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Application of Proton-Transfer-Reaction Mass Spectrometry to the Assessment of Odorant Removal in a Biological Air Cleaner for Pig Production

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Supporting Information

ABSTRACT: There is an urgent need to develop odor reduction technologies for animal production facilities, and this requires a reliable measurement technique for estimating the removal of odorants. The purpose of the present experiment was to investigate the application of proton-transfer-reaction mass spectrometry (PTR-MS) for continuous measurements at a biofilter from SKOV A/S installed at a pig production facility. PTR-MS was able to handle the harsh conditions with high humidity and dust load in a biofilter and provide reliable data for the removal of odorants, including the highly odorous sulfur compounds. The biofilter removed 80−99% of carboxylic acids, aldehydes, ketones, phenols, and indoles and ca. 75% of hydrogen sulfide. However, only ∼0−15% of methanethiol and dimethyl sulfide was removed. In conclusion, PTR-MS is a promising tool that can be used to improve the development of biological air cleaning and other odor reduction technologies toward significant odorants.

KEYWORDS: *proton-transfer-reaction mass spectrometry, biological air cleaning, odorants, odor, pig production*

INTRODUCTION

Odor from pig production can be a serious nuisance for people living close to the production facilities, and it is therefore vital to further develop odor reduction technologies that can ensure low emission of odorants and other gases to the surroundings. Biological air cleaning is a potential method for reducing odor nuisance from modern intensive pig productions.[1] The development of a biological air-cleaning system for pig production is a compromise between cost optimization and environmental effects in relation to odor and ammonia. During the development process as well as the documentation of biological air cleaning, it is important to have a reliable measurement technique that can estimate the removal of odor. At the moment, odor is normally measured with olfactometry, which is based on a dilution-to-threshold assessment of air samples with trained human panelists.[2] This method has some drawbacks in relation to low recovery of odorants in sample bags[3−5] and during analysis in the olfactometer.[6] For some of the odorants that have been demonstrated to be removed by biological air cleaning (carboxylic acids, phenols, and indoles), a particularly low recovery in sampling bags for olfactometry has been observed.[3,5] Additionally, chemical measurements have a potential for providing a more detailed understanding of the processes that occur in biological air-cleaning systems compared to olfactometry. This may aid in identifying factors limiting the efficiency and in optimizing the systems.

Different chemical methods have been used for the collection of odorants and analysis with gas chromatography and mass spectrometry (GC-MS) including solid-phase microextraction (SPME)[7,8] and adsorbent tubes.[9,10] These chemical methods and olfactometry provide only a limited number of discrete measurements and do not reveal diurnal variations and how the odor removal is affected by changes in the function and management of the biological air cleaner. A study with the online technique membrane inlet mass spectrometry (MIMS) at a biological air cleaner has demonstrated that measurement online is a useful tool to give an estimate of the removal of odorants in relation to both the specific compounds and the diurnal variations.[11] MIMS has some drawbacks in relation to sensitivity and specificity, particularly in relation to reduced sulfur compounds, including hydrogen sulfide in air, which cannot be measured by MIMS.[11] Reduced sulfur compounds are considered to be important odorants from pig production facilities due to their low odor threshold values.[12,13]

Proton-transfer-reaction mass spectrometry (PTR-MS) is another online technique that is based on soft chemical ionization with protonated water (H_3O^+) and is an instrument with high sensitivity and specificity.[14−16] In addition, the relative ease of obtaining quantitative results, even for compounds for which calibration standards are not available,[14−16] is a unique advantage. PTR-MS has been applied in some studies in relation to odorants from animal production. In the studies by Ngwabie et al.[17] and Shaw et al.[18], PTR-MS was used to estimate the emission of odorants from cattle production. Feilberg et al.[19] conducted the first study with PTR-MS in pig production and demonstrated that quantitative results could be obtained for odorants and, in particular, the highly odorous sulfur compounds. In the study by Liu et al.,[20] PTR-MS was used for estimating the effect of slurry ozonation on the emission of odorants from pig production. However, PTR-MS has not been investigated in relation to biological air cleaning for pig production, which represents relatively harsh

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sampling conditions with high moisture and dust levels. Additionally, extensive quantitative correlations with chromatographic methods that are more selective than PTR-MS have not been included in previous studies of livestock odorant emissions. It is therefore of great interest to investigate whether PTR-MS could be a suitable method for investigating the removal of odorants in a biological air cleaner for pig production and to give a more precise evaluation of the effect on reduced sulfur compounds compared to the previous study with MIMS.[11]

The aim of the present study was (i) to evaluate the application of the PTR-MS for measuring the removal of odorants under the harsh conditions in a biological air cleaner, (ii) to correlate PTR-MS data collected both before and after an air cleaner with data based on supplementary chromatographic methods, and (iii) to estimate the removal of odorants in a biological air cleaner installed at a full-scale pig production facility.

MATERIALS AND METHODS

Description of the Biofilter. A three-step biofilter manufactured by SKOV A/S (SKOV A/S, Roslev, Denmark) was installed at a pig production facility with 350 growing−finishing pigs. The biofilter was placed in a separate building next to the pig production facility. Four ventilation fans were placed after the biofilter, and the ventilation air was drawn through the biofilter from six outlets (⌀ 60 cm) in the side of the pig production facility. The maximum ventilation rate for the biofilter was ca. 35000 m^3 h^{-1}. The biofilter was designed with three vertical filter walls of cellulose pads (step 1, 2, and 3) (see Figure 1). Steps 1 and 2 were 15 cm wide, and step 3 was 60 cm wide. A 2 cm wide air distribution plate was placed in front of step 1 to ensure equal distribution of air in the biofilter and to lower the load of dust particles. The filter walls in steps 1 and 2 were irrigated with recirculated water from a pond beneath the filter walls. Step 1 was washed regularly with an automatic washing machine to minimize clogging by dust particles. The washing machine flushed the filter wall with recirculated water in the direction opposite to the air flow four times a day. Replacement of water was based on measurements of conductivity in step 1. Water was removed from step 1, and fresh water was added to step 2. An overflow between steps 1 and 2 allowed fresh water to flow back to step 1. The discarded water was transferred to a slurry tank outside the facility. The humidification of the filter wall in step 3 was achieved by the humidified air from steps 1 and 2.

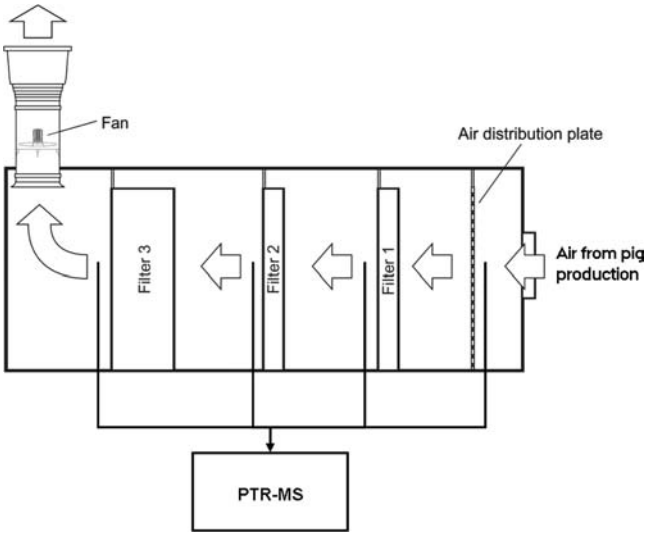

Figure 1. Schematic drawing of the three-step biofilter from SKOV A/S and the setup with odorant measurements by PTR-MS.

PTR-MS. A high-sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) was applied for measuring the removal of odorants in the biofilter. The PTR-MS is based on chemical ionization of compounds by protonated water (H_3O^+) in a drift tube and subsequent detection of ionized compounds in a quadrupole mass spectrometer. Because H_3O^+ is used for protonation, only compounds with a proton affinity higher than that of water (691 kJ/mol) can be measured. In the present study, the drift voltage was set at 600 V and the drift tube pressure was maintained in the range of 2.1−2.2 mbar (E/N value ∼ 135 Td). The temperature of the drift tube was controlled at 75 °C, and the sampling flow was adjusted to ca. 100 mL min^{-1}. An external pump was used to increase the flow in the sampling tubes to ca. 500 mL min^{-1}. The measurements were performed as single ion monitoring with each ion being detected for 200−1000 ms during each cycle. A total of 40 cycles (20 min) were measured on each step in the biofilter in a continuous mode. Between measurements on the biofilter, instrumental background was measured (40 cycles) on contaminant-free air, prepared onsite by purification of room air via a Supelpure HC filter (Supelco, Bellefonte, PA). Four times during the measurement period, a full-scan between m/z 30 and 140 was performed. The sensitivity of the compound of interest was estimated using the rate constant for proton transfer, the estimated drift tube residence time, and the mass-specific transmission factor as described by de Gouw and Warneke.[14] The rate constants were either based on measurements on gas standards or calculated by using the method described by Su and Chesnavich.[21] The mass-specific transmission factors were checked regularly during the measurement period with a mixture of 14 aromatic compounds between m/z 79 and 181 (P/N 34423-PI, Restek, Bellefonte, PA). The measurement of hydrogen sulfide by PTR-MS is humidity dependent, and the concentration of hydrogen sulfide was determined according to the method described by Feilberg et al.[19] The detection limits for PTR-MS were calculated as 3 times the standard deviation on blank samples (see Table 1).

GC-SCD and TD-GC-MS. A gas chromatograph with a sulfur chemiluminescence detector (GC-SCD, GC 7890 A and SCD 355, Agilent Technologies A/S, Horsholm, Denmark) was used to measure the concentration of sulfur compounds in air samples collected in 10 L Tedlar bags (CEL Scientific Corp., Santa Fe Springs, CA). The gas chromatograph was equipped with a capillary column with a stationary phase of dimethylpolysiloxane (DB-1, Agilent Technologies A/S). The column had a length of 60 m, an inner diameter of 0.53 mm, and a stationary phase of 5 μm. The helium carrier gas flow rate was set to 10 mL min^{-1}. The GC oven temperature was held for 1 min at 60 °C, ramped to 200 °C at 20 °C min^{-1}, and held for 1 min at 200 °C. The GC-SCD was equipped with a sample loop at 1.0 mL. At each analysis, the sample loop was flushed with ca. 45 mL of sample air. A gas standard (Air Liquid, Horsens, Denmark) containing hydrogen sulfide (5.33 ± 0.16 μL L^{-1}), methanethiol (5.37 ± 0.27 μL L^{-1}), and dimethyl sulfide (5.84 ± 0.29 μL L^{-1}) was used as a one-point calibration. The detection limit for the GC-SCD was estimated as 3 times the baseline noise (Supporting Information, Table S1).

A thermal desorber (Turbomatrix ATD, Perkin-Elmer, Waltham, MA) coupled with a gas chromatograph and a mass spectrometer (GC/-MS, GC 6890 N and MSD 5973, Agilent Technologies A/S) was used to analyze the air samples collected on adsorbent tubes. The adsorbent tubes were made of stainless steel and packed with Tenax TA (Markes International Ltd., Llantrisant, U.K.) and Carbograph 5TD (Markes International Ltd.). The adsorbent tubes were desorbed in a two-step mode. In the first step, the tubes were purged with helium for 2 min and desorbed for 10 min at 290 °C, and the desorbed compounds were trapped on a cold trap (−20 °C) packed with Tenax TA. In the second step, the cold trap was heated to 300 °C at 40 °C s^{-1}, and the desorbed compounds were transferred to the GC in a transfer line heated to 250 °C. The GC was equipped with a capillary column with a stationary phase of polyethylene glycol (HP-INNOWax, Agilent Technologies A/S). The column had a length of 30 m, an inner diameter of 0.25 mm, and a stationary phase of 0.25 μm. The helium carrier gas flow rate was pressure controlled at 7.5 psi.

Table 1. Average Concentrations of Odorants Measured by PTR-MS in a Three-Step Biofilter from SKOV A/S Installed at a Facility with Growing–Finishing Pigs (n = 237)

				concentration (nL L^{-1} ± SD)			
compound	m/z[a]	DL[b]	OTV[c]	before step 1	after step 1	after step 2	after step 3
hydrogen sulfide	35	3.51	1.9	353 ± 104	322 ± 92	272 ± 83	86 ± 37
acetaldehyde	45	0.22	38	6.8 ± 1.9	4.4 ± 1.2	9.4 ± 4.4	0.5 ± 0.1
methanethiol	49	0.09	0.07	12 ± 3.4	12 ± 3.4	10 ± 3.1	10 ± 3.0
acetone	59	0.08	13000	7.1 ± 2.0	4.8 ± 1.3	5.4 ± 1.3	0.8 ± 0.3
trimethylamine	60	0.30	2.1	12 ± 4.9	4.3 ± 1.4	3.2 ± 1.4	0.8 ± 0.3
acetic acid	61 + 43	0.96	234	314 ± 72	49 ± 20	54 ± 31	1.2 ± 0.2
dimethyl sulfide[d]	63	0.15	4.1	3.0 ± 0.9	2.9 ± 0.8	2.7 ± 0.8	2.7 ± 0.8
2-butanone	73	0.06	4500	3.3 ± 1.0	2.0 ± 0.5	2.4 ± 0.7	0.6 ± 0.2
propanoic acid	75 + 57	0.34	25	67 ± 19	16 ± 5.6	19 ± 9.1	0.5 ± 0.1
2,3-butanedione	87	0.12	0.1	1.2 ± 0.3	0.7 ± 0.2	1.1 ± 0.4	0.2 ± 0.06
butanoic acid[e]	89 + 71	0.21	1.8	42 ± 12	11 ± 3.9	9.4 ± 4.0	0.3 ± 0.1
phenol + dimethyl disulfide	95	0.08	54[g]	2.0 ± 0.4	0.7 ± 0.2	1.9 ± 1.0	0.2 ± 0.07
C_5 carboxylic acids[f]	103 + 85	0.12	1.4	11 ± 3.1	3.2 ± 1.0	2.7 ± 1.0	0.2 ± 0.03
4-methylphenol	109	0.15	0.3	9.5 ± 2.8	2.5 ± 0.8	2.6 ± 0.7	0.2 ± 0.04
indole	118	0.03	0.4	0.7 ± 0.2	0.2 ± 0.05	0.1 ± 0.02	<DL
4-ethylphenol	123	0.07	1.3	1.2 ± 0.3	0.4 ± 0.1	0.5 ± 0.1	<DL
dimethyl trisulfide	127	0.05	1.7	0.1 ± 0.02	0.06 ± 0.01	0.1 ± 0.03	<DL
3-methylindole	132	0.03	0.09	0.4 ± 0.1	0.1 ± 0.05	0.07 ± 0.02	<DL

[a] m/z, mass-to-charge ratio. [b] Detection limit (nL L^{-1}) estimated as 3 times the standard deviation on blank samples. [c] Odor threshold values (nL L^{-1}) were based on reported detection threshold values.[12,13]. [d] Corrected for O^{18} isotopic contribution from acetic acid. [e] Ca. 10% contribution from 2-methylpropanoic acid. [f] Ca. 60% pentanoic acid and 40% 3-methylbutanoic acid. [g] OTV for phenol.

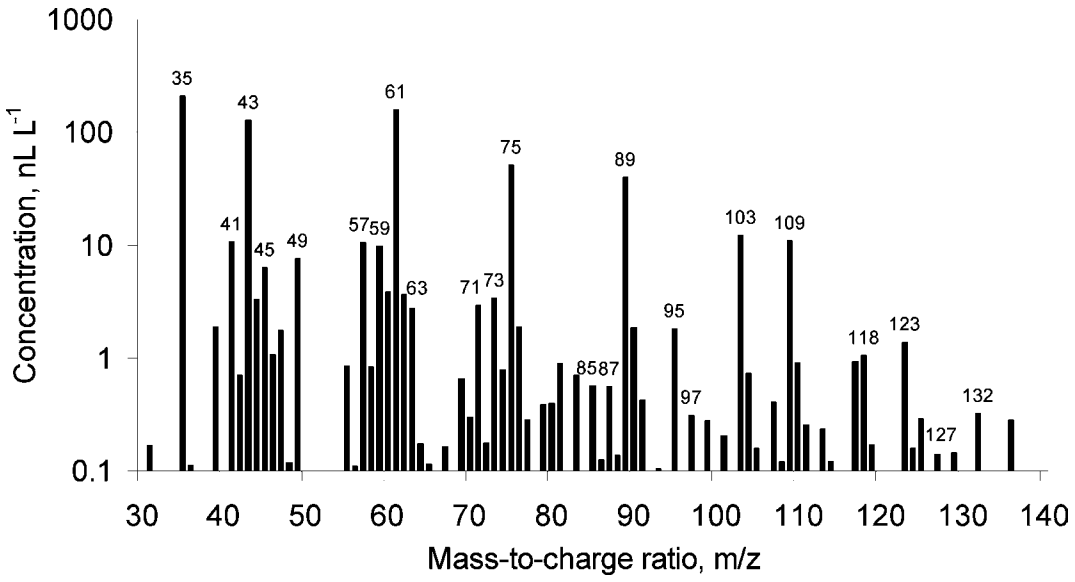

Figure 2. Example of a full-scan mass spectrum measured by PTR-MS in the ventilation air before a biofilter installed at a facility with growing–finishing pigs. The results are presented as nL L^{-1}, and each value represents an average of four consecutive scans. Only peaks with a concentration above 0.1 nL L^{-1} were included. The signal at m/z 35 (hydrogen sulfide) was corrected for the humidity dependency.

The GC oven temperature was held for 5 min at 50 °C, ramped to 250 °C at 10 °C min^{-1}, and held for 5 min at 250 °C. Two liquid calibration standards containing a total of 18 odorants were used as a one-point calibration. Clean adsorbent tubes loaded with 1 μL of the calibration standards and field blank adsorbent tubes were analyzed along with the sample tubes. The detection limit for the TD-GC-MS was estimated as 3 times the baseline noise (Supporting Information, Table S1).

Experimental Setup. The removal of odorants was measured continuously for 13 days with PTR-MS. To achieve maximum load of odorants, the measurements were performed in the summer period with high ventilation rates. All equipments were placed in an insulated room next to the biofilter. A heated Teflon tube (Mikrolab Aarhus A/S, Aarhus, Denmark) with a 5 μm Teflon filter (Millipore, Billerica, MSA) was placed before the biofilter and after each step in the biofilter. The recovery of odorants in the Teflon filter was estimated on sample air before the biofilter. The variation in the concentration of odorants in the six outlets from the pig production facility was measured to validate the setup with one sampling point in the center of each step. The Teflon tubes from the different steps in the biofilter were connected to a heated switchbox (ca. 60 °C) with a five-way PEEK valve (Bio-Chem Valve Inc., Boonton, NJ). The switchbox was controlled by the software of the PTR-MS.

On 5 days during the measurement period, air samples were collected in Tedlar bags and on adsorbent tubes before the biofilter and after each step in the biofilter. The Tedlar bags were filled over a

period of 10 min to 90% of their nominal volume, and the adsorbent tubes were exposed for 20 min with a flow at ca. 100 mL min^{-1}. On each of the 5 days, three sets of samples were collected between 11:00 a.m. and 2:00 p.m. Each set of samples was collected simultaneously. The content of the Tedlar bags was analyzed within 6 h on the GC-SCD, and the adsorbent tubes were kept in a refrigerator and analyzed on the TD-GC-MS within 72 h. The results from the GC-SCD and TD-GC-MS were paired with results from PTR-MS that were within 30 min of the collection time. Consequently, not all measurements by GC-SCD and TD-GC-MS were used for the intercomparison with PTR-MS.

Data Analysis. The last 20 cycles of each measurement by PTR-MS were used to calculate the concentration of the detected compounds. A total of 237 measurements were recorded for each step in the biofilter and the instrumental background. The instrumental background was subtracted from the measurements, and the results are presented as the average ± standard deviation. An average value was calculated only if more than 20% of data was above the detection limit. Linear regression was used for the intercomparison between PTR-MS and the other methods.

RESULTS AND DISCUSSION

Compound Assignment. The mass-to-charge ratios (m/z) monitored during the continuous measurement period on the biofilter are presented in Table 1, along with the corresponding compounds, average concentrations (± standard deviation), detection limits, and odor threshold values. The chosen m/z values were based on a full-scan spectrum for the ventilation air before the biofilter between m/z 30 and 140, as shown in Figure 2. The compound assignment was based on measurements with GC-SCD and TD-GC-MS and previous experiences with odorants from pig production facilities.[9,19] For most of the compounds, an unambiguous compound assignment can be obtained. However, some compound assigments are more difficult due to humidity dependency or overlapping of signals from other compounds or isotopes.

A signal at m/z 35 was assigned to hydrogen sulfide. The proton affinity of hydrogen sulfide (705 kJ mol^{-1}) is close to the proton affinity for water (691 kJ mol^{-1}), which results in a humidity-dependent backward reaction of protonated hydrogen sulfide. In the study by Feilberg et al.,[19] a correction of the measurement of hydrogen sulfide by PTR-MS was described, and that method was applied in the present study. In this method, the concentration of a known gas standard relative to the response from the PTR-MS is expressed as a function of the humidity in the sample air. Measurement of water cluster ($H_3O^+(H_2O)$, m/z 37) relative to the primary ion (H_3O^+, m/z 21) is used an expression of humidity in the sample air. The correction of hydrogen sulfide was established prior to the measurements with the settings used during the whole period (see Figure 3).

The high relative humidity in sample air from the biofilter can also affect the measurement of carboxylic acids because the fragmentation of these compounds will increase as the relative humidity increases.[19] The signals at m/z 61, 75, 89, and 103 can be assigned to acetic acid, propanonic acid, C_4 carboxylic acids (butanoic acid and 2-methylpropanoic acid), and C_5 carboxylic acids (pentanoic acid and 3-methylbutanoic acid). These compounds will also have fragments at m/z 43, 57, 71, and 85, respectively. In the study by Feilberg et al.,[19] it was shown that the sum of the molecular ion and the fragment under various humidity conditions is stable within 5%. The results for carboxylic acids in the present study are therefore presented as the sum of the molecular ions and their respective fragments. According to the TD-GC-MS measurements, the contribution

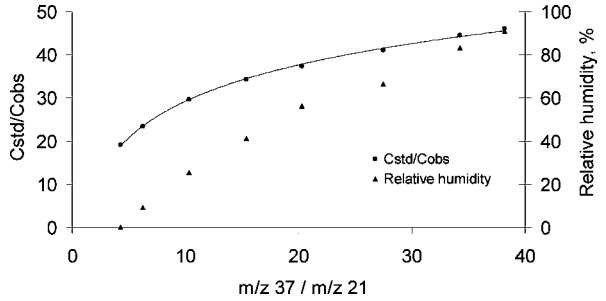

Figure 3. Correction of hydrogen sulfide (m/z 35) measured by PTR-MS expressed as the diluted hydrogen sulfide concentration from a known standard (Cstd) relative to the measured signal by PTR-MS (Cobs) as a function of the water cluster signal ($H_3O^+(H_2O)$, m/z 37) relative to the primary ion (H_3O^+, m/z 21). The fitted line represents the empirical logarithmic function $y = 12.2 \ln(x) + 1.2$, $R^2 = 0.99$.

from 2-methylpropanoic acid was ca. 10% of C_4 carboxylic acids, and m/z 89 + 71 was mainly ascribed to butanoic acid. The distribution between C_5 carboxylic acids was ca. 60% pentanoic acid and ca. 40% 3-methylbutanoic acid. Fragmentation of alcohols can influence the signal for some of the carboxylic acid fragments.[22] According to the TD-GC-MS measurements, the abundance of alcohols was very low compared to that of carboxylic acids (~0−5%) and will have only a limited influence on the measurements of carboxylic acids. The signal at m/z 41 can be ascribed to alcohol fragments.[19]

The signal at m/z 63 was assigned to dimethyl sulfide, and due to the high concentration of acetic acid the signal at m/z 63 was corrected for the O^{18} isotope of acetic acid (m/z 61). Approximately 20% of m/z 63 was due to acetic acid. A signal at m/z 73 was detected during the entire measurement period in all three steps in the biofilter. The signal at m/z 73 can be assigned to C_4 carbonyls; however, according to the TD-GC-MS measurements, it is likely to be 2-butanone. In the same way, the signal at m/z 87 can be assigned to 2,3-butanedione.

A signal was detected at m/z 95, and this signal can be assigned to both phenol and dimethyl disulfide. These two compounds have previously been detected in ventilation air from pig production facilities, although they are often found in the low nanoliters per liter range.[9] Dimethyl disulfide also gives fragments at m/z 79 and 97, but the signals are low (<1 nL L^{-1}) and can be influenced by benzene (m/z 79) and fufural (m/z 97), which are likely to be found as background contaminants. In the TD-GC-MS measurements, phenol and dimethyl disulfide were detected in a ~1:1 ratio. The adsorbent tubes used in the present study were packed with both Tenax TA and a graphitized sorbent (Carbograph 5TD). Graphitized sorbents will cause oxidation of thiols into disulfides.[23,24] It has previously been demonstrated with adsorbent tubes less affected by oxidation of methanethiol (Tenax TA) that phenol was detected at a level approximately 6 times higher than dimethyl disulfide in a facility with growing−finishing pigs.[19] It is therefore likely that dimethyl disulfide was overestimated in the TD-GC-MS measurements and that most of the signal at m/z 95 could probably be ascribed to phenol.

The full scan also demonstrated a number of low-level masses other than those presented in Table 1. It was not possible to assign all of these masses, but they are likely to originate from compound fragments (m/z 58, trimethylamine fragment), aromatic compounds (m/z 107, benzaldehyde and

C_8-aromatics), and C^{13} isotopes (m/z 90, butanoic acid C^{13} isotope).

Removal of Odorants in the Biofilter. The results in Table 1 clearly show that many of the measured odorants were removed to a level close to or below the odor threshold values when the concentrations measured before the biofilter are compared to the concentrations after step 3. The odor threshold values are based on compilations of reported values.[12,13] It has to be stated that the reported odor threshold values demonstrate large variations, and the interpretation has to be done with great care. Particular carboxylic acids, phenols, and indoles were removed to a level below the odor threshold values. The concentrations of butanoic acid and 4-methylphenol in the different steps of the biofilter are shown in Figures 4 and 5, respectively. The removal of these compounds

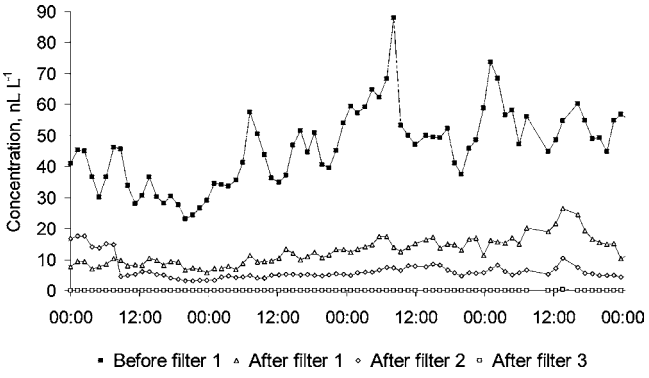

Figure 4. Measured concentrations of butanoic acid (m/z 89 + 71) by PTR-MS in a three-step biofilter from SKOV A/S installed at a facility with growing−finishing pigs. A selected period of 4 days is shown.

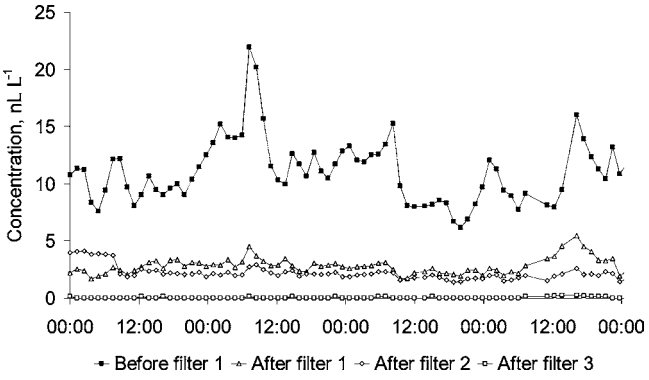

Figure 5. Measured concentrations of 4-methylphenol (m/z 109) by PTR-MS in a three-step biofilter from SKOV A/S installed at a facility with growing−finishing pigs. A selected period of 4 days is shown.

mainly took place in step 1 (60−80%), whereas in step 2 the removal was less pronounced, and in some periods there was even a small increase in step 2. A high removal of carboxylic acids, phenols, and indoles has also been demonstrated for an earlier version of the biofilter from SKOV A/S without step 3.[11] Aldehydes and ketones were also removed in step 1, but only with 30−40%, and an increase in some of these compounds was also seen in step 2. Particularly acetaldehyde was increased to a higher level than before the biofilter. The increase in some compounds in step 2 did not have an effect on the overall removal because these compounds were removed to a high extent in step 3. In general, these results indicate that step 2 in the biofilter had only a small and varying effect on the removal of odorants.

Hydrogen sulfide was the sulfur compound being removed to the greatest extent (ca. 75%) when the concentration before the biofilter was compared with that after step 3. It seems that step 3 was particularly effective in removing hydrogen sulfide, and ca. 70% of the removal took place in this step. Figure 6 shows a

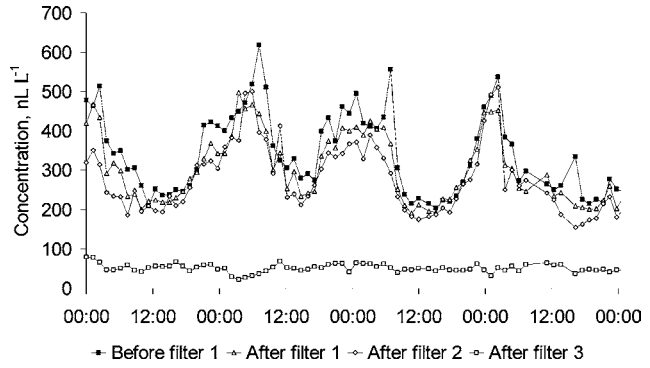

Figure 6. Measured concentrations of hydrogen sulfide (m/z 35) by PTR-MS in a three-step biofilter from SKOV A/S installed at a facility with growing−finishing pigs. A selected period of 4 days is shown.

clear diurnal variation in the hydrogen sulfide concentration before the biofilter and after steps 1 and 2, with the highest concentrations during nighttime when the ventilation rate was low and the lowest concentrations during daytime when the ventilation rate was high. The measured concentration of hydrogen sulfide after step 3 showed much less diurnal variation, which indicates a threshold for the removal of hydrogen sulfide in step 3. However, due to the diurnal variation in the ventilation rate and concentration level, the overall removal efficiency for hydrogen sulfide was lower during the daytime (70−80%) compared to the nighttime (85−95%). Further research is needed to investigate the microbial and chemical conditions responsible for the positive effect of step 3 on the removal of hydrogen sulfide. The removal of methanethiol and dimethyl sulfide was low (~0−15%), and for these compounds step 3 did not have an effect. The low removal of methanethiol and dimethyl sulfide may be due to insufficient mass transfer of these compounds from the gas phase to the liquid phase in the biofilm, which limits the oxidation of these compounds.[25] Figure 7 shows that the removal of methanethiol was low for all three steps in the

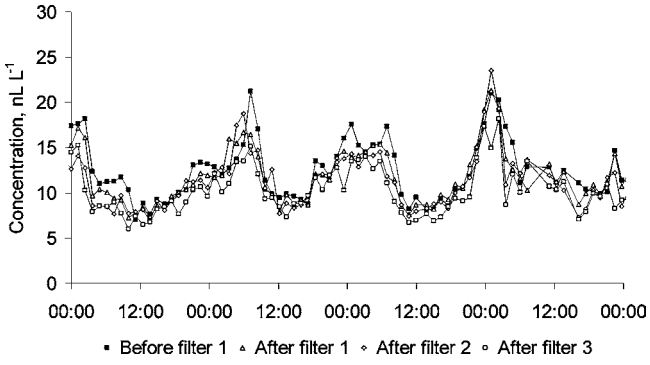

Figure 7. Measured concentrations of methanethiol (m/z 49) by PTR-MS in a three-step biofilter from SKOV A/S installed at a facility with growing−finishing pigs. A selected period of 4 days is shown.

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biofilter both during daytime and nighttime. The same pattern was also seen for dimethyl sulfide (not shown). Despite the high removal of a number of important odorants, hydrogen sulfide and methanethiol were still present at concentrations above the odor threshold value after the biofilter. This emphasizes that further improvement of the odor removal of the biofilter has to focus on these highly odorous sulfur compounds.

Method Evaluation. The application of PTR-MS for estimating the removal of odorants in biological air cleaning for pig production requires that the instrument can handle the hazardous conditions with high relative humidity (70→99%) and dust particles and still provide reliable results. One of the major obstacles is the content of dust particles in the ventilation air. It has previously been estimated in another study that the total inhalable dust concentration in facilities for growing–finishing pigs may be >2 mg m^{-3}.[26] To protect the instrument from this high load of dust particles, a Teflon filter with a pore size at 5 μm was inserted in the end of the Teflon tubing inside the biofilter. In this way, both the tubing and the instrument were protected against dust particles >5 μm and to some extent against suction of liquid water. A measurement with the Teflon filter was compared to a measurement without the Teflon filter to see if there was any effect of the Teflon filter on the odorants (see Figure 8). The Teflon filter mainly had an effect on the

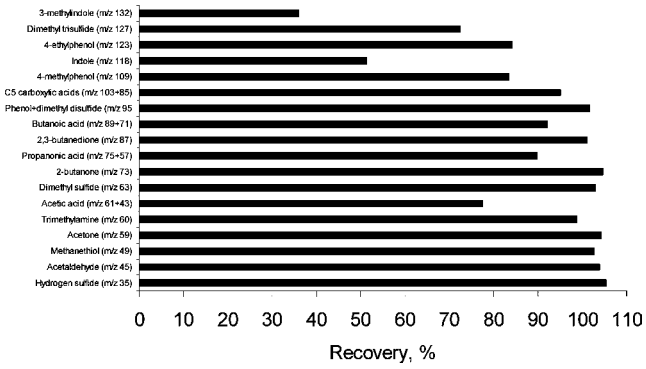

Figure 8. Effect of a 5 μm Teflon filter used for dust filtration on the recovery of odorants measured by PTR-MS in a facility with growing–finishing pigs. The recovery of odorants in the Teflon filter is based on measurements without the filter.

recovery of indoles (35–50%), whereas carboxylic acids (80–90%) and phenols (85–99%) were only slightly affected and sulfur compounds, aldehydes, ketones, and trimethylamine were more or less unaffected. The measurements with and without the Teflon filter were made within 20 min, and the temporal variation should have only a small influence. Some studies have shown that odorants can be associated with dust particles,[27,28] and it is likely that some odorants can be trapped along with the dust on the Teflon filter. Although the Teflon filter was used, the instrument was still affected by the dust particles of <5 μm, and after the measurement period a cleaning of the inlet system was needed. This shows that the Teflon filter is necessary to protect the instrument from dust particles, and depending on the compounds of interest, it will also influence the results to some extent.

The variation in the concentration of odorants in the six outlets from the pig production facility was measured to evaluate the setup with one sampling point in the center of each step (Supporting Information, Table S2). The concentrations in the six outlets varied by 10–15%, which indicates that the horizontal input concentrations in the biofilter were comparable and one sampling point in the center seems reasonable. More sampling points in each step would increase the certainty of the measurements, but it would also increase the temporal variation between the different steps in the biofilter.

An intercomparison between results obtained by PTR-MS, GC-SCD, and TD-GC-MS demonstrated a reasonable correlation (see selected compounds in Figure 9). The data consist of measurements and samples from before the biofilter, between the filter steps, and after the biofilter and, thus, represent different conditions in terms of dust and humidity levels. In general, the concentrations measured by PTR-MS were slightly higher than the concentrations measured by GC-SCD and TD-GC-MS, but the general trends in odorant removal were the same (Supporting Information, Table S1). There could be several reasons for the difference between the methods including uncertainty in calibration, temporal variations, and sampling method. The relative standard deviation for measurement of the calibration standard was ca. 10–15% for TD-GC-MS and 5–10% for GC-SCD. For logistical reasons it was not possible to calibrate the PTR-MS with known standards during the field measurements. The available calibration equipment with gas standards and permeation oven was laboratory-bound and could not easily be moved to a site for field measurements. The mass-specific transmission factor was adjusted regularly during the measurement period with a transportable gas standard (volume = 1 L) and showed only a little variation. The rate constants were based on our own calculations and measurements on gas standards. It has previously been reported that the calculated rate constants are within ±10–15% of measured rate constants.[15] However, field calibration would increase the certainty of the measurements by PTR-MS, and more research is needed to define a functional and reliable field calibration method.

An explanation for the lower concentrations measured by TD-GC-MS could be contaminants on the field blanks. In general, the field blanks had low concentrations of odorants, but the concentration of carboxylic acids was slightly elevated. The samples for analysis of sulfur compounds by GC-SCD were collected in Tedlar bags, which could induce losses due to adsorption to the bag surface or diffusion through the bag material. The samples in the present study were analyzed within 6 h after sampling, and according to other studies the loss of sulfur compounds within this time period should be limited.[4,5] It should also be noted that the analytical results for methanethiol were close to the detection limit of the GC-SCD and, hence, the GC-SCD measurements of this compound are relatively uncertain.

The measurements with PTR-MS require long sampling tubes (3–5 m), which could also influence the results. The potential loss of odorants in the sampling tubes to the PTR-MS was minimized by using Teflon tubing.[29] Furthermore, the Teflon tubes were heated to prevent condensation, and a long equilibration time (10 min, 20 cycles) was used. For most of the compounds of interest in the present study, only a few cycles were needed to achieve a stable signal. However, for compounds such as carboxylic acids, trimethylamine, and 4-methylphenol, 10–15 cycles were necessary to achieve a stable signal. This shows that depending on the compound of interest, the equilibration time could be lowered and even higher time resolution in data can be achieved.

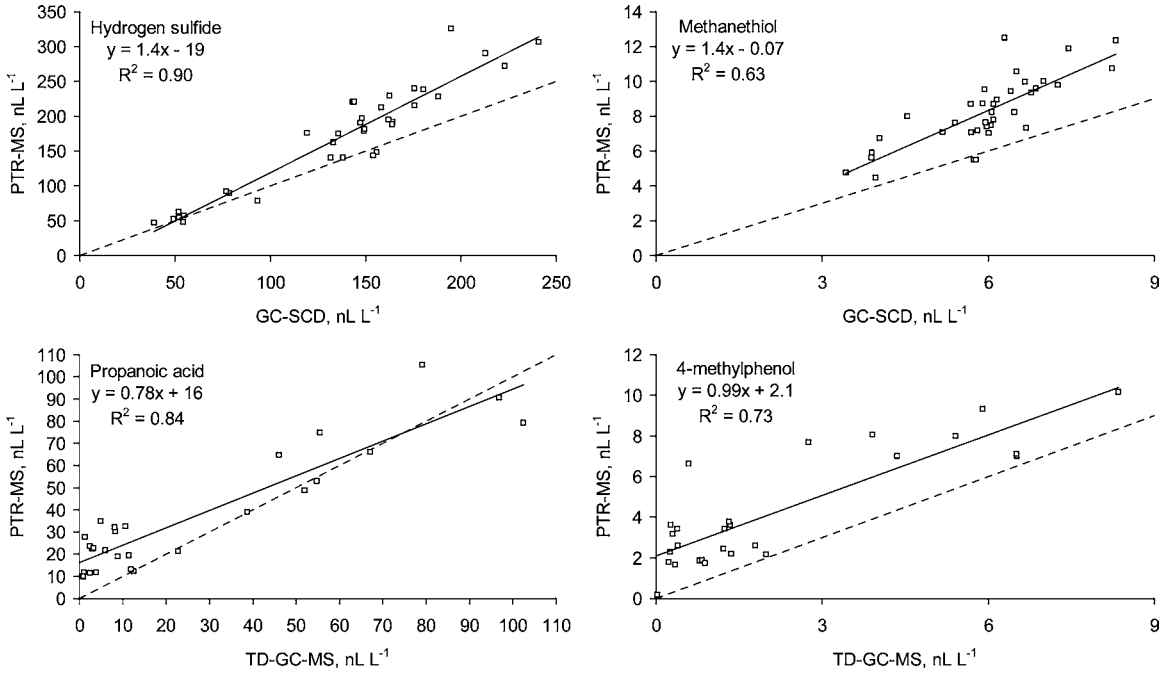

Figure 9. Intercomparison between measurements of odorants by PTR-MS and GC-SCD (n = 36) and TD-GC-MS (n = 27). The measurements by PTR-MS were performed on-site in a three-step biofilter from SKOV A/S installed at a facility with growing−finishing pigs. Samples for GC-SCD and TD-GC-MS were collected in 10 L Tedlar bags and on adsorbent tubes, respectively. The solid line shows the best linear fit to data, and the dashed line is a 1:1 line.

Overall, PTR-MS is assessed to be a robust method for estimating the removal of odorants in a biological air cleaner for pig production because the drawbacks of adsorbent tubes and samplings bags is avoided and dust and humidity can be handled. PTR-MS can also provide high time resolution, which gives valuable information about the diurnal variation in the removal of odorants and how the removal is affected by changes in the function and management of the biological air cleaner. Finally, PTR-MS can provide reliable measurements on the highly odorous reduced sulfur compounds, and this gives an opportunity to improve future research within development of odor reduction technologies for agricultural applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Estimated detection limits for the GC-SCD and the TD-GC-MS and concentrations measured before the biofilter and after each step in the biofilter (Table S1), the measured variation in the concentration of selected odorants in the six outlets from the pig production facility (Table S2), and additional intercomparisons between PTR-MS and TD-GC-MS (Figures S1−S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS USED

MIMS, membrane inlet mass spectrometry; PTR-MS, proton-transfer-reaction mass spectrometry; GC-SCD, gas chromatograph with sulfur chemiluminescence detector; TD-GC-MS, thermal desorbtion coupled with gas chromotograph and mass spectrometry.

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