}_6$ ) (von Hartungen et al., 2004), and m/z 109, respectively. All have previously been associated with animal husbandry VOC emissions. The remaining, significantly enhanced ion signals at m/z 73, 93, 95, and 107, were attributed to methyl ethyl ketone, toluene, phenol, and  $\text{C}_8$  aromatics (xylenes, ethylbenzene, and benzaldehyde) plus hydrated butyric acid, and should be largely free of interference.

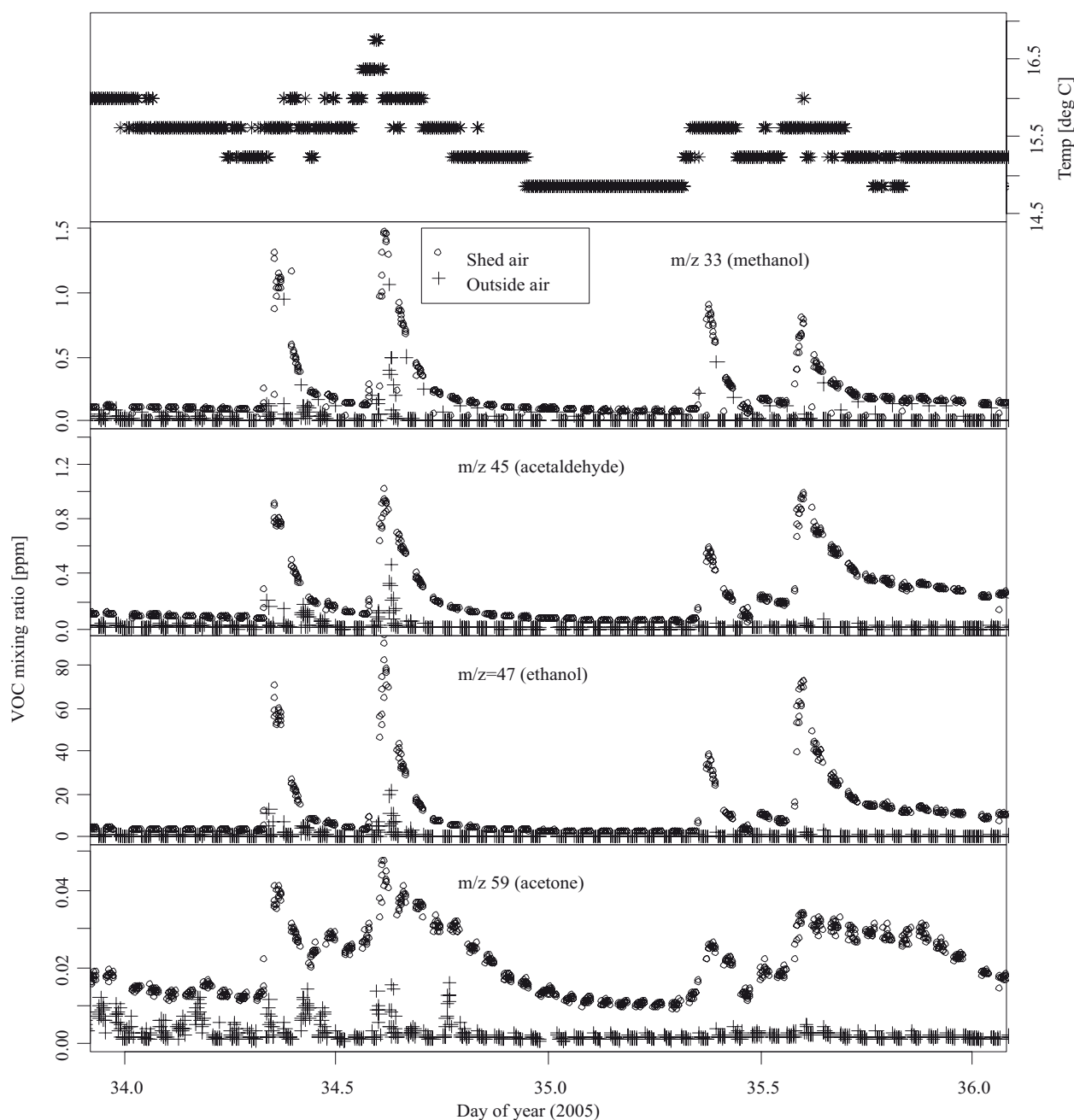


Figure 2:  
Time series of calibrated VOCs in the sheep shed ( $\text{ppm} = \mu\text{mol mol}^{-1}$ )

### 3.2 Trace gas variability

Our discussions here are concentrated on trace gases emitted in the sheep shed as there is little research information on this. Methane, carbon dioxide, ammonia and nitrous oxide exhibited regular daily spikes in both animal sheds much in the same pattern as the VOCs. In particular, methane showed a clear distinction between shed and outside air mixing ratios in the sheep shed indicating a large and constant production source, likely the ruminants' respira-

tion. This distinct separation between shed and reference air was not observed for ammonia in either shed, likely due to its adsorption to the walls inside the model 1302 analyser used in this study. Table 1 lists median values of mixing ratios for these gases including the maximum and minimum values attained in both sheds.

Figure 2 depicts two days of the week long campaign in the sheep shed with the upper panel showing the temperature variation with a mean of  $15 \pm 1$  °C. The shed VOC

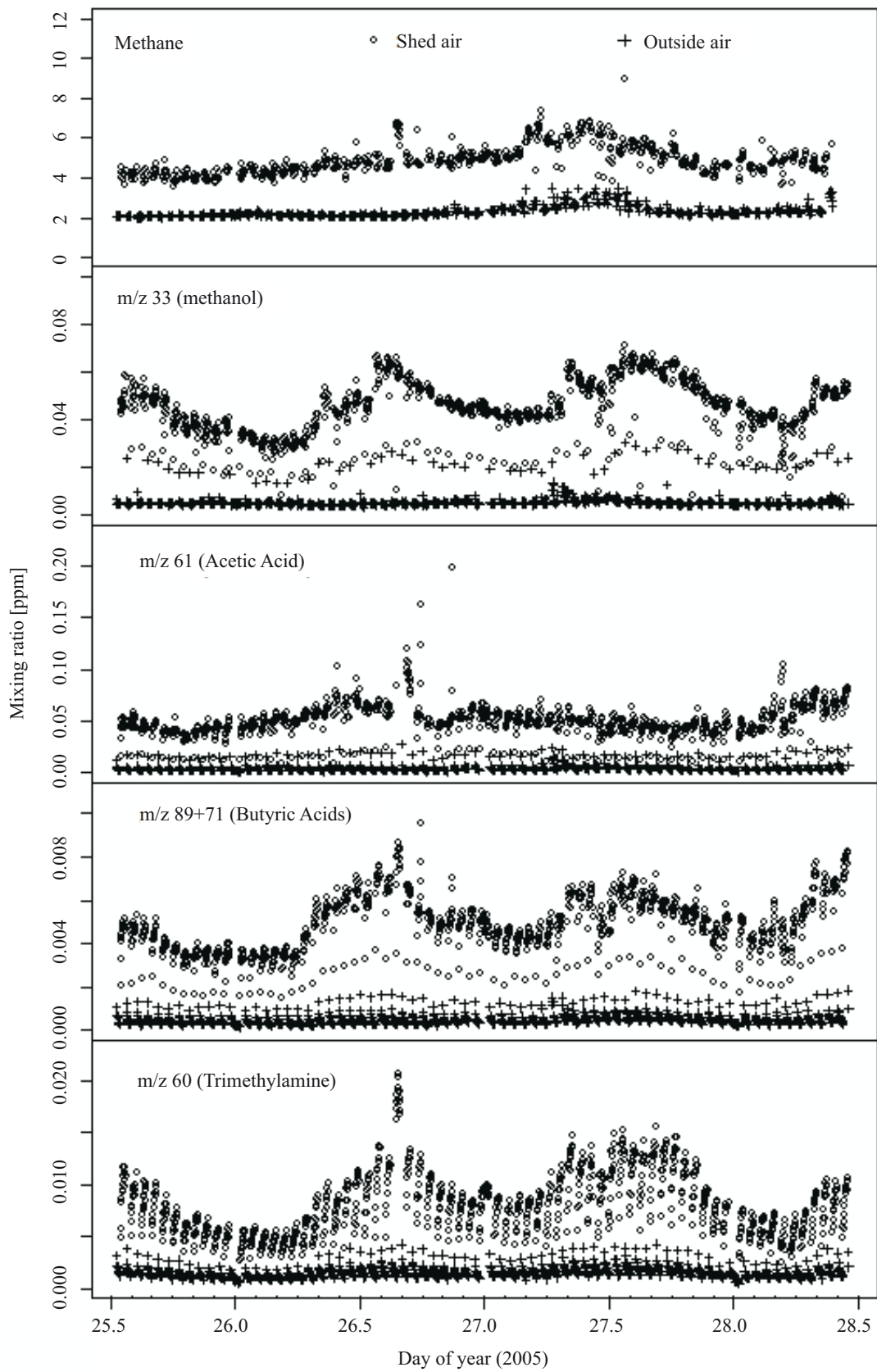


Figure 3:  
A selection of measured VOCs at the pigsty exhaust flue.

mixing ratios showed regular interval spikes, which appeared to decay exponentially. The periodicity of the emission spikes in the sheep shed was associated with regular activities that included cleaning and manure removal and feeding. During this time, the manure underneath the floor was mechanically removed by a conveyor and dumped on a heap outside the shed. At this time, the odour in the shed was the most unpleasant, likely caused by the manure stirring/overturning.

As an example for the concentration variations at the pigsty exhaust flue, Figure 3 shows a selection of measured VOCs with different properties, and methane for comparison. A carryover effect (from shed to ambient air) can be observed for nearly all VOC, increasing from methanol, through the acids, to trimethylamine (TMA). For the latter and for ammonia, true background may not have been observed within the half-hour period of ambient air measurements due to excessive adsorption to the sampling lines. The concentration increase in the afternoon of 26 January was likely caused by the periodic excrement removal, the temporary drop the following day just before noon remains unexplained. Methanol, VFAs, TMA and other VOC mixing ratios (not shown) appeared to correlate with temperature. This can be explained by taking into account that the shed exhaust for this experiment had been fixed at a low flow instead of constantly adjusting to keep pigsty temperature nearly constant, therefore allowing pigsty temperature to vary.

### 3.3 Flux estimates

The accuracy of flux calculations from animal buildings depends on how precisely the trace gas concentrations and the air exchange rates can be measured. It is difficult to calculate the air exchange rate in naturally ventilated buildings. This has commonly been overcome using a tracer gas such as sulphur hexafluoride to determine the ventilation rate indirectly. Though SF<sub>6</sub> has unwanted long-term climatic effects, finding a well mixed and inert tracer in the animal building itself is challenging, further limiting this method. The carbon dioxide mass balance method has been used with the assumption that all carbon dioxide production in the building is through respiration (CIGR, 2002). However, this is hardly the case as carbon dioxide is also produced from other sources such as the manure and litter (Jeppsson, 2000).

Here, we used two different methods to estimate the release rates of selected VOCs from the sheep shed: (i) correlations with ammonia or methane multiplied by previously estimated ammonia or methane fluxes, and (ii) model fits to the concentration profile in the shed to calculate the constant background production and the semi-instantaneous emission rates during cleaning and feeding periods. VOC fluxes for the pigsty unit were estimated using the

correlation method only due to a lack of sufficient data for analysis using method (ii).

#### (i) Flux estimate from correlations

This method has previously been used to estimate fluxes (Berges and Crutzen, 1996; Hobbs et al., 2004; Schade and Crutzen, 1995). Its basis lies much less in the fact that certain VOCs are formed during the same biological processes that produce ammonia or methane, but more in the fact that emissions are often driven by substrate dynamics, such as biological activity in general, or physical substrate disturbance. Hence, observed correlations are most often caused by covariances, not as a result of a biological connection between emitted methane (or ammonia) and VOCs. This explains why some carefully conducted laboratory measurements on various manure substrates do not show strong correlations between these trace gases (Hobbs et al., 2004) in contrast to field studies under typical conditions such as this one. The advantage of the correlation method in this case is based on the comparatively large body of research on livestock ammonia and methane emissions. In Germany, emission rates of methane, ammonia, nitrous oxide and carbon dioxide have been compiled from many sources, and were recently summarized through Germany's reporting duties on greenhouse and related trace gases to the United Nations (Dämmgen, 2004). A value of 0.023 Tg a<sup>-1</sup> (Tg = 10<sup>12</sup> g) of methane for the categories "enteric fermentation" and "manure management", and 0.002 Tg a<sup>-1</sup> of ammonia for the category "manure management" alone have been calculated to come from the holdings of sheep in Germany for the year 2002. For swine, the report lists 0.553 Tg a<sup>-1</sup> of methane (from "enteric fermentation" and "manure management") and 0.123 Tg a<sup>-1</sup> of ammonia (from "manure management") for 2002.

For this study, mass emission ratios for VOCs to methane or VOCs to ammonia were calculated where significant correlations were observed ( $R^2 > 0.5$ ). These were then multiplied with the above methane (ammonia) mass release rates to get estimates of nationwide VOC fluxes. The emission ratio  $E_V$  (here for methane) is given by equation 1:

$$E_V = \frac{\mu(\text{VOC})_{\text{shed}} - \mu(\text{VOC})_{\text{Out}}}{\mu(\text{CH}_4)_{\text{shed}} - \mu(\text{CH}_4)_{\text{Out}}} * \frac{\text{g/mol C in VOC}}{16 \text{ g/mol CH}_4} \quad [\text{g C/g CH}_4] \quad (1)$$

$\mu(\text{VOC})_{\text{shed}} - \mu(\text{VOC})_{\text{Out}}$  is the enhancement of the VOC mixing ratio in the animal shed to that outside and

$\mu(\text{CH}_4)_{\text{shed}} - \mu(\text{CH}_4)_{\text{Out}}$  the enhancement of methane (or ammonia) mixing ratio to the ambient level. Hence, only a

Table 2:

Flux estimates of VOC from sheep shed based on correlation with methane or ammonia. Values for methane and ammonia emissions for 2002 were adopted from Dämmgen (2004)

VOC	Statistics	$E_V$ (g C) / (g CH <sub>4</sub> )	CH <sub>4</sub> / NH <sub>3</sub> Emission (± 30 %) [g a <sup>-1</sup> ]	VOC Emission [Gg a <sup>-1</sup> C]
Methanol	R <sup>2</sup> = 0.88 N = 1017	$(1.2 \pm 0.2) \times 10^{-3}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	0.02 – 0.04
Acetaldehyde	R <sup>2</sup> = 0.89 N = 1049	$(3.8 \begin{smallmatrix} + 1.5 \\ - 1.0 \end{smallmatrix}) \times 10^{-3}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	0.04 – 0.16
Ethanol	R <sup>2</sup> = 0.88 N = 1049	$(128 \begin{smallmatrix} + 73 \\ - 37 \end{smallmatrix}) \times 10^{-3}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	1.5 – 6.0
Acetone	R <sup>2</sup> = 0.94 N = 1049	$(6.8 \pm 1.1) \times 10^{-4}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	0.01 – 0.02
Propanol	R <sup>2</sup> = 0.80 N = 1128	$(6.1 \pm 1.0) \times 10^{-4}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	0.01 – 0.02
DMS	R <sup>2</sup> = 0.96 N = 1128	$(3.5 \pm 0.5) \times 10^{-5}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	< 0.001 (0.6 – 1.6 Mg a <sup>-1</sup> S)
MEK	R <sup>2</sup> = 0.81 N = 1128	$(5.9 \begin{smallmatrix} + 1.8 \\ - 1.3 \end{smallmatrix}) \times 10^{-5}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	< 0.003
Acetic acid	R <sup>2</sup> = 0.88 N = 1128	$(3.0 \pm 0.5) \times 10^{-4}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	< 0.01 – 0.02
Propionic acid	R <sup>2</sup> = 0.84 N = 1049	$(3.6 \begin{smallmatrix} + 1.4 \\ - 1.1 \end{smallmatrix}) \times 10^{-4}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	< 0.015
TMA	R <sup>2</sup> = 0.87 N = 1049	$(4.8 \pm 1.3) \times 10^{-4}$	$0.023 \times 10^{12}$ CH <sub>4</sub>	< 0.01 – 0.02
TMA	R <sup>2</sup> = 0.85 N = 996	$(4.9 \pm 1.5) \times 10^{-3}$	$0.002 \times 10^{12}$ NH <sub>3</sub>	< 0.01 – 0.02 (2.3 – 7.8 Mg a <sup>-1</sup> N)

correct relative difference in the measured quantities is needed. Though errors increase with a decrease in the shed-to-reference abundance, all reported VOCs showed sufficiently large shed to reference concentration differences, as was true for ammonia and methane.

We observed the strongest correlations between trace gases that have similar emission sources within the animal sheds (manure or the animals) or that have a similar biochemical production process, such as acetic acid and methane from fermentation. These species had R<sup>2</sup> values of 0.8 and better. A summary of our findings is presented in Table 2 (sheep shed) and Table 3 (pigsty). In the sheep shed, ethanol had the highest emission with a range of 1.5 – 6.0 Gg a<sup>-1</sup> C but showed no significant correlation with methane in the pigsty. However methanol did have a good correlation with methane emitted from the pigsty and was found to be the largest single emission with a value of 3 – 9 Gg a<sup>-1</sup> C.

#### (ii) Flux estimate from emission profile model in the sheep shed

We analyzed short-term abundance increases and their exponential decay to derive apparent shed air turnover rates and constant background trace gas emission rates. This was

done using equation 2 with the assumptions (i) of observing well-mixed air, (ii) that dilution with reference air from outside the shed was the dominant process that resulted in the decay of the VOC abundance, and (iii) that chemical or physical removal inside the shed is negligible.

$$x(t) = (x_0 - x_{bg}) \times \exp(-D \times t) + x_{bg} + P' \quad (2)$$

In equation 2,  $x$  is the mixing ratio at time  $t$ ,  $x_0$  the mixing ratio at the top of a concentration spike,  $x_{bg}$  the background or reference mixing ratio measured outside the shed,  $D$  the decay constant (dilution rate [h<sup>-1</sup>]),  $t$  the step time being equivalent to 107 s, and  $P'$  the constant mixing ratio added from continuous emissions into the shed during one measurement cycle of 107 s. Using the value of  $P'$  from the non-linear model fit, a constant mass flux  $P$  of the VOC during each period was calculated assuming an instantaneous dilution into the known shed volume. A non-linear least squares routine was fitted using both the morning and afternoon spikes, as there might be differences between them. The results of this analysis for selected VOCs that produced good fits are summarised in Table 4. The dilution rates  $D$  did not vary significantly between the model fit suggesting that the assumptions about the concentration



Table 3:

Flux estimates of VOC from pigsty based on correlation with methane or ammonia. Values for methane and ammonia emissions for 2002 were adopted from Dämmgen (2004)

VOC	Statistics	$E_V$ (g C) / (g CH <sub>4</sub> )	CH <sub>4</sub> / NH <sub>3</sub> Emission (± 30 %) [g a <sup>-1</sup> ]	VOC Emission [Gg a <sup>-1</sup> C]
Methanol	R <sup>2</sup> = 0.92 N = 685	(1.1 ± 0.2) × 10 <sup>-2</sup>	0.55 × 10 <sup>12</sup> CH <sub>4</sub>	6.1 ± 3.1
Acetone	R <sup>2</sup> = 0.96 N = 578	(7.3 ± 1.1) × 10 <sup>-3</sup>	0.55 × 10 <sup>12</sup> CH <sub>4</sub>	4.0 ± 2.0
DMS	R <sup>2</sup> = 0.95 N = 597	(1.5 ± 0.3) × 10 <sup>-3</sup>	0.55 × 10 <sup>12</sup> CH <sub>4</sub>	0.8 ± 0.5 (0.3 – 1.1 Gg a <sup>-1</sup> S)
MEK	R <sup>2</sup> = 0.95 N = 685	(1.1 ± 0.2) × 10 <sup>-3</sup>	0.55 × 10 <sup>12</sup> CH <sub>4</sub>	0.6 ± 0.3
Propionic acid	R <sup>2</sup> = 0.91 N = 685	(4.5 ± 0.9) × 10 <sup>-3</sup>	0.55 × 10 <sup>12</sup> CH <sub>4</sub>	2.5 ± 1.4
Butyric acid	R <sup>2</sup> = 0.92 N = 685	(4.9 ± 0.9) × 10 <sup>-3</sup>	0.55 × 10 <sup>12</sup> CH <sub>4</sub>	2.7 ± 1.5
Valeric acid	R <sup>2</sup> = 0.91 N = 624	(7.0 ± 1.3) × 10 <sup>-4</sup>	0.55 × 10 <sup>12</sup> CH <sub>4</sub>	0.4 ± 0.2
Acetaldehyde	R <sup>2</sup> = 0.94 N = 614	(2.8 ± 0.5) × 10 <sup>-3</sup>	0.12 × 10 <sup>12</sup> NH <sub>3</sub>	0.3 ± 0.2
Acetone	R <sup>2</sup> = 0.93 N = 525	(7.2 <sup>+1.5</sup> <sub>-1.2</sub> ) × 10 <sup>-3</sup>	0.12 × 10 <sup>12</sup> NH <sub>3</sub>	0.9 <sup>+0.5</sup> <sub>-1.4</sub>
Butyric acid	R <sup>2</sup> = 0.93 N = 627	(4.8 <sup>+1.1</sup> <sub>-0.7</sub> ) × 10 <sup>-3</sup>	0.12 × 10 <sup>12</sup> NH <sub>3</sub>	0.6 <sup>+0.3</sup> <sub>-0.2</sub>
TMA	R <sup>2</sup> = 0.92 N = 627	(5.4 ± 0.7) × 10 <sup>-3</sup>	0.12 × 10 <sup>12</sup> NH <sub>3</sub>	0.6 ± 0.3 (0.1 – 0.35 Gg a <sup>-1</sup> N)

decay being largely due to dilution is supported. Production values *P* showed much larger variation as is expected for the different compounds, sources and production rates.

To estimate the contribution of the actual emission surge to the total emissions, we assumed that each abundance spike was caused by a short duration, symmetric emission. This was then modelled as being Gaussian in shape, adjusting the height and width to fit the measurements, assuming the measurements represented a resultant mixing ratio from this nearly instantaneous emission into the shed, with its volume and dilution rate as given parameters. A typical model curve for methanol is depicted in Figure 4. The bell-shaped model curve was then integrated and scaled to the number of sheep in the shed. Lastly, we converted this animal emission factor to an annual flux using a total of 2 spikes in a day, 365 days in a year and 2771100 sheep for Germany (Dämmgen, 2004), with the annual flux derived from the mean of four to eight integrated spikes (Table 4).

Table 4 contains flux estimates from both sub-models, and emission values were estimated for Germany assuming that emission factors do not differ significantly across different sheds and that management systems are fairly constant over the entire country.

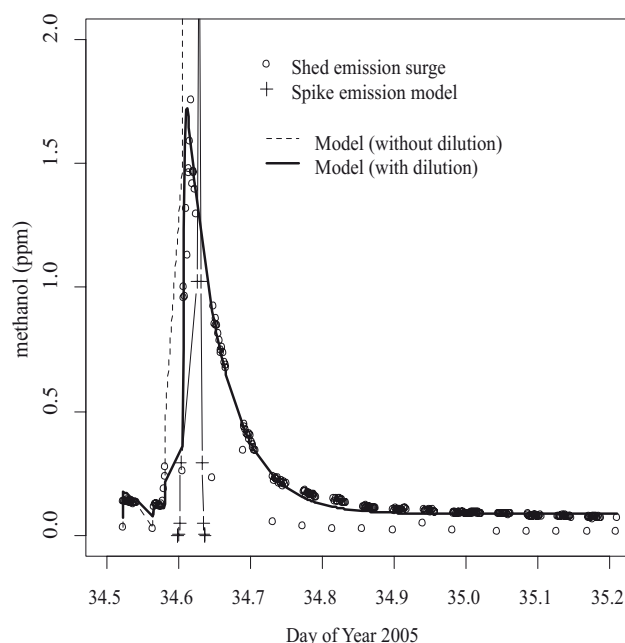


Figure 4:  
Example of modeled mixing ratio curve for methanol in the sheep shed. The spike emission model has a 30 minutes offset in time for clarity

Table 4:  
Selected VOC emissions from spike analysis for sheep. Errors indicate statistical variability

VOC	<i>D</i> [h <sup>-1</sup> ]	<i>P</i> [mg sheep <sup>-1</sup> h <sup>-1</sup> ]	<i>S</i> [mg sheep <sup>-1</sup> spike <sup>-1</sup> ]	Annual flux <sup>‡</sup> [Gg a <sup>-1</sup> C]
Methanol	1.09	26 ± 13	103 ± 52	0.3 ± 0.1
Acetaldehyde	0.82	45 ± 40	60 ± 21	0.7 ± 0.5
Ethanol	1.07	2124 ± 1644	8569 ± 3700	40 ± 20
Acetic acid	0.91	8 ± 5	12 ± 9	0.09 ± 0.05
Propionic acid	1.06	4 ± 2	168 ± 303	0.2 ± 0.3
Butyric acid	1.11	3 ± 2	36 ± 48	0.08 ± 0.06
Valeric acid	0.93	0.2 ± 0.1	1 ± 1	0.005 ± 0.003
Caproic acid	1.15	0.3 ± 0.2	9 ± 14	0.02 ± 0.02

D: Decay rate; P: Constant production; S: Production from emission spikes.  
<sup>‡</sup> 2771100 sheep for Germany (Dämmgen, 2004), 2 Spikes per day, 365 days per year.

On comparing the flux values from both the correlation and the dilution modelling methods in the sheep shed, we observed a difference by an order in magnitude for most of the species (Tables 2 and 4). Though both methods have shortcomings, the most likely factor leading to larger values for the second model is the assumption that the animals spend all year inside the shed, and that the conditions encountered during the campaign were representative under that assumption. In the case of the sheep shed investigated, the above calculation showed a relatively large effect of the spikes on total emissions. Such spikes will hardly occur when the sheep are not inside the shed. Hence, the second model likely creates an overestimate of emissions. The correlation estimate does not include such assumptions, but instead presumes that the relative emission of VOC per ammonia or methane remains nearly constant, whether the animals are inside or outside the shed. Thereafter, the extrapolation gives a mean value under the conditions previously evaluated for the reference emission, i.e. of methane and ammonia.

Generally, the use of emission factors from one animal shed to calculate regional emissions may pose problems as there can be differences in animal nutrition and management systems, and differences in manure management leading to various emission sources within different animal housings. Controlled experiments have shown that factors like temperature, humidity and ventilation rate can also influence emission rates (Nimmermark and Gustafsson, 2005). Another issue of concern is that the CH<sub>4</sub> and

NH<sub>3</sub> fluxes used for VOC flux extrapolation that were for “manure management” plus “enteric fermentation” and for “manure management”, respectively, may not have been representative for the measurement situation. The factors extend to both grazing and housed animals and all types of manure management systems. We used these fluxes with calculated emission ratios from housed livestock only and for a specific manure management system for VOC flux estimation. Therefore our estimates are possibly not comprehensive and may have an associated error of a factor of two at least.

Table 5:  
Emission ratio (*E<sub>V</sub>*) of VOC to NH<sub>3</sub> in Germany and the UK compared

Animal Type	VOC	<i>E<sub>V</sub></i> Germany	<i>E<sub>V</sub></i> UK <sup>‡</sup>
Pigs	Acetone	6 – 9 × 10 <sup>-3</sup>	< 0.1 × 10 <sup>-3</sup>
	Acetic acid	NA	0.1 – 0.2
	Propionic acid	3 – 6 × 10 <sup>-3</sup>	6 – 9 × 10 <sup>-3</sup>
	DMS	1.2 – 1.8 × 10 <sup>-3</sup>	0.05 – 0.15
	Valeric acid	0.6 – 0.8 × 10 <sup>-3</sup>	10 – 30 × 10 <sup>-3</sup>
	p-cresol	1 – 3 × 10 <sup>-3</sup>	70 – 90 × 10 <sup>-3</sup>
Sheep	Acetone	5 – 8 × 10 <sup>-3</sup>	5 – 8 × 10 <sup>-3</sup>
	Acetic acid	2 – 4 × 10 <sup>-3</sup>	10 – 20 × 10 <sup>-3</sup>
	Propionic acid	2 – 4 × 10 <sup>-3</sup>	< 1 × 10 <sup>-3</sup>
	DMS	0.3 – 0.4 × 10 <sup>-3</sup>	0.15 – 0.3

<sup>‡</sup> Hobbs et al., 2004 ; NA = Not Applicable

When we compare our emission ratios (Table 5) to ammonia with published values from the United Kingdom (Hobbs et al., 2004), same order of magnitude results are obtained for a number of VOCs for which data exist in both cases. The largest differences were found for p-cresol and higher volatile fatty acids, as well as for DMS. Differences among the VFA's are not surprising, because differences in manure degradation age and bacterial composition can readily cause different VFA abundances. The difference for DMS remains unexplained.

#### 4 Conclusions

With the use of a proton transfer reaction mass spectrometer we have identified and measured the mixing ratios of major volatile organic compounds emitted by pigs and sheep in Germany. The diurnal variations of carbon dioxide, nitrous oxide, methane, and ammonia have also been monitored with the aid of a photo-acoustic analyser.

The results are summarised as follows:

- 1) Some 17 major VOCs were measured in the sheep shed while in the pigsty we identified 15 main compounds

with the PTR-MS.

- 2) Trace gas emissions showed periodic spikes with emission surges coinciding with manure removal and animal feeding.
- 3) Using VOC correlations with ammonia or methane, we calculated emission factors for Germany. Some of our emission factors are in line with those for the UK calculated by Hobbs et al., (2004). Major deviations were found for p-cresol, higher acids, and with DMS having the largest disagreement.
- 4) Mass release rates of VOCs were also modelled from the emission profiles in the sheep shed. We found large discrepancies likely related to high short-term emissions during manure removal, and the assumption that the animals remain inside the shed all year round.
- 5) Emissions were dominated by methanol in the pigsty and ethanol in the sheep shed.
- 6) Legal threshold limits for livestock and human welfare were not exceeded in both sheds monitored.

Table 6:

VOC Emissions from animal husbandry in Germany in Gg a<sup>-1</sup> C. Calculated from correlation with methane unless stated otherwise.

VOK	Dairy cows <sup>‡</sup>	Pigs	Sheep	Total
Methanol	0.7 – 2.3	3 – 9	0.02 – 0.04	3.7 – 11
Ethanol	4 – 31	NA	1.5 – 6	5.5 – 37
Acetaldehyde	0.3 – 1.2	0.1 – 0.5	0.04 – 0.7	0.4 – 2.4
Acetone	0.4 – 1.3	0.5 – 6	0.01 – 0.02	0.9 – 7.3
MEK	0.1 – 0.3	0.3 – 0.9	< 0.003	0.4 – 1.2
“Propanols”	0.1 – 2	~0.01	0.01 – 0.02	0.1 – 2
Acetic acid	1 – 5	NA	< 0.01 – 0.02	1 – 5
Propionic acid	0.14 – 0.5	1 – 4	< 0.015	1.1 – 4.5
Butyric acid	0.2 – 0.4	0.4 – 4	0.02 – 0.14 <sup>†</sup>	0.6 – 4.5
Valeric acid	0.02 – 0.04	0.2 – 0.6	0.002 – 0.008 <sup>†</sup>	0.2 – 0.6
DMS	0.04 – 0.23	0.3 – 1.3	< 0.001	0.3 – 1.5
TMA	0.3 – 2	0.3 – 0.9	0.01 – 0.02	0.6 – 2.9
Sum	7 – 45	6 – 27	2 – 7	15 – 77

NA = Not Applicable, <sup>‡</sup> Ngwabie et al., 2007,  
<sup>†</sup> Calculated from emission model

A summary of our VOC emission estimates for the three livestock types investigated (Table 6, including previously published work) indicates that emissions are dominated by ethanol and methanol with ethanol mainly released by cows and methanol mainly by pigs, which maybe due to the differences in nutrition and digestive systems. For instance, pigs are not ruminants but receive a higher amount of pectin in their diets compared to cows, with pectin a

potentially dominant source of emitted methanol (Galbally and Kirstine, 2002). On the other hand, if the main source of acetone is animal respiration (fat metabolism), then this would explain our measurements (and the discrepancy to the UK measurements, Table 5), as there was no strong tendency for a dominant acetone emission from a certain animal species.

The total annual VOC emissions from the measured animal groups were estimated to range from as low as 15 to as high as 77 Tg carbon. Taking into account that the German cow population is three times as high including all other than just dairy cows, and that poultry emissions were not investigated in this study, likely increases the actual emissions by a factor of two. Considering further that the numbers in Table 6 are likely only accurate to a factor of two, we estimate that German VOC emissions from animal husbandry likely range from 100 to 200 Gg C per year. Though this is only slightly smaller to the previous estimate or ~230 Tg C (Dämmgen, 2004), which was based on the work of Hobbs et al. (2004), the determined VOC composition is much different. That is to say, emissions are dominated by short-chained alcohols, and not VFAs and DMS. Interestingly, the magnitude compares well with VOC emissions of car traffic in Germany, estimated by the German Umweltbundesamt to have been 250 Gg C per year in 2002. However, the animal emissions are of fundamentally different origin and composition. While car traffic emissions are dominated by partially highly reactive hydrocarbons, animal emissions are dominated by relatively unreactive alcohols, acetone, and acids. Hence, the impact of animal husbandry VOC emissions on tropospheric ozone is likely smaller, though not confined to the atmospheric boundary layer but possibly affecting free tropospheric ozone chemistry.

Our measurements are a starting point and a reference for further VOC identification and quantification from animal husbandry. To augment these measurements, there is need to access trace gas emissions from other animal categories, such as bulls, and birds for a full impact on the environment. In addition, the effects of different holding types and manure treatment types among the dominant emitters needs close examination. Though there has been research into some methods to reduce emissions during feeding like spraying with water droplets or a water/oil mixture, and addition of tallow to animal feed, much work still has to be done to find ways to avoid large spikes during active periods as shown by our measurements. In addition, better ventilation and management practices may go a long way to reducing emissions from animal manure and reducing exposure to farm workers and the animals themselves.

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