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Multivariate prediction of odor from pig production based on in-situ measurement of odorants

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HIGHLIGHTS

- Analytical and sensory measurements were carried out in parallel.
- Sampling in bags was avoided by using direct on-site measurements.
- A partial-least-squares regression model using on-site data was achieved.
- On-site measurements of odor clearly improved the model validation ($R^2 = 0.77$).

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ABSTRACT

The aim of the present study was to estimate a prediction model for odor from pig production facilities based on measurements of odorants by Proton-Transfer-Reaction Mass spectrometry (PTR-MS). Odor measurements were performed at four different pig production facilities with and without odor abatement technologies using a newly developed mobile odor laboratory equipped with a PTR-MS for measuring odorants and an olfactometer for measuring the odor concentration by human panelists. A total of 115 odor measurements were carried out in the mobile laboratory and simultaneously air samples were collected in Nalophan bags and analyzed at accredited laboratories after 24 h. The dataset was divided into a calibration dataset containing 94 samples and a validation dataset containing 21 samples. The prediction model based on the measurements in the mobile laboratory was able to explain 74% of the variation in the odor concentration based on odorants, whereas the prediction models based on odor measurements with bag samples explained only 46–57%. This study is the first application of direct field olfactometry to livestock odor and emphasizes the importance of avoiding any bias from sample storage in studies of odor-odorant relationships. Application of the model on the validation dataset gave a high correlation between predicted and measured odor concentration ($R^2 = 0.77$). Significant odorants in the prediction models include phenols and indoles. In conclusion, measurements of odorants on-site in pig production facilities is an alternative to dynamic olfactometry that can be applied for measuring odor from pig houses and the effects of odor abatement technologies.

1. Introduction

Odor from pig houses is a severe problem that causes substantial nuisance to the neighbors and it prevents the farmers from developing their production. Odor nuisance can either be lowered by placing the pig houses further away from the neighbors or by applying abatement technologies. Abatement of odor nuisance requires a method that can be used to document how much the nuisance is lowered. Dynamic olfactometry (CEN, 2003) is often used to estimate the effect on odor. However, this method relies on the use of human panelists that despite the attempts to standardize the panelist performance are associated with great variation (Clanton et al., 1999; Klarenbeek et al., 2014). Furthermore, this method has some drawbacks such as impaired recovery of odorants

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in sample bags used for collection of air samples (Koziel et al., 2005; Trabue et al., 2006; Mochalski et al., 2009; Parker et al., 2010; Hansen et al., 2011) and in the olfactometers used for sample dilution (Hansen et al., 2010, 2013). It has been suggested that a method with analytical measurements of odorants could be an alternative to dynamic olfactometry since it can provide data with a relatively high precision and reproducibility. The challenge, however, is to predict the highly variable sensory response from the human nose based on the more precise chemical measurement of odorants. A few studies have developed a prediction model based on a synthetic mixture of odorants relevant for livestock production with a fairly high correlation (R^2: 0.76–0.8) between measured and predicted odor measurements in manure systems (Hobbs et al., 2001; Zahn et al., 2001). However, the development of a prediction model for pig houses should be based on complex real samples and, preferably, measurements without storage of air samples in sample bags. In a study with measurements of odorants in pig houses by solid phase micro-extraction (SPME) and gas chromatography and mass spectrometry (GC/MS) a poor correlation ($R^2 < 0.3$) was found between measured and predicted odor concentration (Gralapp et al., 2001). This study only included a limited number of odorants and no sulfur compounds were included. The shortcomings of using dynamic dilution olfactometry based on bag samples as a reference for odor prediction models were emphasized in a previous study (Trabue et al., 2011), which also highlighted the challenges in selecting suitable analytical methods to cover the odorant composition. In food sensory science multivariate statistics like partial least squares (PLS) regression are routinely used to find complex relations between chemicals and odor with success (Aznar et al., 2003; Biasioli et al., 2006).

A different approach is to correlate the sum of odor activity values (concentration divided by odorant threshold value) of measured odorants and compare this with odor concentration (Kim and Park, 2008). This was recently further developed by Wu et al. (2016) to include both threshold value and the relationship between odor intensity and odor concentration (the Weber-Fechner law). This approach does not rely on multivariate statistics, but is on the other hand dependent on the access to single compound threshold values of all odorants.

Regardless of the approach used, reliable measurement methods are pivotal for using analytical methods for predicting odor. Recent studies have revealed that on-line Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a fast and sensitive method to investigate the effect of abatement technologies on odorants from pig houses that can measure relevant odorants including sulfur compounds (Liu et al., 2011; Hansen et al., 2012b). PTR-MS has previously been applied in semi-field studies regarding prediction of odor from composting facilities (Biasioli et al., 2004) and pig houses (Hansen et al., 2012a). In these studies, odor concentration and concentrations of odorants where measured in air samples collected in sample bags and the analyses were synchronized in order to achieve the same sampling storage time. In the study of pig house air samples (Hansen et al., 2012a), a reasonable correlation ($R^2 = 0.53$) was found between measured and predicted odor concentration, but the influence of sampling storage was also emphasized. Based on previous work, there is a strong need to examine if the prediction of the odor concentration can be improved if both odor concentration and odorants are measured on-site at the pig production facilities without any interference from the collection of air samples in sample bags.

The aim of the present study was to 1) develop a multivariate statistical prediction model (PLS) based on on-site measurements of odor concentration measured by dilution-to-threshold with human panelist and chemical measurements of odorants by PTR-MS and 2) identify important odorants that should be included in evaluation of odor emission and abatement technologies for pig houses. The use of simultaneous field olfactometry and online mass spectrometry has not been attempted previously for complex pig production odor and will overcome some of the challenges mentioned previously (Trabue et al., 2011). The approach will eliminate loss of compounds in sampling bags and will therefore provide a much more realistic comparison of odor and odorant composition than what has been obtained so far. In order to achieve a suitable range of odor levels, measurement locations with and without odor abatement technology have been carefully selected. The aim of this was to include high, low and intermediate odor/odorant concentrations in the prediction model in order to achieve a relatively high distribution of data. In addition, the data also provides insights into the effects of abatement technologies on odorant composition.

2. Materials and methods

2.1. Analytical methods

A TO8 olfactometer (Odournet GmbH, Kiel, Germany) was used to estimate the odor concentration. The olfactometer was based on the yes-no response method and was designed for four panelists. The olfactometer was able to dilute the samples from 65,536 to 4 times dilution with a step factor of 2. The presentation time at each dilution step was set at 2.2 s. All olfactometric procedures, including selection of panelists, were carried out according to the European standard for odor analysis (CEN, 2003).

A high sensitivity PTR-MS (Ionicon Analytik GmbH, Innsbruck, Austria) was used to measure odorants in pig house air. In PTR-MS, chemical ionization is performed by using H_3O^+ as a primary ion to protonate all compounds with proton affinities above water (691 kJ mol^{-1}). The principle of the PTR-MS has been described in detail in several review papers (Lindinger et al., 1998; Hewitt et al., 2003; de Gouw and Warneke, 2007) and the application of PTR-MS for measuring pig house odorants including details on quality assurance procedures have been detailed in previous papers (Feilberg et al., 2010; Hansen et al., 2012b). The detection limits depend on the dwell time on each ion and the specific detection limits determined in this case are included as Supplementary Information. Comparison of PTR-MS measurements of odorants with discrete measurements by thermal desorption GC/MS has been provided by Hansen et al. (Hansen et al., 2012b). Standard drift tube conditions were applied with a pressure between 2.1 and 2.2 hPa, a voltage at 600 V and a temperature at 60 °C. The inlet temperature was set at 60 °C. These settings suppress the formation of water clusters that may otherwise affect quantification. The PTR-MS was operated in scan mode between m/z 22–200 with a dwell time at 200 ms. Instead of using raw ion counts as input to the statistical model, all m/z intensities were converted to concentration in units of ppb as described previously (de Gouw and Warneke, 2007) by using a general proton transfer rate constant of 2×10^{-9} cm^3 s^{-1}. The advantage of this is that data is converted into an approximate concentration and becomes independent of specific measurement conditions (temperature, pressure and primary ion concentration). Transmission factors used for converting ion counts to concentrations (de Gouw and Warneke, 2007) were determined routinely based on a certified mixture of aromatics (TO-14, Restek, USA). More accurate concentrations of selected compounds (see Table 1) were determined using compound-specific rate constants either available as experimental values or calculated by the method recommended by Cappellin et al. (2012). This approach has been observed to provide accurate concentrations within an uncertainty of ±10% (Cappellin et al., 2012). Including the uncertainty of the transmission mixture, we estimate