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Non-methane volatile organic compounds predict odor emitted from five tunnel ventilated broiler sheds

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HIGHLIGHTS

- The relationship between poultry NMVOCs and odor was determined using chemometrics.
- A small set of NMVOCs provided strong predictions of odor.
- High litter moisture favored sulfurous odorants but did not affect odor concentration.
- High bird density favored non-sulfurous odorants and slightly increased odor.
- The dominant odorants were primarily associated with the litter, manure and feed.

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ABSTRACT

Non-methane volatile organic compounds (NMVOCs) emitted from mechanically ventilated poultry sheds in similar stages (32–36 d) of broiler production were measured by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS), then identified using parallel factor analysis (PARAFAC2) and the NIST11 database. Calibration models predicting odor measured by dilution olfactometry from NMVOC concentrations via orthogonal projection to latent structures (O-PLS) made good predictions (R^2_p = 0.83–0.87, $RMSE_p$ = 137–175 OU) using one to eight NMVOCs with either one or two latent variables representing odor concentration and character, respectively. Similar changes in odorant composition were observed in each sampling campaign, with samples collected early in the day more odorous and more sulfurous than samples collected later in the day. High litter moisture favored sulfur-containing odorants over alcohols, aldehydes and ketones but had little bearing on perceived odor, whereas high bird density favored alcohols, aldehydes and ketones over sulfur-containing odorants. Eight VOCs that were important predictors of odor across all sheds in order of decreasing importance were dimethyl sulfide (DMS), dimethyl trisulfide (DMTS), 2-3 butanedione, 3-methyl-butanal, 1-butanol, 3-methyl-1-butanol, acetoin, and 2-butanone. Four additional NMVOCs also influenced perceived odor although less predictably; these were *n*-hexane, 2-butanol, dimethyl disulfide (DMDS), and 1-octen-3-ol. All of the odorants are associated with microbial or fungal activity in the litter and manure, except *n*-hexane, which may originate from hexane-extracted soybean meal in the chicken feed. The organosulfides measured in this study may have arisen from the field sites as well as from the degradation of thiols captured on sorbent tubes during analysis by TD-GC/MS.

1. Introduction

The expansion of intensive animal farming practices to meet greater demand from increasing meat consumption is resulting in greater incidence of odor annoyance at the same time that community tolerance for poor air quality is diminishing (Powers et al., 2005). Developing cost-effective strategies for reducing odors requires the major contributing odorants to be identified from the soup of potential odorants present, allowing odor-reduction strategies to be targeted toward the compounds that contribute most greatly to annoyance. A better understanding of the relationship between odorants and odors is also needed to improve the design of non-specific sensor arrays for online odor monitoring (Stuetz et al., 1999; Hobbs et al., 2001; Sohn et al., 2008).

In broiler sheds where poultry are raised for human consumption, odorants are released from the birds or generated in the litter, then expelled to the surroundings by ventilation fans. The composition and concentration of bird odor varies according to age, activity, and diet (Robertson et al., 2002). In the litter, the aerobic biodegradation of uric acid, animal fats and proteins results in odorous nitrogen-containing compounds including ammonia, amines and volatile fatty acids (Jiang and Sands, 2000). Reduced litter moisture is reported to inhibit anaerobic bacterial activity

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limiting the formation of anaerobically-produced odorous gases, and further plays a role in microbial and fungal community composition (Wadud et al., 2012).

Gas chromatography coupled with mass spectrometry (GC/MS) is used widely to identify and quantify VOCs emitted by livestock operations (Schiffman et al., 2001; Filipy et al., 2006; Trabue et al., 2010, 2011; Blanes-Vidal et al., 2012). In complex GC/MS datasets containing many unknown compounds, chemometrics can assist in separating overlapping elution peaks, increasing the accuracy and sensitivity with which compounds are identified and quantified (Amigo et al., 2010; Murphy et al., 2012). However, an operational difficulty is that the functions relating odorant concentration with annoyance vary greatly between VOCs, confounding the interpretation of these data. Furthermore, odor perceived at the human receptor is the product of many volatile chemicals interacting in complex ways that are as yet poorly understood (Ferreira, 2012). These limitations may be at least partly addressed by coupling GC/MS data with measurements of human-perceived odor in order to sift out the important VOCs influencing odor detected by the human receptor (Jacobson et al., 1997; Blanes-Vidal et al., 2009; Akdeniz et al., 2012). Perceived odor is most commonly determined using dilution olfactometry, which involves presenting a series of diluted air samples to a panel of selected human assessors according to a standardized protocol and identifying an odor concentration (OU m^{-3}) equal to the minimum concentration perceived by 50% of the population (Standards Australia/Standards New Zealand, 2001). In the case that the air samples contain a mixture of odorants, this method can provide useful information on the synergistic impact of various odorants at the human receptor.

Multivariate calibration techniques can be used to relate properties of a chemical system that are difficult or expensive to measure, such as perceived odor, with more easily measured attributes, such as NMVOC concentrations. Potential non-linearities between the predictor attributes and the properties of interest can be handled using a linear model such as partial least squares (PLS) regression (Sjöström et al., 1983) in combination with appropriate transformations or non-linear expansions of the input variables (Taavitsainen and Korhonen, 1992). If the attributes are accurately measured and responsible for the properties of interest, it is theoretically possible to develop robust models that accurately predict these from the easily-measured variables (Martens, 2001). In the case where odors are sourced from livestock facilities, NMVOCs both contribute to odor and are much more easily quantified than is odor itself, making multivariate calibration an efficient means of developing testable predictions relating odor to odorants, and in so doing, identifying which NMVOCs have the greatest influence on perceived odor.

Odor-odorant models have been developed previously for environmental samples collected at wastewater (Stuetz et al., 1999) and pig production facilities (Gralapp et al., 2001; Zahn et al., 2001a; Blanes-Vidal et al., 2009; Akdeniz et al., 2012; Hansen et al., 2012), but have not led to a clear consensus regarding the most important predictors of livestock odor (Bunton et al., 2007). Compounds proposed as predictor odorants for livestock odors include hydrogen sulfide (Hobbs et al., 2001; Blanes-Vidal et al., 2009), however, correlations between odors in environmental samples and measured H_2S are often weak particularly when data are pooled across sites (Jacobson et al., 1997; Guo et al., 2000). This suggests an important contribution of NMVOCs and other compounds present within the emissions from intensive livestock operations to perceived odors (Zahn et al., 2001b).

In this study, multivariate calibration models were developed to study the relationship between NMVOCs and odor in five broiler sheds, each containing 35 000–45 000 birds aged between 32 and 36 d. The aims were threefold; first, to accurately predict perceived odor from measured NMVOC concentrations; second, to identify "ubiquitous odor predictors", defined as NMVOCs which improved the prediction of odor in all five sheds; and third, to identify relationships between ubiquitous odor predictors and other measured NMVOCs that were less robust predictors of odor, but may still have contributed to odor in some sheds.

2. Methods

2.1. Experimental design

Samples were collected from five broiler houses in Queensland, a dry subtropical region in northeastern Australia, during April and May, 2008. The broiler houses were long, narrow tunnel sheds and were mechanically-ventilated by axial fans located at one end. Sampling was conducted over a 1–2 d period at each farm, timed such that birds were at similar stages in their production cycles (aged 32–36 d). The stage prior to the first harvest at around 35 d was chosen for study since bird mass and odor emissions were expected to be at a maximum. Management practices at each shed were similar, with wood shavings comprising the litter material.

On each sampling day, up to 6 pairs of replicate samples for each chemical and olfactometry analysis were collected between 0700 and 1300 h from the face of one of the tunnel-ventilation fans; these are referred to as 'fan-face samples'. Additional samples were collected from within the broiler houses if access could be gained after the first batch of birds had been removed when approximately 35 d of age. These 'wind tunnel' samples were collected directly from the litter, using the wind tunnel apparatus previously described by Hudson et al. (2009). Ventilation rates in the sheds were determined by the in-shed environmental control system, and generally increased with ambient temperature throughout each sampling campaign. Thus ventilation rates differed between pairs of replicate samples collected on the same day.

2.2. Odor measurement by dynamic olfactometry

The olfactometry data used in this study represent a subset of data presented by Dunlop et al. (2010) in their study of odor emission rates at nine Queensland poultry farms. The current analysis is restricted to five farms at which paired GC/MS and olfactometry data were obtained (Farms D-I). Odor emission rates in these sheds were reported by Dunlop et al. (2010) to be between 330 and 1800 OU s^{-1} per 1000 birds.

Apparatus and methods used for collecting the olfactometry samples have been described in detail by Dunlop et al. (2010) and references therein. Briefly, replicate odor samples were collected in customized 120-L drums lined with a specially prepared polyethylene terephthalate (PET, Melinex®, 15 mm, DuPont Teijin FilmsTM, Chester, VA, USA) bag. The bags were filled using negative pressure over approximately 10 min. Odor samples were transported to the laboratory and analyzed within 8 h of collection. In the laboratory, olfactometry analysis was performed using an 8-panellist, triangular, forced-choice dynamic olfactometer operated by DAFF, Toowoomba, constructed and operated in compliance with the requirements of the Australian/New Zealand Standard for Dynamic Olfactometry, AS/NZS 4323.3:2001 (Standards Australia/Standards New Zealand, 2001). In this procedure, 8 panelists compared various dilutions of odor samples with clean air in several independent presentations (rounds), reporting whether they detected an odor difference. Panelists were first screened using *n*-butanol to ensure their detection threshold was within the required concentration range of 20–80 ppb (v/v). A robust geometric mean representing each sample's odor was determined, and the arithmetic mean was calculated for each pair of replicate samples