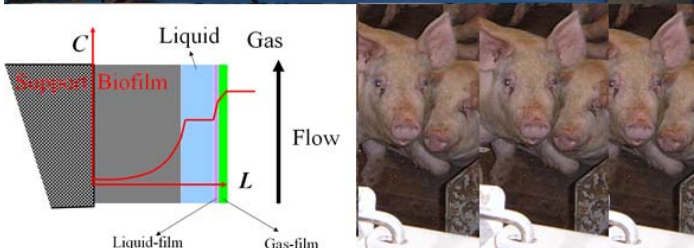




APPLICATION OF PTR-MS FOR OPTIMIZATION OF ODOUR REMOVAL FROM INTENSIVE PIG PRODUCTION WITH EMPHASIS ON BIOFILTRATION

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Keywords: Biofilters; Biotechnology; Emission; Environmental engineering; Mass transfer; Odour and air quality; PTR-MS

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Dezhao Liu

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Abstract

Odour emission from intensive livestock production is becoming a nuisance to neighbors. Biofiltration is the most cost-effective technology for odour reduction. In this PhD study, PTR-MS was demonstrated to be a unique tool both for online evaluation of odour removal and for estimation of key parameters in biofiltration process. Kinetic study indicated the removal of odour is related both to mass load of the odourants and the air loading rate. Partition coefficients of sulfur compounds in biotrickling filter liquids were found to be generally very close to the corresponding partition coefficients in deionized water. Mass transfer coefficients of sulfur compounds in the biofilter packing media were determined through an established method based on breakthrough curves measured by PTR-MS.

Preface

The present PhD thesis is the outcome of the my PhD study of three years at the Department of Engineering, Faculty of Science and Technology, Aarhus University. The study was conducted under the project of ‘Cost-Effective Biofilter for Odour Nuisance Abatement for intensive pig production (CEBONA)’ financed by the Danish Council for Strategic Research. The financial support is acknowledged indeed. The project was a collaboration between SKOV A/S (Roslev, Denmark), Weber A/S (Randers, Denmark), Danish Agriculture & Food Council (Pig Research Centre), Aalborg University (Department of Biotechnology, Chemistry and Environmental Engineering) and Aarhus University (Department of Bioscience, Microbiology and Department of Engineering).

I would especially like to thank my main supervisor Anders Feilberg for the numerical supports, help, guidance and proofreading whenever and whatever I needed. I would also like to thank many times to my supervisor Anders Peter Adamsen for all the help, guidance and supports. Many thanks for both supervisors for their patience and for all the inspirational and motivating discussions.

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Last but not least, I would like to thank my loving wife Li and our lovely son Ian for their love, support, encouragement and understanding.

种瓜得瓜，种豆得豆！

October 2012, Foulum

Dezhao Liu

刘德钊

Summary

Odour emission from livestock production and manure management is increasingly becoming a nuisance to neighbors in the local surroundings and hence a limitation for production growth. Livestock odour emissions consist of a range of odorous compounds potentially contributing to perceived odour nuisance. Treatment of ventilation air by various types of biological air filters has emerged as the most cost-effective technologies for reduction of both odour nuisance and ammonia emissions from animal production facilities. However, previous studies have shown that whereas water soluble odour compounds (e.g. carboxylic acids and phenols) are removed efficiently (>90%), emissions of poorly soluble volatile sulfur compounds are more difficult to remove. Volatile sulfur compounds from livestock production include hydrogen sulphide (H_2S) and methanethiol (CH_3SH), which have been identified as potentially important odorants. Due to difficulties in measuring low concentrations of these compounds, only limited information is available about the processes and parameters that control the removal of these compounds. Proton-transfer-reaction mass spectrometry (PTR-MS) can offer fast, sensitive and time-resolved measurements with low detection limits for odorants monitoring and process monitoring. The objectives of this study are: (1) to evaluate the odour reduction techniques by on-line measurements applying PTR-MS (the emphasis is on biological air treatment, but a full scale slurry ozonation is included for comparison); (2) to evaluate and estimate key parameters (e.g., partition coefficient and mass transfer coefficient) limiting the removal of volatile sulfur compounds in biofilters by applying PTR-MS; (3) to evaluate further optimization and development of biofilters according to estimated key parameters. On-line PTR-MS measurements demonstrated that the slurry ozonation system can give overall odour reduction of ca. 49% (based on odour activity values) and 77% of H_2S reduction. However, the study indicated the emissions of odorants other than hydrogen sulphide mainly originate from sources other than the treated slurry, which limits the potential for further optimization of this technology. On-line PTR-MS application on full scale biological air filters demonstrated that carboxylic acids, aldehydes, ketones, phenols and indoles consistently have high removal efficiencies (80 - 99%). H_2S can be removed with moderate efficiency (ca. 30 - 75%) with higher removal only under special conditions, whereas low removal (0 - 20%) of methanethiol and dimethyl sulphide is generally observed. Removal of these compounds is assumed to be limited by mass transfer process due to the low partitioning to water. Experiments of air-biofilter liquid partitioning by PTR-MS indicated that the partition coefficients of sulfur compounds in the

biotrickling filter liquids were generally very close to the corresponding partition coefficients in deionized water, despite the ionic strength and presence of co-solutes in the biotrickling filter liquids. Based on breakthrough curves measured by PTR-MS and a dispersion-diffusion model, a method for mass transfer coefficient determination was established. The application of the method on Leca® material demonstrated the dependence of mass transfer coefficients on gas velocity, particle size, specific surface area and contaminant chemical properties (e.g., Henry's law constant). Further investigation on other packing materials demonstrated the dependence of mass transfer coefficients on gas and liquid velocities and specific surface area. Normalizing mass transfer coefficients to pressure drop indicated a potential of ceramic saddles due to higher mass transfer coefficients and a potential of cellulose pads due to low pressure drop, respectively, compared to other materials. The kinetic analysis of on-line PTR-MS data for removal of odorants in biological air filters indicated that the Stover-Kincannon model and the Grau second-order model, which were commonly used for simulation of wastewater biofiltration processes, could be applied for the analysis of the contaminants removal in the biotrickling filter. Whereas the Stover-Kincannon model demonstrated that pollutant removal rates were positively related to the mass loading rates, the Grau second-order kinetic model indicated that the removal efficiencies were negatively dependent on air loading rates. Thus the design of the biofilter should focus on increasing of the mass loading rates and decreasing the air loading rate at the same time. Field measurements by PTR-MS of two biological filters treating odorants indicated that a grinded Leca® filter performed better than an untreated Leca® filter and this may be due to the enlargement of the surface area of Leca® by the grinding process. The low ventilation rate and low temperature may benefit the removal of volatile sulfur compounds, which may be mass transfer limited in the biofilter. Furthermore, a small-scale test of the Leca® biofilter indicated that more than half of the H₂S reduction was due to the oxidation by iron oxides contained in Leca® pellets. Whereas another test with cellulose biofilter indicated that fungi takes up H₂S and oxidize it without being energetically favorable for the fungi. The average removal efficiency (RE) for H₂S was 17.6% without bloom and 64.3% when fungi were visually present in the same filter. Therefore the maintenance of the biofilter and the fungi is also important in order to get stable removal of H₂S. To summarize, removal of volatile sulfur compounds by biological air treatment is challenging due to the low water solubility of the compounds and the relatively high air loading in filters for livestock production facilities. The present work expands the knowledge on key limiting factors,

and points to application of fungi-loaded filters or metal-ion catalyzed degradation as potential future technologies that need to be further investigated.

Resumé

Udledning af lugt fra husdyrproduktion og gyllehåndtering udgør i stigende grad en gene for naboer i de nære omgivelser og er dermed blevet en begrænsning for udvidelser af husdyrproduktion. Lugt fra husdyrproduktion skyldes en række lugtstoffer, der potentielt kan bidrage til de erkendte gener. Rensning af ventilationsluft ved hjælp af forskellige typer biologiske filtre har vist sig at være en mulig omkostningseffektiv teknologi til reduktion af såvel lugtgener som ammoniak-emission fra husdyrproduktion. Tidligere undersøgelser har vist, at det er muligt at fjerne forholdsvis vandopløselige lugtstoffer (f. eks. carboxylsyrer og phenoler) med en acceptabel rensningsgrad. Derimod er flygtige svovlforbindelser vanskeligere at fjerne, hvilket fortrinsvis tilskrives den lavere vandopløselighed for disse stoffer. Blandt disse stoffer er hydrogen sulfid (H_2S) og methanethiol (CH_3SH) foreslået at være blandt de vigtigste lugtstoffer. Der er imidlertid kun begrænset viden om de processer og parameter, der har betydning for fjernelsen af disse stoffer i biologiske filtre, hvilket til dels skyldes begrænsninger i de anvendte målemetoder. PTR-MS (proton-transfer-reaction mass spectrometry) er en nyere online måleteknik, der er kendetegnet ved høj følsomhed, hvilket er relevant for at kunne måle de forholdsvis lave koncentrationer, der findes i ventilationsluft fra stalde. Samtidig har PTR-MS høj tidsopløsning, hvilket kan være vigtigt for at kunne undersøge dynamiske processer i biologiske filtre.

Formålene med dette PhD-projekt er: 1) at evaluere lugtreducerende teknologier ved hjælp af PTR-MS med fokus på biologisk luftrensning, men til sammenligning er ozonbehandling af gylle tillige undersøgt, 2) at evaluere og estimere nøgleparametre (relateret til masse-overførsel og vand/luftfordeling) for flygtige svovlforbindelser ved anvendelse af PTR-MS og 3) at afdække muligheder for optimering og yderligere udvikling af biologiske filtre ud fra de bestemte nøgleparametre. On-line PTR-MS viste i dette projekt, at en gyllebehandling, der indbefatter ozonbehandling, kunne give en lugtreduktion på ca. 49% (baseret på lugtaktivitetsværdier) og en H_2S -reduktion på 77%. Denne undersøgelse indikerede dog også, at lugtstoffer udover H_2S i højere grad end forventet blev emitteret fra andre kilder end den opsamlede gylle under gulvet, hvilket begrænser effekten af ozonbehandling af gyllen. Anvendelse af PTR-MS til undersøgelser af et fuld-skala biologisk luftfilter baseret på cellulose pads viste, at carboxylsyrer, aldehyder, ketoner, phenoler og indoler blev fjernet med høj effektivitet (80 - 99%). H_2S kan fjernes med moderat og varierende aktivitet (ca. 30 - 75%) med høje rensningsgrader under specielle betingelser, hvorimod methanethiol og

dimethylsulfid kun i meget begrænset omfang fjernes (0 - 20%). Fjernelse af sidstnævnte stoffer formodes at være begrænset af luft-vand masseoverførsel som følge af lav optagelse i vand.

Undersøgelser af stof-fordelingen mellem luft og væsker fra et biofilter viste, at fordelingskoefficienterne for biofiltervæsker generelt var sammenlignelige med de tilsvarende fordelingskoefficienter for rent vand. Det vurderes således, at ionstyrke og forekomsten af co-solutter er af begrænset betydning.

Baseret på gennembrudskurver målt med PTR-MS med lav tidsopløsning samt en dispersions-diffusionsmodel er der udviklet en metode til bestemmelse af masse-overførselskoefficienter. Anvendelse af metoden på LECA[®]-materiale viste, at masse-overførslen afhænger af lufthastighed, partikel-størrelse, specifikt overfladeareal og det specifikke stofs vand-luft fordeling (Henry's konstant). Yderligere undersøgelser af andre filtermaterialer bekræftede, at masseoverførslen afhænger af lufthastighed og specifikt overfladeareal. Endvidere synes hastigheden for væsketil sætning at have en betydning. Ved at normalisere masse-overførsel ud fra filtermaterialets tryktab (lavere tryktab kan give mulighed for større filtervolumen) blev to materialer med lovende egenskaber udpeget ud fra undersøgelser af ialt 11 materialer: 1) keramiske "Saddles" på grund af høj masseoverførsels-hastighed og 2) cellulose-pads på grund af exceptionelt lavt tryktab.

Undersøgelser af kinetikken for fjernelse af lugtstoffer i biologiske filtre viste, at to modeller overvejende gav gode overensstemmelser med data: Stover-Kincannon-modellen og Grau's andenordens model. Disse har hidtil været anvendt til simulering af biologisk rensning af spildevands, men er her vist at kunne anvendes til biologisk luftrensning. Stover-Kincannon-modellen indikerede at fjernelsen er relateret til den masse-specifikke belastning, mens Grau-modellen indikerede, at fjernelsen var negativt relateret til den luft-belastningen. Øget filter-effektivitet synes derfor at kunne opnås ved både at øge masse-belastningen og ved at reducere lufthastigheden.

Feltmålinger med PTR-MS på to beslægtede biologiske filtre til rensning af luft fra en svinestald viste, at et filter bestående af LECA med groft slebet overflade generelt havde højere effektivitet end et filter med ubehandlet LECA, hvilket kan tilskrives større specifik overflade. Endvidere er det vist at lav ventilationshastighed og lav temperature øgede fjernelsen af lugtstoffer. En supplerende test af filtermaterialerne i mindre skala viste, at mere end halvdelen af reduktionen af H₂S kunne tilskrives kemisk oxidation, formentlig som følge af tilstedeværelsen af jern-oxider på overfladen af LECA. En anden opfølgende undersøgelse af cellulose-biofiltret viste, at svampe kan optage H₂S og oxidere dette på trods af, at dette ikke er energetisk favorabelt for svampene.

Rensningseffektiviteten for H₂S var i gennemsnit 17.6% med lav svampevækst og 64.3% med synlig svampevækst på filtret.

Sammenfattende kan det siges, at fjernelse af flygtige svovl-forbindelser ved biologisk rensning af luft er en udfordring på grund af den begrænsede optagelse i vand og den høje luft-belastning af filtre til husdyrproduktion. Dette PhD-projekt udvider kendskabet til de vigtigste faktorer, der begrænser effektiviteten af sådanne filtre og peger på anvendelse af svampe-begroede filtre eller jern-katalyseret nedbrydning som to mulige udviklingsområder.

List of abbreviations

ADO	Average-Dipole-Orientation
AOPs	Advanced oxidation processes
E/N	Electric field / number density of gas molecules
GC-MS	Gas chromatograph and mass spectrometry
H ₃ O ⁺	Protonated water molecule
m/z	mass per charge ratio
OAV	Odor activity value
OTV	Odor threshold value
ppbv	Part per billion by volume
PTR-MS	Proton-Transfer-Reaction mass spectrometry
PTR-TOF-MS	Proton-Transfer-Reaction Time-of-Flight mass spectrometry
sccm	Standard Cubic Centimeters per Minute
VOCH ⁺	Protonated volatile organic compound molecule
VOCs	Volatile organic compounds
VSCs	Volatile sulfur compounds

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Appendix I: Paper I-X (full text)

Appendix II: List of other publications/paper drafts

1 Introduction

The global production of pigs has increased by 50 percent in the last 15 years (Best, 2010). The pig production in Europe and the USA is characterized by intensive and large-scale farms, where the production is associated with a number of environmental pollutants, e.g., ammonia, odour and VOCs, particulate matter and greenhouse gases (CO₂, CH₄ and N₂O). Odour emissions from intensive animal facilities and related activities have particularly become a severe nuisance to people living in the vicinity (Wing et al., 2008; Godbout et al., 2008; Nimmermark, 2011). Besides the nuisance, the odour emissions may have negative effects on human health. A study by Schiffman et al. (1995) showed that people living near intensive large-scale pig facilities were affected by odours and experienced significantly more depressions, more anger, more confusion, more tension and more fatigue compared to the control subjects. In another study by Wing and Wolf (2000), people who lived near to the intensive livestock production suffered more from sore throats, headaches, runny noses, diarrhoea, coughing and burning eyes compared to residents living outside livestock operation areas. Even a short-term exposure of low concentrations (ppbv level) of odour and ammonia may cause headaches, eye irritation and nausea (Schiffman et al., 2005). Further, hydrogen sulphide and a number of gases related to animal production are recognised as hazardous substances, despite their low concentrations (Nimmermark, 2004).

Therefore, odour emissions need to be reduced in order to reduce the nuisance and potential negative effects on human health. In addition to feed management and optimisation of house and ventilation system, techniques could be applied to manure slurry or to the vented air (end-of-pipe techniques) in order to reduce emissions. Techniques that have been implemented for manure slurry in Denmark mainly include drainage of slurry pits (Jonassen and Lyngbye, 2010; approximately 45% reduction in H₂S), slurry ozonation Lyngbye et al., 2008b; approximately 52% odour reduction measured by olfactometry and approximately 82% reduction in H₂S) and combination of slurry separation, ozonation and acidification (Jonassen et al., 2010; approximately 40% odour reduction, point measurements by olfactometry). Slurry ozonation seems to be a slightly better method (from the point of view of reduction of H₂S and odour), but further

developments and optimisations are needed – for example, dosage of ozonation and reduction of costs (Bildsoe et al., 2012). It should be noted that slurry treatment for emission reduction in some cases could be combined with energy production (e.g., biogas production by using anaerobic digestion; Masse et al., 2011) or as a fertilizer by soil injection (Feilberg et al., 2011).

As an alternative to slurry treatment, the ventilation air containing odours from the pig production facility could be treated before being emitted. Generally, many techniques can be employed for odour and VOC reduction. Adsorption, absorption, biological treatment (biofilter/biotrickling filter, bioscrubber and other bioreactors), oxidation (advanced oxidation processes (AOPs), thermal and catalytic oxidation, incineration, etc.), condensation, membrane systems are commonly used odour and VOC reduction techniques (Smet et al., 1998; Devigny et al., 1999; Delhomenie and Heitz, 2005; Kennes and Veiga, 2010). However, the suitability of technologies generally depends on the nature of the pollutants, concentration of the pollutants and flow rate. For example, Fig.1 shows that the biological process is more relevant when pollutant concentration is low and gas flow rate is relatively high. This process is specifically suitable for the treatment of ventilation air from pig facilities due to the high ventilation rate used and low concentrations of chemical compounds (Feilberg et al., 2010a). On the other hand, incineration or condensation is usually only be economical when pollutant concentrations are high. Recent research indicates that bioreactors could also be applied for treating high-concentration pollutants at low gas flow rates (Fig.2; Kennes et al., 2009; Kennes and Veiga, 2010), although the biofilter may be clogged if exposed to excessively large concentrations (Dorado et al., 2012).

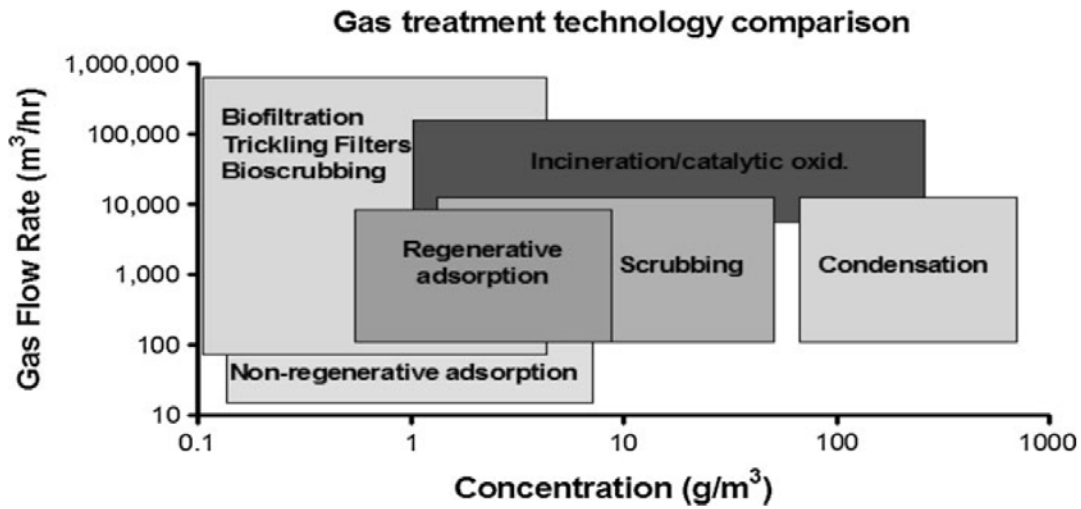


Fig.1 Applicability of various air pollution control technologies based on air flow rate and concentrations to be treated (Detchanamurthy and Gostomski, 2012).

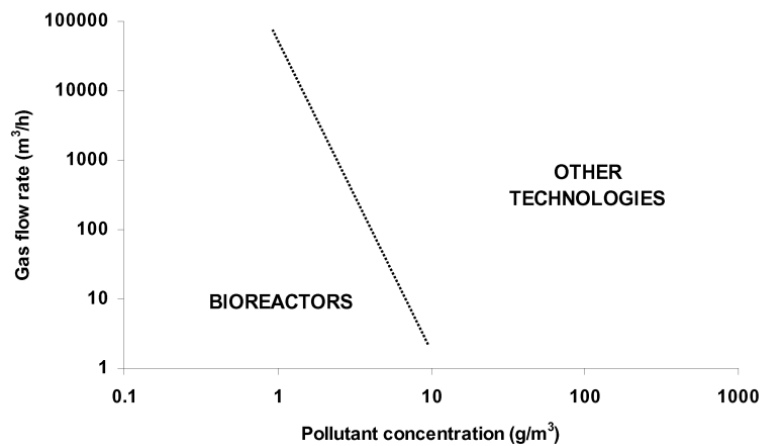


Fig.2 Comparison of the application range of the bioprocess and non-biological treatment technologies in terms of gas flow rates and pollutant concentrations (Kennes et al., 2009).

Overall, treatment of ventilation air by various types of bioreactors has emerged as one of the very few competitive technologies for reduction of both odour nuisance and ammonia emissions from animal production facilities (O'Neill et al., 1992; Nicolai and Janni, 2001; Melse and Ogink, 2005; Jensen and Hansen, 2006; Riis and Lyngbye, 2008; Chen et al., 2008; Feilberg et al., 2010a). Other technologies employed for removing odours from pig production include membrane scrubber technology (Lyngbye et al., 2008a) and AOPs (Andersen et al., 2010; Yao et al., 2012). However, these systems have only been tested

on a small scale and need further investigation and optimisation in order to reduce costs and/or improve performance before they can be up-scaled to commercial applications. Therefore the biological air treatment seems to be the most cost-effective technology for odour reduction so far.

The major odorants in the ventilation air from pig facilities include ammonia, H₂S and volatile organic compounds (VOCs; Ni et al., 2012). Table 1 shows the most abundant compounds detected in the ventilation air or air samples inside the pig house together with typical mean concentrations or concentration ranges, odour threshold values (OTV) and odour activity values (OAV). OTV refers to the smallest concentration of an odorant that can be detected by an average human nose. There are two types of odour threshold values – the detection threshold and the recognition threshold (van Gemert, 2003). The detection threshold is the minimum concentration that can be detected without any requirements for identification or recognition of the odorant. The recognition threshold is the minimum concentration at which an odorant can be identified or recognized. Thus the recognition threshold is always higher than the detection threshold. In table 1, OTVs are estimated by geometric means of detection threshold from van Gemert (2003) or Devos (1990). The OAV for each compound are calculated based on typical concentrations based on various sources divided by the OTV of the compound. In the case of the typical concentration range given in the literature, the arithmetic mean was applied to the range before taking the geometric mean with concentrations taken from other literature. For the data from the study by Mårtensson et al. (1999), only the group of data from the insulated pig house was included in Table 1 (thus the data from the pig house without insulation was excluded). As can be seen from Table 1, the compounds with the highest OAVs are H₂S, methanethiol, butanoic acid and 4-methylphenol. It should be noted that two of the four odorants above are sulphur-bearing compounds.

It should also be noted that methanethiol was typically detected in manure or near the manure surface (Banwart and Bremner, 1975; Schaefer, 1977; Willig et al. 2004; Eriksen et al., 2010), but was only detected quantitatively in ventilation air in a few reports (e.g., Willig et al., 2004; Kim et al., 2007) before the application of PTR-MS (Feilberg et al., 2010b). This may be due to the difficulties of sampling and measuring low concentrations with other instruments than PTR-MS.

Table 1 Most abundant odorants found in ventilation air or air samples from pig facilities.

	MW (g/mol)	Typical concentration (ppbv)	OTV ^a (ppbv)	OAV ^b
ammonia	17	720~67640 ⁸	3548 ²	1.97
methanol	32	ND~42.92 ⁹	63780 ²	0.00
H ₂ S	34	265 ¹ ,353 ⁶	2.3 ²	133
acetaldehyde	44	6.8 ⁶ , 4.1 ⁷ , ND~40.12 ⁹	164 ²	0.05
ethanol	46	0.73~155.41 ⁹	84526 ²	0.00
methanoic acid	46	3.2 ¹⁰	13647 ²	0.00
methanethiol	48	4 ¹ , 12 ⁶	0.07 ²	99
acetone	58	5.1 ¹ , 7.1 ⁶ , ND~27.4 ⁹	13000 ³	0.00
trimethylamine	59	9.4 ¹ , 12 ⁶	2.1 ²	5.06
acetic acid	60	209.5 ¹ , 314 ⁶ , 30 ⁷ , 791 ¹⁰	236 ²	0.84
dimethyl sulphide	62	4.9 ¹ , 3.0 ⁶ , ND~14.41 ⁹	5.9 ²	0.80
2-butanone	72	2.2 ¹ , 3.3 ⁶	4500 ³	0.00
propanoic acid	74	66.0 ¹ , 67 ⁶ , 13 ⁷ , 7~96 ⁸ , 304 ¹⁰	25 ²	2.47
2,3-butanedione	86	1.3 ¹ , 1.2 ⁶	0.6 ²	2.08
butanoic acid	88	55.6 ¹ , 22 ⁴ , 42 ⁶ , 61.2 ⁷ , 5~172 ⁸ , 211 ¹⁰	1.9 ²	33
3-hydroxy-2-butanone	88	1.0 ⁷	4448 ⁵	0.00
lactic acid	90	9.2 ¹⁰	2447 ²	0.00
phenol	94	0.5 ¹ , 1.0 ⁶ , 2.0 ⁷ , 0.5~11.2 ⁸	54.6 ²	0.03
dimethyl disulphide	94	0.2 ¹ , 1.0 ⁶ , 0.91 ⁷ , ND~2.05 ⁹	7.4 ²	0.09
Pentanoic acid	102	6.3 ¹ , 6.6 ⁶ , 1.44 ⁷ , 1.44~15.1 ⁸	1.4 ²	3.37
3-methylbutanoic acid	102	3.2 ¹ , 4.4 ⁶	1.4 ²	2.68
4-methylphenol	108	3.9 ¹ , 9.5 ⁶ , 0.45~17 ⁸ , 0~43.41 ⁹	0.3 ²	31
Hexanoic acid	116	0.84 ⁷ , 0~2.1 ⁸	19.7 ²	0.05
4-methylpentanoic acid	116	0.06 ⁷	7.8 ²	0.01
indole	117	0.12 ¹ , 0.7 ⁶ , 0.1 ⁷ , 0.02~0.42 ⁸	0.4 ²	0.52
4-ethylphenol	122	0.34 ¹ , 1.2 ⁶	1.3 ²	0.49
dimethyl trisulphide	126	ND ¹ , 0.1 ⁶	0.4 ²	0.25
Heptanoic acid	130	0~0.56 ⁸	11.3 ²	0.02
3-methyl-1H-indole	131	0.38 ¹ , 0.4 ⁶ , 0.02~0.37 ⁸	0.09 ²	3
Octanoic acid	144	0~0.85 ⁸	5.3 ²	0.08
Nonanoic acid	158	0~0.62 ⁸	7.6 ²	0.04

a – Odour threshold value (OTV); b – Odour activity value (OAV); 1 – Feilberg et al., 2010b; 2 – van Gemert, 2003; 3 - Devos, 1990; 4 – Hammond et al., 1981; 5 – Backman, 1917 (odour recognition threshold value); 6 – Hansen et al., 2012; 7 - Schiffman et al., 2001; 8 - Hartung, 1988; 9 - Blunden et al., 2005; 10 - Mårtensson et al., 1999.

Previous studies show only poor to average (35-60%) odour reductions (measured by olfactometry) with biofiltration (Melse and Mol, 2004; Riis and Lyngbye, 2008; Feilberg

et al., 2010a). Chemical measurements have demonstrated that water-soluble odour compounds are removed effectively (>90%), whereas poorly soluble sulphur compounds (methanethiol and dimethyl sulphide) are hardly removed (Feilberg et al., 2006; Feilberg et al., 2010a). Due to difficulties in measuring low concentrations of these compounds, only limited information is available about the processes and parameters that control the removal of these compounds.

The commonly used method for odour measurement in Denmark and most other countries is dynamic olfactometry, where an odour sample is diluted with non-odorous air to the odour threshold value. The limitations of this method are the low recovery of odorants in sampling bags (Koziel et al., 2005; Trabue et al., 2006; Mochalski et al., 2009; Hansen et al., 2011) and wide variation due to the use of human panelists (Clanton et al., 1999; Riis, 2012a & 2012b). Chemical measurement of odorant could give a more precise and repeatable estimation, but requires detailed information on odour threshold value in order to substitute olfactometry. Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) has emerged as a fast and reliable on-line measurement instrument for volatile organic compound (VOC) measurements at low concentrations (Lindinger et al., 1998; Hewitt et al., 2003; Shaw et al., 2007; de Gouw and Warneke, 2007; Ngwabie et al., 2008). Just before the start and during the very beginning of this PhD study, identification and quantification of the odorant emissions from intensive pig production facility were performed by on-line PTR-MS (Feilberg et al., 2010b). More recently, a chemometric odour prediction model based on PTR-MS data has been presented by Hansen et al. (2012). It would therefore be very relevant to apply this new instrument for evaluating the odour reduction technologies (especially of sulphur compounds) and for studying the key processes involved in biofiltration in order to optimize odour removal by this technology. Application of PTR-MS will also enable sensitive and selective time-resolved measurements in order to quantitatively determine the essential limiting parameters for removal of VSCs, which have previously only been estimated theoretically.

2 Objective of this study

PTR-MS is introduced as a unique instrument for the direct and rapid measurement of volatile sulphur compounds with superior sensitivity and time resolution. Previous studies have indicated that the reduction of volatile sulphur compounds in biofilters is mainly limited by mass transfer, and improved sulphur removal can only be achieved by combining experimental parameterisation of mass transfer and related processes with comprehensive modeling (Nielsen et al., 2009). Therefore the objectives of this study were:

- (i) to evaluate the odour reduction techniques by on-line measurements with PTR-MS; The emphasis is on biological air treatment, but a full-scale slurry ozonation is included for comparison.
- (ii) to evaluate and estimate key parameters (e.g., partition coefficient and mass transfer coefficient) limiting the removal of volatile sulphur compounds in biofilters by applying PTR-MS;
- (iii) to evaluate further optimisation and development of biofilters according to estimated key parameters.

The PhD thesis will focus on answering the following questions:

- Can PTR-MS give reliable on-line measurements for evaluating the reduction of odorous compounds by odour reduction techniques?
- Can air-biofilter liquid partitioning be determined by PTR-MS and how will that deviate from partitioning between air and pure water? How is the obtained information used in relation to biofilter modelling?
- Can mass transfer coefficients of VSCs for packing materials used in biofilters be determined by PTR-MS and how is the obtained information regarding biofilter design and improvement of VSCs removal used?
- Can the online PTR-MS data be used for analysis of the kinetics of the removal of odorants, and how is the obtained information used for further development of biofiltration for odorant removal?

3 Content of thesis

This thesis is composed of two parts. The first part is an overview of the existing knowledge of PTR-MS and biofiltration processes (sections 4 and 5). The second part includes the scientific work related to the objective of this study, both general discussions (related to the questions posed above; Section 6) and the appendix, where all papers are presented.

Papers included in this thesis are listed below (full papers can be found in the Appendix). The relationships between the papers included and the scientific themes are outlined in Fig. 3.

- Paper I: **Liu, D.**, Feilberg, A., Adamsen, A.P.S., Jonassen, K.E.N. The effect of slurry treatment including ozonation on odorant reduction measured by in-situ PTR-MS. *Atmospheric Environment*. 2011, 45(23), p. 3786-3793.
- Paper II: Hansen, M.J., **Liu, D.**, Guldborg, L.B., Feilberg, A. Application of Proton-Transfer-Reaction Mass Spectrometry to the Assessment of Odorant Removal in a Biological Air Cleaner for Pig Production. *Journal of Agricultural and Food Chemistry*. 2012, 60(10), p. 2599-2606.
- Paper III: **Liu, D.**, Feilberg, A., Nielsen, A.M., Adamsen, A.P.S. PTR-MS measurement of partition coefficients of reduced volatile sulfur compounds in liquids from biotrickling filters. *Chemosphere*. 2012. Article in Press.
- Paper IV: **Liu, D.**, Andreasen, R.R., Poulsen, T.G., Feilberg, A. Experimental determination of mass transfer coefficients in biofilter media measured by Proton-Transfer-Reaction Mass Spectrometry. 2012. Submitted to *Chemical Engineering Journal*.
- Paper V: Andreasen, R.R., **Liu, D.**, Ravn, S., Feilberg, A., Poulsen, T.G. Air-water mass transfer of sparingly soluble odorous compounds in granular biofilter media. 2012. Submitted to *Chemical Engineering Journal*.

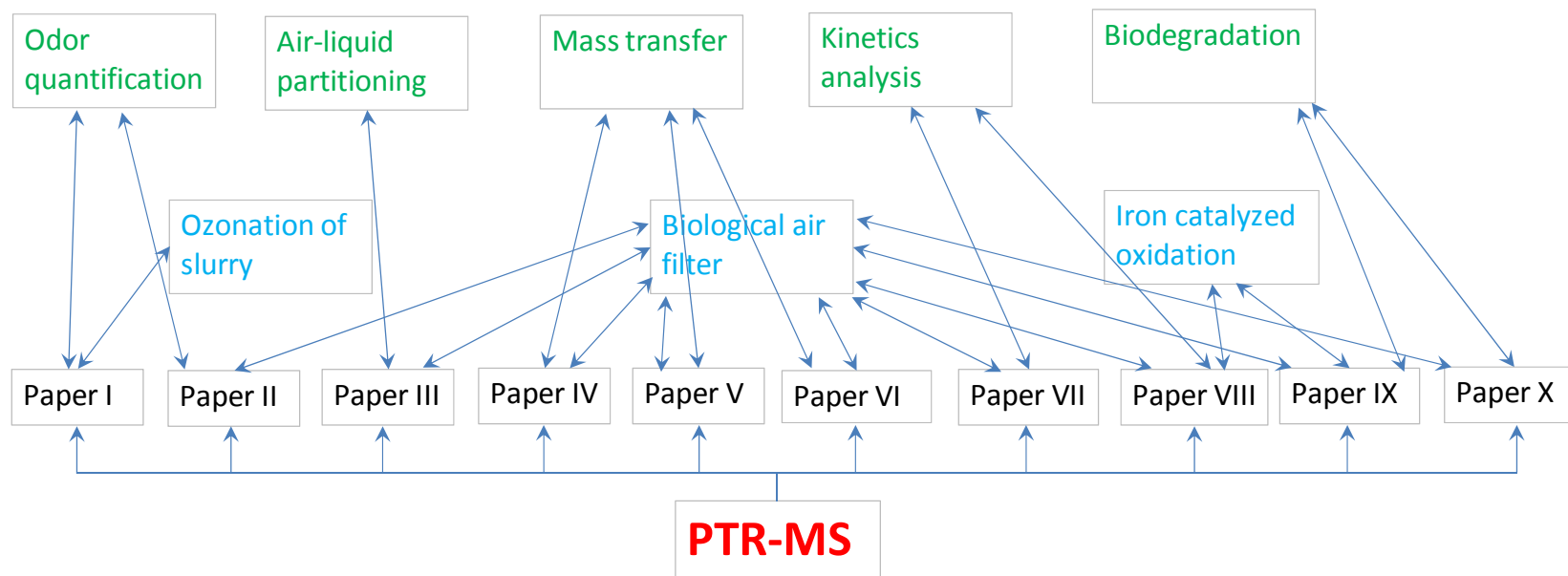


Fig.3 Structure profile of this thesis.

- Paper VI: *Liu, D.*, Adamsen, A.P.S., Andreasen, R.R., Poulsen, T.G., Feilberg, A. A comparative study of mass transfer coefficients of reduced volatile sulfur compounds regarding packing materials for biofiltration. 2012. Paper draft.
- Paper VII: *Liu, D.*, Hansen, M.J., Guldberg, L.B., Feilberg, A. Kinetic evaluation of removal of odor contaminants in a three-stage biological air filter. *Environmental Science and Technology*, 2012, 46(15), 8261-8269.
- Paper VIII: *Liu, D.*, Feilberg, A., Løkke, M.M., Riis, A.L. Performance evaluation of two air biofilters in treating odor pollutants from intensive pig production. 2012. Paper draft.
- Paper IX: Pedersen, C.L., *Liu, D.*, Feilberg, A., Nielsen, L.P. Hydrogen sulfide oxidation rates in active and pasteurized filter material from a trickling biofilter. 2012. Paper draft.
- Paper X: Pedersen, C.L., *Liu, D.*, Feilberg, A., Nielsen, L.P. Presence of fungi in a biofilter treating waste air from a pig farm. 2012. Paper draft.

4 Proton-Transfer-Reaction Mass Spectrometry

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) was first developed by professor Werner Lindinger and co-workers in the late 1990s (Lindinger et al., 1998) and its use has grown tremendously and in a wide variety of applications since then. PTR-MS has a proven robustness and it is currently the only instrument which can provide time-resolved (< 1 s) selective measurements of individual VOCs at very low levels (down to pptv).

4.1 Description of method

A PTR-MS instrument (Ionicon Analytik, Innsbruck, Austria) typically consists of four key components which are 1) discharge ion source, 2) drift tube reaction chamber, 3) quadrupole mass analyser and 4) ion detection unit (Fig.4). PTR-MS utilises proton transfer reactions (in drift tube reaction chamber) from hydronium ions (H_3O^+ ; produced in discharge ion source) to VOCs in the air sample in the drift tube and this produces protonated VOCs, which then are separated in a quadrupole mass filter according to the mass/charge ratio and finally detected by an ion detection unit. PTR-MS utilises low-

energy chemical ionization technique (ion-molecule reactions) instead of electron impact ionization (as used in GC-MS) and thus causes much less fragmentation combined with higher sensitivity and good precision under a short integration time (Lindinger et al., 1998; Hewitt et al., 2003). However, the identification and validation of the measured ions need to be combined with other instruments (for example, GC-MS) or to use PTR-TOF-MS (Warneke et al., 2003; Pozo-Bayon et al., 2008; Cappellin et al., 2010a; Cappellin et al., 2012).

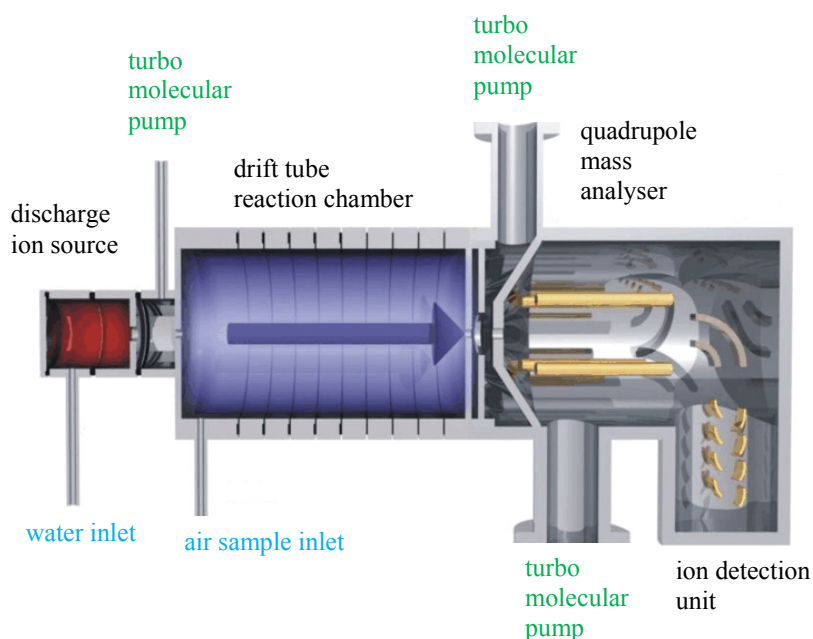


Fig.4 Schematic of main parts of PTR-MS (University of Innsbruck; Ionicon Analytik).

The discharge ion source produces a high concentration of H_3O^+ from very pure water vapour via a hollow cathode. While the ions produced from the hollow cathode are transported through the short intermediate tube (between discharge ion source and drift tube), they are further converted to H_3O^+ . These H_3O^+ ions are conveyed into the drift tube (reaction chamber) via a venturi inlet system. Under normal operation conditions, more than 10^7 H_3O^+ ions per second are detected in PTR-MS. The efficiency of producing H_3O^+ by pure water vapour can reach 99%, the main impurities of O_2^+ and NO^+ being produced by back-diffusion of air from the drift tube reaction chamber. In this

study, standard ion drift tube conditions for the PTR-MS were mostly used, which means drift tube voltage was set to 600 V, drift tube pressure was maintained in the range of 2.15~2.2 mbar, the temperature was set to 60 °C. The E/N value (where E is the electric field on the drift tube and N is the density of the drift tube buffer gas molecules, i.e. air molecules) was thus maintained at 135 Td (1 Td = 1 Townsend = 10^{-17} cm² V).

4.2 Drift tube ion chemistry, water cluster, fragmentations and humidity dependence

Table 2 Proton affinities for selected volatile emissions from pig production facilities.

Substance	Formula	Mass	Proton affinity (kcal mol ⁻¹)
oxygen	O2	32	100.6
nitrogen	N2	28	118
water	H2O	18	165.2
hydrogen sulphide	H ₂ S	34	170.2
acetaldehyde	C ₂ H ₄ O	44	183.8
acetic acid	C ₂ H ₄ O ₂	60	186.9
methanethiol	CH ₄ S	48	187.4
propanoic acid	C ₃ H ₆ O ₂	74	190.6
2,3-butanedione	C ₄ H ₆ O ₂	86	192.1
acetone	C ₃ H ₆ O ₂	58	194.1
H₃O⁺(H₂O)	H₃O⁺(H₂O)	37	194.4
4-methylphenol	C ₇ H ₈ O	108	194.5
phenol	C ₆ H ₆ O	94	195
dimethyl disulphide	C ₂ H ₆ S ₂	94	195
2-butanone	C ₄ H ₈ O	72	197.8
butanoic acid	C ₄ H ₈ O ₂	88	198.5
Pentanoic acid	C ₅ H ₁₀ O ₂	102	200
3-methylbutanoic acid	C ₅ H ₁₀ O ₂	102	200
dimethyl sulphide	C ₂ H ₆ S	62	200.5
ammonia	NH ₃	17	204.1
indole	C ₈ H ₇ N	117	223.2
trimethylamine	C ₃ H ₉ N	59	225.1

In the PTR-MS drift tube, collisions of gaseous pollutants (VOCs) with H₃O⁺ ions can result in proton-transfer reactions and VOCs can be ionized if the proton affinities of the VOCs are higher than that of water (165.2 kcal mol⁻¹; see Table 2):



The major components in the air samples (nitrogen and oxygen) undergo non-reactive collisions with H₃O⁺ ions due to their typically lower proton affinities nitrogen: 118.0

kcal mol⁻¹; oxygen: 100.6 kcal mol⁻¹) than that of water. Thus, these components act as buffer gases and are subsequently removed by the turbo molecular pump.

In addition to reaction in eq. (1), H₃O⁺ ions and RH⁺ ions can cluster with H₂O molecules in the air sample (de Gouw and Warneke, 2007).

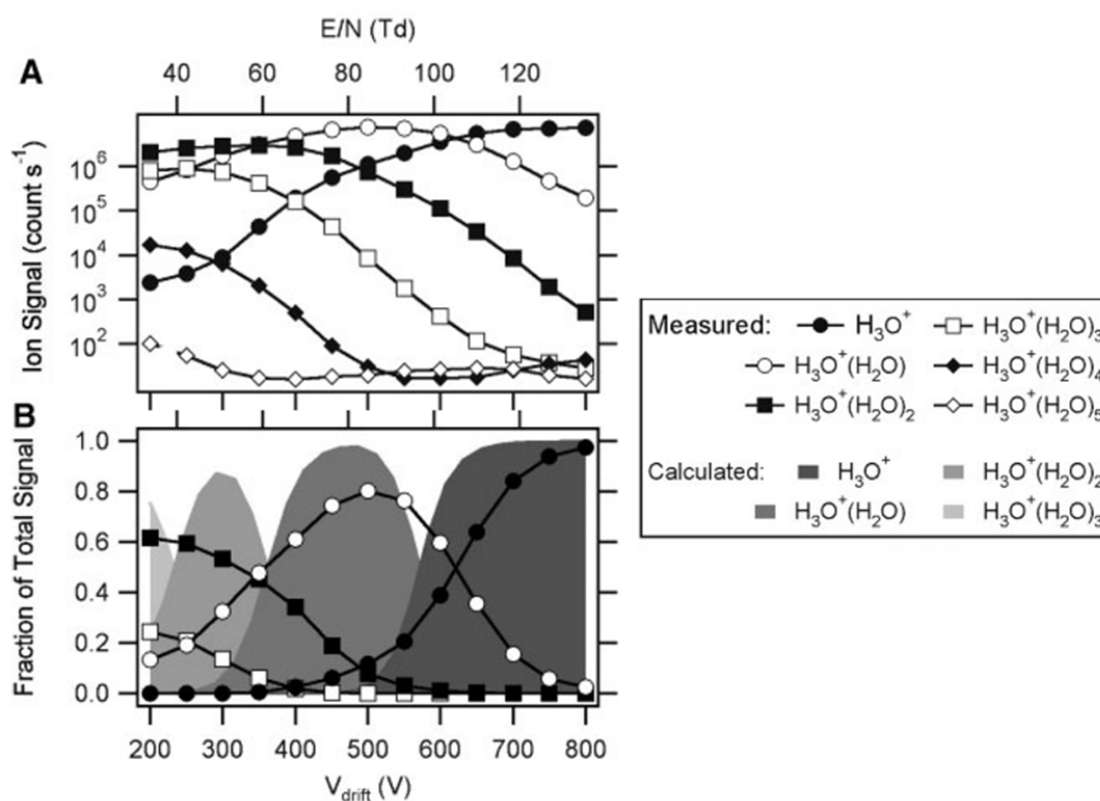
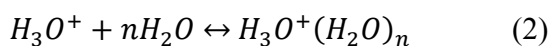


Fig.5 Example of reagent ion distribution as a function of drift tube E/N and drift voltage (de Gouw and Warneke, 2007).

The presence of water clusters complicates the interpretation of the mass spectra and therefore is not desirable when operating the PTR-MS. Depending on the electric field and pressure in the drift tube, H₃O⁺(H₂O) cluster ions can still react with VOCs if the proton affinities of VOCs are higher than that of H₃O⁺(H₂O) cluster ions (approx. 194.4 kcal mol⁻¹):





Thus, depending on the proton affinity of the target compound (higher or lower than that of $H_3O^+(H_2O)$ ion), the sensitivity of the measurement will depend on the humidity of the air sample (Blake et al., 2009). Further, the distribution of cluster ions in the drift tube has been proven to be closely related to the E/N value, which is positively related to ion kinetic energy, as shown by an example in Fig.5. Suppression of water clusters is therefore desirable by either increasing the electric field (E) or decreasing the drift tube pressure (N). However, the product ion fragmentations are commonly increased due to the higher ion kinetic energy in the drift tube (Fig. 6; Brown et al., 2010).

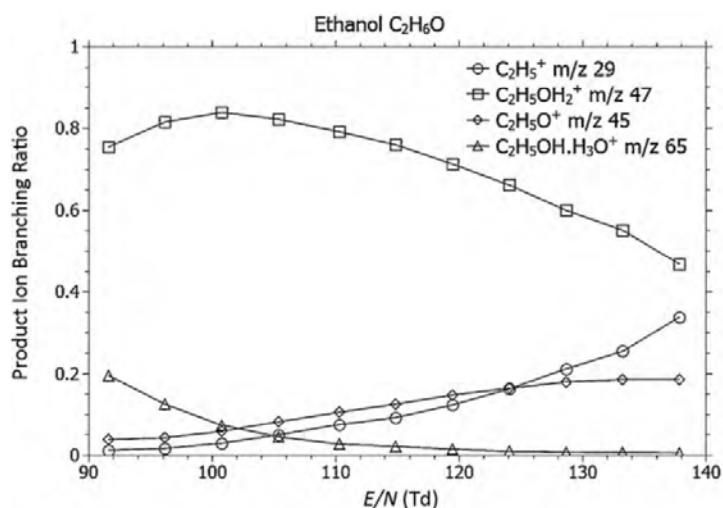


Fig.6 Product ion distribution as a function of E/N for ethanol (Brown et al., 2010).

Fragmentation is preferably avoided within the PTR-MS operating conditions in order not to complicate the analysis. However, it may help to identify and separate compounds. The fragmentation pattern is very dependent on compound type. For example, alcohols generally have a high degree of fragmentation, whereas aldehydes fragment less (for short chains) and sulphides and ketones hardly showed any fragmentations (Buhr et al., 2002). Carboxylic acids typically fragment and lose one water molecule under PTR-MS operation conditions, depending on both humidity levels and E/N value (Lindinger et al., 1998; Feilberg et al., 2010b). In general, for the same type of compounds fragmentation increases with the increase of carbon chain length (Buhr et al., 2002).

Table 3 gives the intensities of major ions measured by PTR-MS under similar E/N conditions for selected odorants identified in ventilation air from pig facilities. Most of the odorants have low fragmentation which can benefit the on-line application of PTR-MS for process monitoring and control of air pollutants emitted from pig house.

Table 3 Intensities of major ions measured by PTR-MS for selected odorants detected in pig facilities.

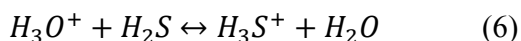
	MW (g/mol)	Type	Relative fragmentation intensity of major ions
ammonia	17	amines	18(100) ¹
methanol	32	alcohols	33(100) ^{1,3,4,5} , 34(1.1) ⁷
H ₂ S	34	sulfur	35(100) ^{1,2,6}
acetaldehyde	44	aldehydes	45(100) ^{1,3} , 46(3.1) ⁷
ethanol	46	alcohols	47(100) ^{1,3} , 45(37) ⁴ , 65(6) ⁴ , 45(40) ⁵ , 29(93) ⁵ , 48(2.7) ⁷
methanoic acid	46	acids	47(100) ¹
methanethiol	48	thiols	49(100) ^{2,3}
acetone	58	ketones	59(100) ^{1,2,8} , 60(3.4) ⁷ , 46(1.3) ⁷
trimethylamine	59	amines	60(100) ²
acetic acid	60	acids	61+43 ^{1,2}
dimethyl sulphide	62	sulfides	63(100) ^{1,2,3}
2-butanone	72	ketones	73(100) ² , 74(5) ⁴
propanoic acid	74	acids	75+57 ²
2,3-butanedione	86	diketones	87(100) ² , 59(35) ⁶ , 43 (7) ⁶
butanoic acid	88	acids	89+71 ²
3-hydroxy-2-butanone	88	ketones	
lactic acid	90	acids	
phenol	94	phenolics	95(100) ¹
dimethyl disulphide	94	sulfides	95(100) ³ , 79(14) ³
Pentanoic acid	102	acids	103+85 ²
3-methylbutanoic acid	102	acids	103+85 ²
4-methylphenol	108	phenolics	109(100) ²
Hexanoic acid	116	acids	
4-methylpentanoic acid	116	acids	
indole	117	nitrogen heterocycles	118(100) ²
4-ethylphenol	122	phenolics	123(100) ²
dimethyl trisulphide	126	sulfides	127(100) ²
Heptanoic acid	130	acids	
3-methyl-1H-indole	131	nitrogen heterocycle	132(100) ²
Octanoic acid	144	acids	
Nonanoic acid	158	acids	

1 - Lindinger et al., 1998; 2 - Feilberg et al., 2010b (E/N value = roughly 135 Td); 3 - Aprea et al., 2007 (E/N value = 120 Td); 4 - Buhr et al., 2002 (drift voltage = 600 V); 5 - Brown et al., 2010 (E/N value = 138 Td); 6 - Beauchamp et al., 2010 (E/N value = 122 Td); 7 - Schwarz et al., 2009 (E/N value = ca. 126 Td); 8 – Kilpinen et al., 2012 (E/N value = ca. 135 Td).

It should be noted that a few odorants emitted from pig house have lower proton affinities (e.g., 186.9 and 187.4 kcal mol⁻¹ for acetic acid and methanethiol, respectively) than that of H₃O⁺(H₂O) ion (194.4 kcal mol⁻¹) and thus the sensitivity and fragmentation may be dependent on E/N value which influences the ratio between the H₃O⁺ ion and the H₃O⁺(H₂O) ion. Although little dependence on E/N value was observed in our lab for methanethiol measurement, it is preferable that the E/N value should be kept relatively a high number in order to keep the high percentage of the H₃O⁺ ion.

In any case, the dependency of sensitivity on E/N value should always be examined and for certain compounds needs to be taken into account. Besides the E/N value dependence, the fragmentation pattern and measurement of acetic acid (and other carboxylic acids, although to a minor extent) is dependent on the humidity of the sampled air (Feilberg et al., 2010b). This is obviously important in practice since the humidity of the sample air could be changed dramatically during the measurements. For acetic acid, it has been demonstrated that even though fragmentation was humidity-dependent (Feilberg et al., 210b), the sum of parent ion (m/z 61) and fragment ion (m/z 43) was relatively constant over a range of humidities. Therefore, in cases where m/z 43 and m/z 61 can unambiguously be ascribed to acetic acid, the sum of the two masses can be used to quantify acetic acid with no or very little influence of humidity. In cases where only m/z 61 can be used (if m/z 43 is influenced by, for example, alcohols), a humidity-dependent calibration should be used.

The measurement of H₂S by PTR-MS, on the other hand, is a different situation from that of acetic acid. Since the proton affinity of H₂S (170.2 kcal mol⁻¹) is only slightly higher than that of water (165.2 kcal mol⁻¹), a back-reaction of protonated H₂S is relevant:



Although the reaction rate constant of H₂S protonation by H₃O⁺ (forward reaction) is significantly higher than the rate constant of the back reaction of (6), the presence of water in the reaction chamber (mainly from the sample air) enhances the back reaction. This results in a significant loss of sensitivity of H₂S and a dependency on sampling humidity (Feilberg et al., 2010b; Fig. 7). Furthermore, The E/N value also has influence on the sensitivity of the H₂S measurement. For example, the lower E/N value gives rise

to a higher percentage of $H_3O^+(H_2O)$ ions and lower intensity of H_3O^+ ions (Fig. 5). Thus the sensitivity of the H_2S measurement decreases since the proton affinity of $H_3O^+(H_2O)$ is much higher than that of H_2S and there is no proton transfer reaction between $H_3O^+(H_2O)$ and H_2S . Therefore, a humidity-dependent calibration for the H_2S measurement always needs to be carried out at instrument settings identical to those being used in the measurements. It has previously also been demonstrated for other compounds with relatively low proton affinities (e.g., hydrogen cyanide and formaldehyde, both with proton affinity of $170.4 \text{ kcal mol}^{-1}$) that PTR-MS calibration could be obtained by taking into account the back reaction of eq. (6) (Inomata et al., 2008; Knighton et al., 2009).

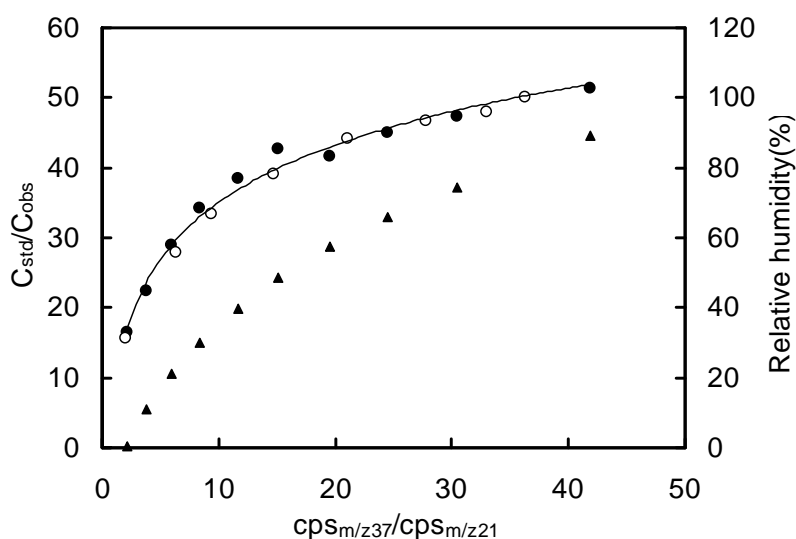


Fig. 7 Relative response of PTR-MS to hydrogen sulphide as a function of humidity at two different concentrations (\bullet : 830 ppb; \circ : 280 ppb). Relative humidity (\blacktriangle) is also included. Vertical axis represents the ratio between C_{std} (known standard concentration) and C_{obs} (observed concentration); Horizontal axis represents the ratio between water cluster signal intensity ($\text{cps}_{m/z37}$) and H_3O^+ signal intensity ($\text{cps}_{m/z21}$). (Feilberg et al., 2010b).

4.3 Sensitivity, calibration, detection limit and transmission

4.3.1 Sensitivity

Under the assumption of trace quantities of VOCs present in the air sample ($[VOCH^+] \ll [H_3O^+]$), the concentration of produced $VOCH^+$ is given by (Hansel et al., 1995; Lindinger et al., 1998):

$$[VOCH^+] = [H_3O^+]_0(1 - e^{-k[VOC]t}) \approx [H_3O^+]_0[VOC]kt \quad (6)$$

where $[H_3O^+]_0$ represents the density of the primary ions injected from the ion source; k is the reaction rate constant for the proton-transfer reaction, eq.(1); t is the average time the reagent ions spend in the drift tube and $[VOC]$ is the concentration of gas pollutant in the air sample. If the transmission efficiencies are included in eq. (6), then the following equation can be used for calculation of VOC concentration (de Gouw et al., 2003):

$$[VOC] = \frac{1}{kt} \times \frac{I_{VOCH^+}}{I_{H_3O^+}} \times \frac{T_{H_3O^+}}{T_{VOCH^+}}; \quad \left(\frac{[VOCH^+]}{[H_3O^+]_0} \approx \frac{[VOCH^+]}{[H_3O^+]} = \frac{I_{VOCH^+}}{I_{H_3O^+}} \times \frac{T_{H_3O^+}}{T_{VOCH^+}} \right) \quad (7)$$

Where I_{VOCH^+} and $I_{H_3O^+}$ are the observed counts of $VOCH^+$ ions and for H_3O^+ ions, respectively, and T_{VOCH^+} and $T_{H_3O^+}$ are the transmission efficiencies for $VOCH^+$ and H_3O^+ ions, respectively. Thus the concentration of VOCs in PTR-MS can be calculated directly from eq. (7) if the concentration of the pollutant is low. The sensitivity and accuracy of eq. (6) is largely dependent on reaction rate constant k and the transmission efficiency of $VOCH^+$ ions, since t can be determined more precisely.

Instrument sensitivity refers to its capability of responding reliably and measurably to changes in analyte concentration and thus refers to the slope of the calibration curve (Harris, 2007).

$$Sensitivity = slope\ of\ calibration\ curve = \frac{change\ in\ signal}{change\ in\ analyte\ concentration} \quad (8)$$

Thus, the unit of sensitivity is cps/ppbv for PTR-MS measurement where cps is the signal unit of counts per second and ppbv is the concentration unit of parts per billion by volume (Jordan et al., 2009). Or in another way, the sensitivity of PTR-MS can be expressed as the signal of $VOCH^+$ ions obtained at a VMR (volume mixing ratio) of 1

ppbv and normalized to a H_3O^+ signal of 10^7 counts/s and thus has a unit of normalized counts/s/ppbv (ncps/ppbv) (de Gouw et al., 2003):

$$\text{Sensitivity} = 10^{-2} \times \frac{kL}{\mu_0 N_0} \times \frac{N^2}{E} \times \frac{T_{\text{VOCH}^+}}{T_{\text{H}_3\text{O}^+}} \quad (9)$$

where L is the length of the drift tube, μ_0 is the reduced mobility, N_0 is the gas number density at standard pressure (1 atm) and temperature (273.15 K), N is the number density of the gas in the reaction chamber, and T_{VOCH^+} and $T_{\text{H}_3\text{O}^+}$ are the transmission efficiencies for VOCH^+ and H_3O^+ ions, respectively. The sensitivity of PTR-MS is limited by the uncertainties of the reaction rate constant k (up to 50%) and the ratio of T_{VOCH^+} to $T_{\text{H}_3\text{O}^+}$ (25%) (de Gouw and Warneke, 2007). The accuracy can therefore be improved by calibration of the PTR-MS by standard mixtures of VOCs.

4.3.2 Calibration and detection limit

Calculations of concentrations from PTR-MS directly may suffer variable errors including uncertainty of rate constant k , uncertainty in the transit time of ions across the drift tube t , variation of transmission ratio $\frac{T_{\text{H}_3\text{O}^+}}{T_{\text{VOCH}^+}}$, and uncertainty of mobilities of H_3O^+ and VOCH^+ , which alone can contribute an error in excess of 20% (Keck et al., 2007; Blake et al., 2009). Thus, calibration by gas standards is typically recommended whenever possible, although the standard mixture is not always easy to obtain. For compounds which may be humidity-dependent (e.g., hydrogen sulphide), calibration is especially important since the dependence can be different under different operational conditions and may change from one occasion to the next, especially after moving the PTR-MS. However, it can be difficult to perform precise and fast calibration under field conditions.

Calibration of PTR-MS for specific compounds commonly uses a standard mixture containing target compounds and a controlled dilution system for obtaining various levels of concentration of the compounds. Zero air (ambient air filtered to contain less than 0.1 parts per million of total hydrocarbons) is typically used for the dilution system and one well-calibrated mass flow controller is normally needed for the dilution system in order

to minimize the uncertainty of the dilution ratio. A series theoretical concentrations can then be derived:

$$[VOC]_d = \frac{[VOC]_s \times Q_s}{Q_s + Q_d} \quad (10)$$

where $[VOC]_d$ is the theoretical concentration after dilution, $[VOC]_s$ is the concentration from the standard mixture, Q_s and Q_d are the flows of the VOC from the standard mixture and from the dilution system, respectively.

Thus a plot of the various theoretical concentrations and the corresponding response of the PTR-MS (signals) can be obtained from which a calibration equation can be derived through a weighted least-square linear regression.

Accuracy refers to the closeness of the result from a measurement to the true value of the sample. The accuracy of calibration-based measurement is dependent on the accuracy of the calibration gas standard (typically 5~10%) and errors in the dilution system (mainly error from the mass flow controller which produces typically 5% uncertainty). The accuracy of a calculated-based concentration measurement, on the other hand, is mainly dependent on the accuracy of reaction rate constant k and the transmission efficiency of the compound.

Precision refers to the reproducibility of a result (Harris, 2007). The precision of PTR-MS can be calculated by the standard deviation of the product ion counts ($\sigma = \sqrt{N_i} = \sqrt{I_{VOCH^+} \times dwell\ time}$) assuming that the counting statistics is a Poisson distribution. Thus the precision can be increased by increasing the dwell time.

Detection limit refers to the smallest quantity of analyte that is 'significantly different' from the blank (Harris, 2007). In practice, the detection limit is commonly defined as three times the noise level of blank measurements (e.g., Feilberg et al., 2010b).

4.3.3 Transmission

The transmission efficiency of protonated ions is important for detection and for the concentration calculation. The transmission efficiency is limited by (de Gouw and Warneke, 2007): (1) the extraction efficiency of ions in the lens system between the reaction chamber and the detection system; (2) the transmission efficiency of the

quadrupole mass spectrometer and (3) the detection efficiency of the electron multiplier. The largest mass-dependent differences may be introduced by the quadrupole mass spectrometer and there may be more scatter loss for light ions. The transmission can typically be measured by a gas standard mixture which contains high-stability and well-calibrated compounds (e.g., aromatic compounds with concentrations close to 100 ppb with 10% uncertainty; e.g. Restek, P/N 34423-PI). The other technique is to use a very high-concentration VOC and monitor the decay of H_3O^+ and the increase of VOCH^+ , which gives the ratio of the transmission factors. The transmission should be determined from time to time, since it can be dependent on operation parameters and vary over time, especially when the electron multiplier ages.

4.4 Reaction rate constant

Calibration by reference standards is preferred whenever reliable standards are available. In this circumstance, the optimisation of the calculation of reaction rate constant is needed in order to improve the accuracy of the measured concentration. As discussed above, the calculated concentration from PTR-MS measurement relies heavily on the accuracy of the reaction rate constant, k , which may err by up to 50%.

Provided a large exothermicity ($> 4.8 \text{ kcal mol}^{-1}$; Bouchoux et al., 1996) of the proton transfer reaction between H_3O^+ and VOCs, the reaction can then occur at collision rate and ion-neutral molecule collision theories can therefore be applied. A commonly used model for the prediction of ion-molecule collision rate constants is the average-dipole-orientation (ADO) theory (Su and Bowers, 1973a, b), which is given as:

$$k_{ADO} = (2\pi q/\mu^{1/2})[\alpha^{1/2} + C\mu_D(2/\pi k_B T)^{1/2}] \quad (10)$$

Where q is the charge of the ion, μ is the reduced mass of the reactants ($\mu^{-1} = m_{\text{VOC}}^{-1} + m_{\text{H}_3\text{O}^+}^{-1}$), α is the polarizability of the neutral reactant (VOC), T is temperature, k_B is Boltzmann's constant, μ_D is the permanent dipole moment of the neutral reactant, and $C = f(\mu_D/\alpha^{1/2})$ is a parameter between 0 and 1 and is dependent on temperature T . The ADO theory generally fits well with experimental ion-neutral molecule reaction rate constants with typical errors of between 10~20% (Mackay et al.,

1976). Zhao and Zhang (2004) employed the ADO theory for reaction rate constant prediction in the application of PTR-MS in atmospheric studies.

However, the employment of room temperature in the ADO theory for calculating the ion-neutral molecule collisions taking place in a drift tube as in PTR-MS has been questioned recently, because the translational energy of the colliding ion leads to a center-of-mass energy largely exceeding that of thermal collisions (Blake et al., 2009; Cappellin et al., 2010b). The center-of-mass energy (KE_{cm}) can be calculated as below (Wannier, 1951):

$$KE_{cm} = \frac{m_n}{m_i+m_n} \left(KE_{ion} - \frac{3}{2} k_B T \right) + \frac{3}{2} k_B T \quad (11)$$

where KE_{ion} is the kinetic energy of the ion and can be calculated as:

$$KE_{ion} = \frac{3}{2} k_B T + \frac{1}{2} m_b v_d^2 + \frac{1}{2} m_i v_d^2 \quad (12)$$

where v_d is the drift velocity of the ion, m_i is the mass of the ion (H_3O^+), m_n is the mass of the neutral molecule (VOC) and m_b is the mass of buffer gas (air). The high center-of-mass energy may lead to a significantly higher effective temperature than the temperature of the drift tube (see eq. (13)) and a marked decrease in the reaction rate constant as compared to thermal conditions (drift tube temperature T) (Blake et al., 2009; Cappellin et al., 2010b):

$$T_{eff} = T + \left(\frac{v_d^2}{3k_B} \right) \left[\frac{m_N(m+M)}{m+m_N} \right] \quad (13)$$

where T_{eff} is effective temperature for the center-of-mass kinetic energy for ion-neutral molecule collision, v_d is the drift velocity of the ion, m is the mass of the ion (H_3O^+), m_N is the mass of the neutral molecule (VOC) and M is the mass of buffer gas (air).

For example, under the standard conditions used in our lab (drift tube voltage 600 V, length 9.2 cm, drift tube temperature 60 °C, drift tube pressure 2.2 mbar), the ion drift velocity is approximately 1025 m/s. The effective temperature is calculated to be around 1900 K for dimethyl sulphide as neutral reactant. Thus it can be seen that the effective temperature is much higher than drift tube temperature.

A model including the kinetic energy and temperature dependence may consequently give more reasonable results for reaction rate constants calculation (Cappellin et al., 2010b). Su (1994) made a benchmark test for predicting the rate constants of ion-polar molecule capture collisions (eq.(14)) with a wide range of center-of-mass kinetic energies (from thermal to a few eV) and temperature (50-1000 K). The report error for the calculated rate constant for ion-molecule systems was within 5%. Therefore this model is suggested for estimating the reaction rate constants used in the concentration calculations from PTR-MS data:

$$\left. \begin{aligned}
 k_{cap}(T, KE_{cm}) &= K_c q \left(\frac{\pi \alpha}{\mu \epsilon_0} \right)^{\frac{1}{2}} \\
 K_c &= 1 + c_1 \tau^{0.4} \epsilon^2 S + c_2 (1 - S) \times \sin\{c_3 [c_4 + \ln \tau]\} \tau^{0.6} (\epsilon - 0.5)^{\frac{1}{2}} \\
 \tau &= \frac{\mu_D}{(\alpha T)^{\frac{1}{2}}} \\
 \epsilon &= \frac{\mu_D}{(\alpha KE_{cm})^{\frac{1}{2}}} \\
 S &= \begin{cases} \exp[-2(\epsilon - 1.5)]; & \epsilon > 1.5 \\ 1; & \epsilon \leq 1.5 \end{cases}
 \end{aligned} \right\} \quad (14)$$

In overall, PTR-MS has been proved to be a robust tool for online VOCs monitoring with fast, sensitive and time-resolved measurements of VOCs with low detection limits. For our purpose of removing odorants from intensive pig production, it is interesting to apply this robust tool for monitoring the odour removal and for determining and understanding the removal process especially by biofiltration process. Next section will focus on the biofiltration which is recognized as the most cost-effective technology for removing the odorants from intensive pig houses.

5 Biofiltration

Biofiltration generally refers to the biological treatment techniques including mainly biofilters, biotrickling filters and bioscrubbers (Delhom nie and Heitz, 2005; Kennes et al., 2009; Detchanamurthy and Gostomski, 2012). As discussed in the introduction, biofiltration is cost-effective for treating large quantities of air containing low-concentration pollutants. Biofilters have increasingly been used for the control of ammonia and odour emissions from livestock buildings since the 1980s starting in

Germany and the Netherlands (O'Neill et al., 1992; Ergas and Gonzalez, 2004). For the laboratory biofilter research, very high removal efficiencies (close to 100%) were observed for ammonia, H₂S and VOCs under high inlet concentrations (a few to 200 ppm) and long residence times (typically 20 to 100 s) (Kim et al., 2002; Choi et al., 2003; Kastner et al., 2004; Chung et al., 2007). This may be due to the well-controlled conditions for humidity, temperature and loading. On-site research for both biofilters and biotrickling filters, on the other hand, showed highly fluctuating removal efficiencies of ammonia, H₂S and odour with typically much lower concentrations of individual odorants (Nicolai and Janni, 1997; Janni et al., 2001; Martinec et al., 2001; Melse and Mol, 2004; Feilberg et al., 2006; Riis and Lyngbye, 2008). Packing materials for biofilters are usually a mixture of materials such as compost, wood chips, wood bark, coconut fibre, peat, perlite, granular activated carbon, etc. Some of the materials provide a rich community of bacteria and good conditions for biofilm growth, but long-term treatment of exhaust air directly drawn from the animal house usually brings problems with clogging, preferential flow paths and quick acidification due to the high load of dust and ammonia (Melse and Ogink, 2005). The biofilters, therefore, were suggested to be used as secondary filters after the biotrickling filter or wet scrubbers as the dust and ammonia will be reduced dramatically after the trickling filter (Melse and Ogink, 2005; Chen and Hoff, 2009).

Packing materials, media moisture content and empty bed residence time were recognized as the most important factors influencing biofilter performance (Chen and Hoff, 2009). However, the poorly water-soluble odour compounds (e.g., sulphur compounds) generally have low removal efficiencies and this may be limited by external mass transfer rather than biodegradation in the biofilm (Kim and Deshusses, 2005; Nielsen et al., 2009; Feilberg et al., 2010a). A few recent studies have indicated that the addition of an organic co-solvent to the water phase may increase the availability of the odorants to the bacteria and thus increase the biodegradation efficiency (Davidson and Daugulis, 2003; Quijano et al., 2009; Yeom et al., 2010; Galindo et al., 2011), but the studies have so far been limited to laboratory tests.

Further, the underlying mechanism of biofiltration is complex although there is general agreement on the biofilter/biotrickling filter mechanisms as shown in Fig. 8 (Devanny and

Ramesh, 2005). Important processes involved in the biofiltration mechanisms include partitioning, pollutant mass transfer, biodegradation and oxygen transfer. Due to the large air flow rate applied in biofilters, it is dominated by aerobic processes and thus oxygen supply generally is more than enough even for complete oxidation of air pollutants.

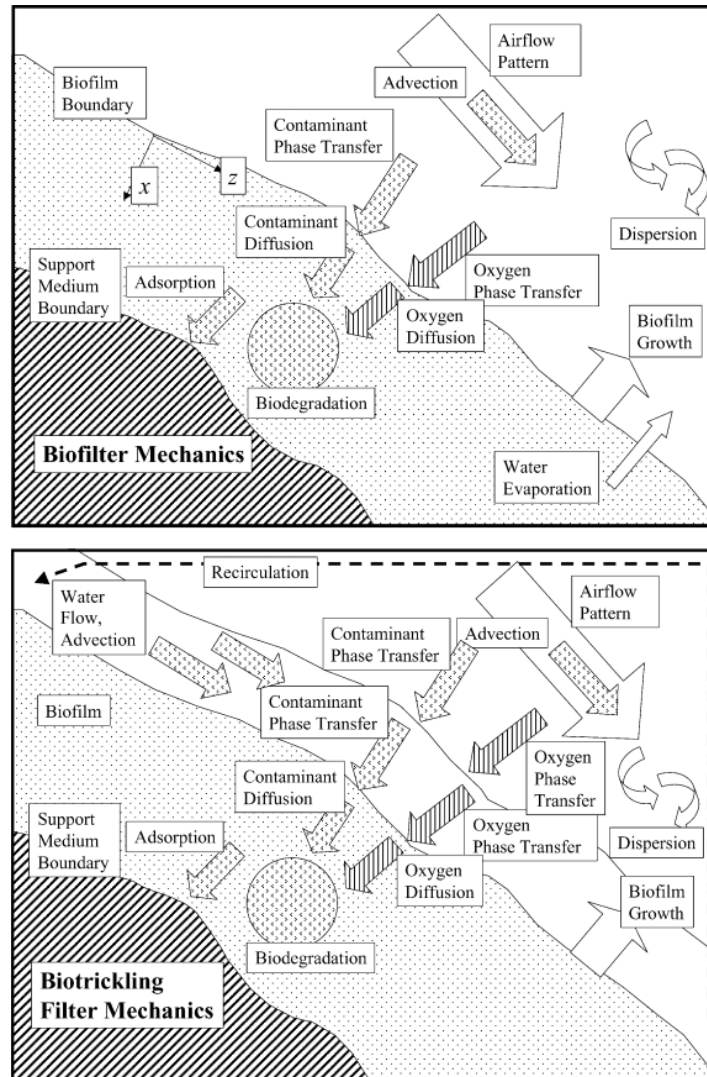


Fig. 8 Phenomena involved in the operation of biofilters and biotrickling filters (Deviny and Ramesh, 2005).

5.1 Air-liquid Partitioning

Movement of the pollutants from the air to the water phase (or biofilm in which 99% is water) occurs according to the partitioning equilibrium of the compound between two phases. The equilibrium could be described by Henry's law when pollutant concentration is low. Thus the equilibrium concentration in the liquid phase will be proportional to those in the air:

$$HC_G = C_L^* \quad (15)$$

where C_G is the pollutant concentration in the gas phase (g m_G^{-3}), C_L^* is the equilibrium concentration in the liquid phase (g m_L^{-3}) and H is the partition coefficient or dimensionless Henry's law constant ($\text{g m}_L^{-3}/\text{g m}_G^{-3}$). The unit of H is described in this way, thus the number reflects directly the partitioning ratio between the water and the air phase. Generally, more pollutant is partitioned in the water than in the air (for the same volume of air and water), even for hydrophobic compounds (e.g., for H_2S , methanethiol and dimethyl sulphide, the values of H are approximately 2.4, 7.5 and 13.7, respectively (NIST database)). For hydrophilic compounds, H is a very large number (e.g., for acetic acid, H is in the region of $1.5 \cdot 10^5$).

However, the presence of different compounds in water (e.g., salts in sea water) could significantly change the air-liquid partitioning when certain concentrations are reached (Dacey et al., 1984; Suleimenov and Krupp, 1994; Peng and Wan, 1998; Iliuta and Larachi, 2007; Coquelet et al., 2008). Due to the complex compositions (e.g., suspended particles and salts) contained in the biofilter/biotrickling filter liquids, there might be significantly different partition coefficients of air pollutants from that in pure water. Furthermore, organic co-solvents (highly water-soluble organic compounds – acetic acid, for example) may influence the solvation properties of an aqueous phase (Schwarzenbach et al., 2003). Thus the partition coefficients of the target pollutants should preferentially be determined experimentally under realistic biofilter/biotrickling filter operating conditions, in order to optimize the filter operation.

The equilibrium static headspace technique (Hála et al., 1967; Richon et al., 1985) and the dynamic stripping technique (Leroi et al., 1977; Mackay et al., 1979) are the two

customary experimental approaches for determination of partition coefficients. The former relies on the static determination of headspace concentrations and may result in large estimation errors of the measured partition coefficient, especially for sparingly-soluble compounds (Leroi et al., 1977). The latter, on the other hand, applies a flow that strips dissolved compounds out of the solution and leads to a decrease of the concentration in the solution. The partition coefficient can be calculated through measuring the drop in the concentration of the compound in the gas phase. The experimental error can in this way be reduced to <10% (Leroi et al., 1977) and the method can take advantage of the online measurements by PTR-MS (Lindinger et al., 1998; Karl et al., 2003; Pollien et al., 2009).

Besides partitioning pollutants into the liquid phase, the sorption of air pollutants in biofilters is essential since sorbed pollutants may be available for biodegradation and the mass adsorbed may be much greater than that dissolved in water. The sorption involved in biofiltering may include simple dissolution in the water phase, adsorption to the medium surface, adsorption on the surface of the biomass and biofilm, absorption in the biofilm, uptake by living cells, and adsorption at the air-water interface (Devinny et al., 1999). The effect of sorption and desorption of pollutants could be described by the retardation factor, which is the ratio between mass adsorbed on the medium (unit volume) and mass in the gas phase (unit volume). Thus the retardation factor is closely related to the mass partition coefficient which contains the partition coefficient between water and air (Hodge and Devinny, 1994; Deshusses and Johnson, 2000; Avalos et al., 2009).

5.2 Mass transfer

Pollutant mass transfer is especially important since the process supplies the potential substrates for the microbiological community and thus should be as efficient as possible. The two-film model (Whitman, 1923) is generally used for describing the pollutant mass transfer process in biofilters (Fig.9):

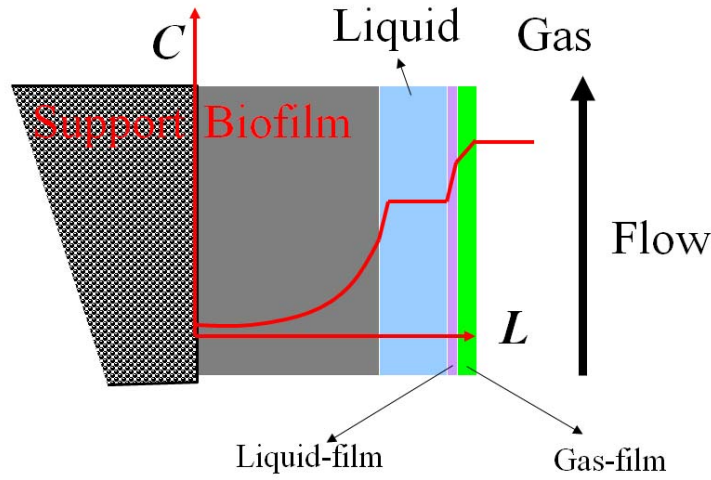


Fig.9 Schematic of the concentration gradient from gas phase to biofilm and two-film model.

$$\left. \begin{aligned} -\frac{HdC_G}{dt} &= \frac{dC_L}{dt} = K_L a (HC_G - C_L) \\ \frac{1}{K_L a} &= \frac{1}{Hk_L a} + \frac{1}{k_G a} \end{aligned} \right\} \quad (16)$$

where C_L is the local pollutant concentration in the liquid phase (g m_L^{-3}), K_L , k_L and k_G are the overall mass transfer coefficient (m s^{-1}), the liquid-film mass transfer coefficient (m s^{-1}) and the gas-film mass transfer coefficient (m s^{-1}), respectively and a is the specific surface area over unit volume of the packing material ($\text{m}^2 \text{m}^{-3}$). Thus the overall mass transfer rate $K_L a$, the liquid-film mass transfer rate $k_L a$ and the gas-film mass transfer $k_G a$ have a unit of s^{-1} . The model describes the decrease of pollutant concentration per unit time in the gas phase equal to the increase of pollutant concentration per unit time in the liquid phase. The latter is proportional to the overall mass transfer coefficient and concentration gradient between the saturated liquid concentration (due to partitioning equilibrium) and the local liquid concentration. The overall mass transfer resistance ($1/K_L a$) is equal to the sum of gas-film mass transfer resistance ($1/k_G a$) and liquid-film mass transfer resistance ($1/Hk_L a$). Generally, the pollutants in the bulk air flow move by convection, but the flow becomes laminar near the air-water interface where transport is dominated by molecular diffusion. Thus the mass transfer may be limited by the diffusion process since it is much slower than turbulent transport. Due to the lower molecular

diffusion rate in water than in air, mass transfer is likely controlled by liquid-film resistance especially for low-water-soluble compounds ($H \ll H_{critical} = 975$ (critical Henry's law constant, Schwarzenbach et al., 2003); $k_{Ga} \gg Hk_{La}$; $K_{La} \approx Hk_{La}$). On the other hand, mass transfer may be controlled by the gas-film for highly water-soluble compounds ($H \gg H_{critical} = 975$; $k_{Ga} \ll Hk_{La}$; $K_{La} \approx k_{Ga}$).

It is likely that the removal of volatile sulphur compounds by biofiltration is limited by the mass transfer resistance from the gas phase to the wet surface of the biofilter medium rather than biodegradation of these compounds (Devinny et al., 1999; Kim and Deshusses, 2005; Nielsen et al., 2009; Feilberg et al., 2010a). In order to enhance the performance and design of biofilters, a better understanding of the level and limitations of the mass transfer rates of volatile sulphur compounds is therefore important (Kim and Deshusses, 2005). Currently only limited experimental work has been done on mass transfer for packing materials used in biofilters or biotrickling filters (Kim and Deshusses, 2008; Dorado et al., 2009). Although there are plenty of mass transfer correlation data obtained mainly from wet scrubbers, they are not necessarily suitable for usage in biofiltration processes due to the large difference in superficial gas velocities or liquid velocities employed between biofiltration conditions and wet scrubbers (Kim and Deshusses, 2008). Furthermore, most of the mass transfer data obtained are for oxygen (which is important for aerobic conditions) and those data cannot with certainty be expanded to cover other compounds such as sulphur compounds due to the difference in diffusion and partitioning coefficients. Thus the experimental determination of mass transfer coefficients of volatile sulphur compounds for the related packing materials commonly used for biofilters or biotrickling filters is necessary.

5.3 Biodegradation

Biodegradation is the key process of biological treatment using biofilm (microorganisms) to destroy air pollutants. Thus the biofilm needs to be very active in order to make the biofiltration a success. Furthermore, greater biodegradation allows a smaller biofilter which is more economical. The efficient biodegradation requires strict control of the environments for microorganisms (Delhom nie and Heitz, 2005). Critical parameters for the optimization include: (1) pH (Lu et al., 2002; Liu et al., 2008; Taylor and Bouwer,

2009; Omri et al., 2011), (2) water content (Swanson and Loehr, 1997; van Lith et al., 1997; Ranasinghe and Gostomski, 2003; Shareefdeen et al., 2010), (3) nutrients (N, P, K, for example) (Morgenroth et al., 1996; Prado et al., 2002; Morita et al., 2012), (4) temperature (Swanson and Loehr, 1997; Sorial et al., 1997; Yoon and Park, 2002; Pedersen et al., 2007).

Depending on target air pollutants, biofilters may support different structures and groups of microorganisms (Ralebitso-Senior et al., 2012). For the elimination of VOCs, heterotrophic microorganisms (most likely fungi or bacteria) predominate, since organic compounds are the carbon and energy sources for these microorganisms (Delhom nie and Heitz, 2005). But the structure of the complex microbial ecosystem and the biofilm in real reactors is still poorly known. The bed inoculation, depending on the nature of air pollutants and filter materials, commonly employs consortia isolated from similar operating biofilters or extracted from sewage sludge. In some cases, enrichment and isolation of the microbial community may be considered in order to obtain appropriate cultures for the target compounds (Ralebitso-Senior et al., 2012).

The kinetics of pollutant degradation is often described by the Michaelis-Menten equation (eq. 17) or Monod kinetics (eq. 18):

$$-\frac{dC_L}{dt} = \frac{k_{max}C_L}{K_S+C_L} \quad (17)$$

$$-\frac{dS}{dt} = \frac{kSX}{K_S+S} \quad (18)$$

Where k_{max} is the maximum degradation rate ($\text{g mL}^{-3} \text{s}^{-1}$), K_S is the half-saturation constant (g mL^{-3}), S is the substrate concentration (g mL^{-3}), in this case $S = C_L$, k is the maximum substrate utilization rate (s^{-1}), and X is the biomass concentration (g mL^{-3}). Where the pollutant concentration is high compared to the half-saturation constant ($C_L \gg K_S$), the degradation rate follows zero-order and is independent of pollutant concentration. In contrast, the degradation rate will be proportional to the pollutant concentration (first order), where the pollutant concentration is low compared to the half-saturation constant ($C_L \ll K_S$).

The biodegradation of volatile sulphur compounds (e.g., H_2S , methanethiol and dimethyl sulphide) in biofilters is in many cases attributed to the microorganism *Thiobacillus*

thioparus. Table 4 shows a few examples of the Michaelis-Menten model simulation parameters for the sulphur degradation in biofilters. In most of the literature dealing with mixtures of sulphur compounds, the removal of dimethyl sulphide and dimethyl disulphide is significantly affected by the presence of H₂S and methanethiol, but the presence of dimethyl sulphide and dimethyl disulphide has no influence on the removal of H₂S and methanethiol (e.g., Hirai et al., 1990; Wani et al., 1999; Li et al., 2003; Cáceres et al., 2012). A few studies indicate that the oxidation of volatile sulphur compounds by *Thiobacillus* follows a sequence in which the methylated volatile sulphur compound is assumed to be first oxidized to H₂S (Kelly et al., 2005; Schäfer et al., 2010; Cáceres et al., 2012).

Table 4 A few examples of Michaelis-Menten model parameters for simulation of sulphur degradation.

Compound	H ₂ S	methanethiol	dimethyl sulphide	H ₂ S
k _{max}	5	0.9	0.38	1.33~1.41
Unit of k _{max}	g-S/d kg-dry peat	g-S/d kg-dry peat	g-S/d kg-dry peat	g-S/d kg-dry bead
K _S	55	10	10	47.2~56.0
Unit of K _S	ppm	ppm	ppm	ppm
Microorganisms	suspected to be <i>Thiobacillus thioparus</i>	suspected to be <i>Thiobacillus thioparus</i>	suspected to be <i>Thiobacillus thioparus</i>	<i>Pseudomonas putida</i> CH11
Packing	Peat	Peat	Peat	cell-laden Ca-alginate beads
Ref.	Hirai et al., 1990	Hirai et al., 1990	Hirai et al., 1990	Chung et al., 2001

6 General discussions

6.1 Online PTR-MS for evaluating odorant reduction (Paper I and II)

As discussed in the introduction, identification and quantification of the odour emissions from intensive pig production facilities were performed by online PTR-MS (Feilberg et al., 2010b) just before the start of the project and during the very beginning of the project. During the summers of 2009 and 2010, online PTR-MS was applied to two full-scale odour reduction technologies. One technology was a slurry treatment including ozonation (Paper I) and the other a biological air filter (Paper II). For the slurry ozonation (combined with solid-liquid pre-separation and acidification), the highest average removal efficiencies were for H₂S (77%), 3-methyl-indole (62%), phenol (53%) and acetic acid (46%). The online chemical measurement confirmed the study by Lyngbye et

al. (2008b) which showed H₂S removal of approximately 82% by slurry ozonation. The overall reduction of odour activity value (OAV; calculated as the mean concentration divided by the odour threshold value (OTV) for each compound) by slurry ozonation was approximately 49%. Based on OTV, methanethiol, butanoic acid, 4-methylphenol, hydrogen sulphide and C₅ carboxylic acids are estimated to contribute significantly to the odour nuisance after slurry ozonation. The study indicated that emissions of odorants other than hydrogen sulphide mainly originate from sources other than the treated slurry, which limits the potential for further optimization of this technology.

During the summer of 2010 the PTR-MS was applied for evaluating the performance of a newly designed three-stage biological air cleaner (SKOV A/S) in the field (Paper II). The PTR-MS was tested for its ability to provide reliable measurements at high-humidity and high-dust loads (via a 5- μ m Teflon filter to the PTR-MS) in the biofilter. The tested three-stage biofilter could efficiently remove carboxylic acids, aldehydes, ketones, phenols and indoles (80-99%). The filter can also remove H₂S relatively efficiently (approximately 75%), but only about 0~15% of methanethiol and dimethyl sulphide. The low removal performance of methanethiol and dimethyl sulphide may be due to the low partition coefficients of these two compounds in water and therefore the process may be mass-transfer limiting rather than biodegradation limiting (Devinny et al., 1999; Nielsen et al., 2009). Hydrogen sulphide differs from methanethiol and dimethyl sulphide in that the concentrations are much higher and that H₂S is a weak acid that dissociates at alkaline pH.

6.2 Air-liquid partitioning of VSCs in biological air-filter liquids (Paper III)

As discussed above, the low partition coefficient in the water phase may be a limiting factor in the ability of the biofilter to treat methanethiol and dimethyl sulphide. However, the partition coefficient in the biofilter liquid was significantly different from that in pure water due to the complex compositions (e.g., suspended particles and salts) in the biofilter/biotrickling filter liquids. Thus the partition coefficients of the target pollutants should be determined experimentally using the true biofilter/biotrickling filter liquids in order to optimise the filter operation and for biofilter modelling purposes. During the spring and early summer of 2010, the partition coefficients of the reduced volatile sulphur

compounds were measured for biotrickling filter liquids and using a dynamic method applying PTR-MS at a temperature range of 3 to 45 °C (Paper III). The biotrickling filter liquids were collected from a full-scale two-stage biotrickling filter. The results were compared to the partition coefficients in pure water and NaCl solutions also measured in this study. Despite the ionic strength and presence of co-solutes in the biotrickling filter liquids, the partition coefficients of organic sulphur compounds in the biotrickling filter liquids were generally very close to the corresponding partition coefficients in deionized water. This study also indicated that the salting-out effects in biotrickling filter liquids are of no importance for these compounds. Thus the co-solute effects for sulphur compounds can generally be neglected in numerical biofilter models, and the uptake of volatile sulphur compounds in biotrickling filter liquids cannot be increased by decreasing ionic strength.

6.3 Mass transfer coefficients of VSCs for packing materials used in biological air filters (Paper IV, V and VI)

Due to the low partition coefficients of sulphur compounds present in the biofilter, the mass transfer from the air phase to the liquid phase may therefore be limiting to the performance of biofilters. Thus a better understanding of the limitations of mass transfer is essential for further optimization of the biofilters.

From summer 2010 to spring 2011, a method was developed for determination of overall mass transfer coefficients of volatile sulphur compounds based on breakthrough curves measured by PTR-MS in combination with a numerical model developed in Paper IV. Traditionally, the mass transfer coefficients have been determined under conditions for wet scrubbers with only a few studies performed under conditions for biofilter/biotrickling filters through CO₂ (for gas-film mass transfer coefficient), O₂ (for liquid-film mass transfer coefficient) or toluene experiments (for overall mass transfer coefficient) (Kim and Deshusses, 2008; Dorado et al., 2009). Our method established the mass transfer coefficient for a range of target pollutants for biofilter/biotrickling filter purposes. The breakthrough curves were optimized in order to get the best reproducibility of the profiles for different injection strategies (injection modes, locations, chemical phases). The breakthrough curves were then used in a numerical model developed for

fitting dispersion-diffusion equations in order to estimate mass transfer coefficients. The method was demonstrated for the application range for VOCs measurements and compared to literature data of mass transfer coefficients.

Within the same period, the established method was then tested with a commercially available medium with different fractions (Leca[®]: Light Expanded Clay Aggregates) (Paper V). In paper V, the investigation and application of the method was focused on the dependency of overall mass transfer coefficients of volatile sulphur compounds in media (Leca[®]) for biofilters on particle size, gas velocity and pollutant chemical properties. Mass transfer coefficients were found to be closely related to particle size compound solubility, particle size range, specific surface area and gas velocity. The link of mass transfer coefficients to gas velocity, media specific surface area, particle size, partition coefficient of the pollutant and gas-film mass transfer coefficient (by CO₂ measurements) was established and validated through a developed predictive model.

During summer and autumn in 2011, the measurements for overall mass transfer coefficients of volatile sulfur compounds by application of the established method were further expanded (paper VI). The study was focus on the dependence of mass transfer coefficients and pressure drop on packing materials, gas velocities and liquid velocities for each volatile sulfur compound. The purpose was to compare the mass transfer coefficients of VSCs in different packing materials used for biofilters/biotrickling filters. While the overall mass transfer coefficients increased rapidly with the increased air velocity, the dependence on liquid velocity is less important. The results of normalized mass transfer coefficients to pressure drop showed a potential of ceramic saddles due to higher mass transfer coefficients and a potential of cellulose pads due to low pressure drop, respectively, compared to other materials. Thus these two materials are recommended for the biofiltration purpose regarding the removal of volatile sulfur compounds in terms of mass transfer coefficients.

6.4 Kinetic analysis for odorant removal in the biological air filter (Paper VII)

The data collected from the 2010 summer campaign for application of online PTR-MS for evaluating the performance of the biotrickling filter were further investigated through kinetic analysis. The kinetic analysis can promote a better understanding of the

biofiltration process and the optimisation of the filter operations. Seven macrokinetic models were tested for simulating the performance of the biotrickling filter for measured volatile compounds. Traditionally applied kinetic models (e.g., plug flow model with Michaelis-Menten kinetics) only give moderate simulation performance for the removal of the compounds. The Stover-Kincannon model and Grau second-order model, which are commonly used for simulation of the wastewater biofiltration process, were introduced to demonstrate pollutant removal in the biotrickling filter. Whereas the Stover-Kincannon model demonstrated that pollutant removal rates were positively related to the mass loading rates, the Grau second-order kinetic model indicated that the removal efficiencies were negatively dependent on air loading rates. Thus the design of the filter should focus on increasing the mass loading rates while decreasing the air loading rate.

6.5 Performance evaluation Leca biofilter and iron catalyzed H₂S oxidation (Paper VIII and IX)

During the late summer and autumn in 2011, on line PTR-MS was applied to monitor two biofilters dealing with odorants emitted from two identical pig houses. The purpose of paper VIII was to compare the performance of the two biofilters of which one packed with untreated Leca and the other one was packed with grinded/shaved Leca. In overall the grinded Leca filter had higher removal efficiencies for most of the odorants than the removal efficiencies by the untreated Leca filter. This enhancement of the performance may due to the enlargement of the surface area of Leca by the grinding process. On the other hand, the observed removal efficiencies during the last period were significantly higher than that during the first period in both biofilters. The low ventilation rate and low temperature may benefit the removal of volatile sulfur compounds, which may be mass transfer limited in the biofilter.

During the online PTR-MS evaluation on the performance of the two Leca biofilters, a small-scale setup was made with filter material from the grinded Leca biofilter. The purpose of paper IX was to investigate and distinguish the biological activity from the iron catalyzed H₂S oxidation, as Leca material was found to be able to chemical adsorb H₂S and methanethiol (Tabase et al., 2012). Since the metal ions such as iron oxide

contained in Leca have been found to catalyze H₂S oxidation, this could potentially improve the H₂S removal in the biofilters. With the controlled loading rates experiments performed under intact, pasteurized and clean Leca conditions, the results indicated that the more than half of the reduction of H₂S was due to the non-biological activities in the Leca biofilter. For methanethiol, on the other hand, more than 85% of the reduction was signed to the biological activity.

6.6 Presence of fungi in a biofilter treating waste air from a pig farm (Paper X)

During 2011 air samples from a full scale biofilter packing with cellulose (SKOV A/S) were collected in Tedlar bags and measured by PTR-MS. The purpose was to investigate the temporal presence of fungal aerial hyphae and accordingly the removal of volatile sulfur compounds. The results indicated that the removal rates of H₂S were positively correlated with temporal presence of fungal aerial hyphae, which suggests that the fungi takes up H₂S and auto oxidize it without being energetically favorable for the fungi. The average removal efficiency for H₂S was 17.6% without bloom and 64.3% when fungi were visually present in the same biofilter. On the other hand, fungal bloom had no significant change on removal efficiencies of methanethiol or dimethyl sulfide in the same biofilter. Fungi did not occur over the whole measuring period, suggesting that the H₂S oxidation is not energetically favorable and we hypothesize that H₂S oxidation is catalyzed by iron containing enzymes in the fungal respiration system.

7. Conclusion

The present PhD thesis is a step towards a better understanding of volatile sulfur odorants removal through biofiltration process by the application of PTR-MS as a key tool. Based on the present PhD thesis, the following can be concluded:

- PTR-MS is a valuable tool both for online odorants monitoring and also a unique tool for parameters estimation for example partition coefficient and mass transfer coefficient determination in biofilters.
- Slurry ozonation gave a moderate reduction (approximately 50%) of the odorants but further optimization may be limited.

- Volatile sulfur compounds have relatively low removal efficiencies in biofilters and may be limited by mass transfer process, due to the low water solubility.
- Partition coefficients of volatile sulfur compounds in biotrickling filters are generally very close to the corresponding partition coefficients in deionized water. This simplifies the modeling of biofiltration process.
- Mass transfer coefficients of volatile sulfur compounds in packed columns used for biofilter/biotrickling filters were observed to be related to gas velocity, liquid velocity, particle size, specific surface area and pollutant chemical properties (e.g., Henry's law constant).
- Kinetic analysis of on-line PTR-MS data indicated the removal rates of odorants were positively related to the mass loading rates, whereas the removal efficiencies were negatively correlated to air loading rates. Thus the design of the biofilter for odorants removal should focus on the increase of mass load while decrease the air load at the same time.
- The grinded Leca biofilter performed better removal efficiencies than untreated Leca biofilter and this may due to the higher surface area by the grinding process. Low ventilation rate and low temperature may benefit the removal of volatile sulfur compounds in Leca biofilters. Lab-scale test indicated that more than half of the reduction of H₂S was due to the non-biological activities.
- The removal rates of H₂S in cellulose biofilter were positively correlated with temporal presence of fungal aerial hyphae. The average removal efficiency for H₂S was 17.6% without bloom and 64.3% when fungi were visually present in the same biofilter. Therefore the maintenance of the biofilter and the fungi is very important in order to get stable removal of H₂S.

8. Future research perspectives

The present PhD thesis has demonstrated that the PTR-MS is a promising and unique tool for odorants removal evaluation and determination of key parameters in biofiltration process. However, the removal of volatile sulfur compounds by biological air treatment is kept to be challenging due to the low water solubility of the compounds and the relatively

high air load in biofilters for livestock production facilities. Based on this PhD thesis, the following research can be identified:

- Fungi-loaded biofilters: Since the presence of fungi was demonstrated to be important for the removal of H₂S, further research and development is needed in order to find the conditions for maintaining the fungi community or enhance the fungi community by optimized operation.
- Enhanced removal of VSCs through combined iron oxidation and biofiltration: Since the iron oxides can help to remove the volatile sulfur compounds especially H₂S, thus a combined system of iron oxidation and biofiltration may enhance the removal of VSCs. The system needs to be developed with key focus on materials, reaction rate and conditions.
- Partial air treatment/concentrated air treatment by biofiltration: Since the present PhD thesis demonstrated that odorant removal rates are positively related to mass load and the removal efficiencies are negatively related to air load, thus a partial air treatment or concentrated air treatment by biofilter/biotrickling filters will be expected to improve the performance of the filters but further research and development of the biofilter system are needed.
- Advanced oxidation of ventilation air after biofiltration: An alternative way to improve the performance of the treatment of odorants is to apply multi-step treatment for example to apply AOPs technique to the air after biofiltration. The hypothesis is that the reaction between AOPs and sulfur compounds is fast and thus the cost is kept in a reasonable range due to the low concentrations of odorants after the biofiltration.

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Appendix:

Paper I: Liu, D., Feilberg, A., Adamsen, A.P.S., Jonassen, K.E.N. The effect of slurry treatment including ozonation on odorant reduction measured by in-situ PTR-MS. Atmospheric Environment. 2011, 45(23), p. 3786-3793.

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Paper V: Andreasen, R.R., Liu, D., Ravn, S., Feilberg, A., Poulsen, T.G. Air-water mass transfer of sparingly soluble odorous compounds in granular biofilter media. Chemical Engineering Journal. 2013, 220, p.431-440.

Paper VI: Liu, D., Adamsen, A.P.S., Andreasen, R.R., Poulsen, T.G., Feilberg, A. A comparative study of mass transfer coefficients of reduced volatile sulfur compounds regarding packing materials for biofiltration. 2013. Paper draft.

Paper VII: Liu, D., Hansen, M.J., Guldborg, L.B., Feilberg, A. Kinetic evaluation of removal of odor contaminants in a three-stage biological air filter. Environmental Science and Technology, 2012, 46(15), 8261-8269.

Paper VIII: Liu, D., Feilberg, A., Løkke, M.M., Riis, A.L. Performance evaluation of two air biofilters in treating odor pollutants from intensive pig production. 2013. Paper draft.

Paper IX: Pedersen, C.L., Liu, D., Feilberg, A., Nielsen, L.P. Hydrogen sulfide oxidation rates in active and pasteurized filter material from a trickling biofilter. 2013. Paper draft.

Paper X: Pedersen, C.L., Liu, D., Feilberg, A., Nielsen, L.P. Presence of fungi in a biofilter treating waste air from a pig farm. 2013. Paper draft.

The full text of the papers is not included here due to copyright issue; please contact Dezhao Liu (Dezhao.Liu@agrsci.dk) if you are interested.

Dezhao Liu, Application of PTR-MS for optimization of odour removal from intensive pig production with emphasis on biofiltration, 2013