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ScienceDirect

Atmospheric Environment 42 (2008) 3332–3341

ATMOSPHERIC ENVIRONMENT

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# Field sampling method for quantifying volatile sulfur compounds from animal feeding operations

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Received 5 October 2006; received in revised form 17 March 2007; accepted 18 March 2007

## Abstract

Volatile sulfur compounds (VSCs) are a major class of chemicals associated with odor from animal feeding operations (AFOs). Identifying and quantifying VSCs in air is challenging due to their volatility, reactivity, and low concentrations. In the present study, a canister-based method collected whole air in fused silica-lined (FSL) mini-canister (1.4 L) following passage through a calcium chloride drying tube. Sampled air from the canisters was removed (10–600 mL), dried, preconcentrated, and cryofocused into a GC system with parallel detectors (mass spectrometer (MS) and pulsed flame photometric detector (PFPD)). The column effluent was split 20:1 between the MS and PFPD. The PFPD equimolar sulfur response enhanced quantitation and the location of sulfur peaks for mass spectral identity and quantitation. Limit of quantitation for the PFPD and MSD was set at the least sensitive VSC (hydrogen sulfide) and determined to be 177 and 28 pg S, respectively, or 0.300 and 0.048 $\mu g\,m^{-3}$ air, respectively. Storage stability of hydrogen sulfide and methanethiol was problematic in warm humid air (25 °C, 96% relative humidity (RH)) without being dried first, however, stability in canisters dried was still only 65% after 24 h of storage. Storage stability of hydrogen sulfide sampled in the field at a swine facility was over 2 days. The greater stability of field samples compared to laboratory samples was due to the lower temperature and RH of field samples compared to laboratory generated samples. Hydrogen sulfide was the dominant odorous VSCs detected at all swine facilities with methanethiol and dimethyl sulfide detected notably above their odor threshold values. The main odorous VSC detected in aged poultry litter was dimethyl trisulfide. Other VSCs above odor threshold values for poultry facilities were methanethiol and dimethyl sulfide.
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*Keywords:* Volatile sulfur compounds; Animal feeding operations; CAFO; Odor

## 1. Introduction

There is much agreement as to the source of odor in rural landscapes; however, there is little agreement and understanding as to what constitutes odor from animal feeding operations (AFOs). The presence of odors in rural communities has been shown

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*Abbreviations:* AFO, animal feeding operation; VSC, volatile sulfur compound; PFPD, pulsed flame photometric detector; RH, relative humidity; FSL, fused silica lined; OAV, odor activity value; ppmv, parts-per-million volume; ppbv, parts-per billion volume; SPME, solid phase microextraction.

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1352-2310/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2007.03.016

to affect not only the quality of life surrounding these facilities (Thu et al., 1997; Wing and Wolf, 2000) but also the property values of homes in their general vicinity (Palmquist et al., 1997). Schiffman and Williams (2005) have speculated that odors are not only a nuisance but also have potential environmental and health effects associated with them. However, data linking odors to any type of respiratory impairment are scant (Schiffman et al., 2005) with most health-related effects being based on self-reporting of symptoms (i.e., headaches, runny nose, etc.) in both laboratory studies (Schiffman et al., 2005) and rural community surveys (Thu et al., 1997; Wing and Wolf, 2000). Consequently, understanding the source of odor may help in determining potential health risks associated with odor and help in the development of odor abatement strategies.

Until recently, most air quality monitoring studies at AFOs typically focused on volatile organic compounds (VOCs), hydrogen sulfide, and ammonia as odorous pollutants (Zahn et al., 1997, 2001; Schiffman et al., 2001; Gralapp et al., 2001; Lim et al., 2003; Wright et al., 2005). Little attention has been given to the importance of volatile sulfur compounds (VSCs), and the techniques employed in these studies may actually preclude detecting many of these compounds. Despite the analytical sampling shortcomings of these studies, conclusions of many of these papers are that VSCs are not a significant contributor to odor from AFOs (Zahn et al., 1997; Schiffman et al., 2001; Wright et al., 2005). These conclusions regarding VSCs may be erroneous given the low odor threshold values of most VSCs (Devos et al., 1990) and the fact these compounds have been identified as the dominant odorants emitted from both municipal sewage systems and pulp and paper mill facilities.

In general, hydrogen sulfide is the only VSC monitored at AFOs, but recent work by Willig et al. (2004, 2005) measured methanethiol at a swine facility as high as $160\,\mu g\,m^{-3}$ (Willig et al., 2005), which is more than 70 times above its odor threshold value. This may indicate that methanethiol adds significantly to odor; however, no study to date has focused on VSC emitted from AFOs. The extent to which other VSCs contribute to odor is largely unknown since sampling and analysis of VSCs is challenging due to the volatility (Wardencki, 1998; Lawrence et al., 2000); reactivity (Chen and Morris, 1972; Millero et al., 1987; Devai and DeLaune, 1994; Wardencki, 1998; Bandosz, 2002; and Bentley and Chasteen, 2004); loss on surfaces (Kuster and Goldan, 1987; and Sulyok et al., 2002); and low concentrations in ambient air (Wardencki, 1998). Methods need to be developed that are robust enough to handle typical environmental conditions at AFOs (i.e., temperature, humidity, and dust), while at the same time being able to speciate and quantify VSCs.

Field sampling of VSCs for speciation purposes consist of either pre-concentration of select compounds or whole air samples. Pre-concentration of VSC in ambient air using solid-phase microextraction (SPME) has been demonstrated to be inadequate for quantitative purposes due to competitive sorption/reverse diffusion of other volatile compounds (Murray, 2001; Lestremau et al., 2003a, b), transformation of compounds during analysis (Nielsen and Jonsson, 2002a; Lestremau et al., 2004), and difficulty of calibrating fibers matching the sampling air matrix (Haberhauer-Troyer et al., 1999; Nielsen and Jonsson, 2002b; Lesteremanu et al., 2003a, b). While there has been some success in the use of sorbent tubes for VSC analysis (Tangerman, 1986; Radford-Knoery and Cutter, 1993; Simo et al., 2003), relative humidity (RH) (Steudler and Kijowski, 1984) and transformation of VSC during analysis (Baltussen et al., 1999; Lestremau et al., 2004) are still major obstacles faced when using sorbent tubes.

Whole air sampling has many of the same issues that pre-concentration techniques have since air samples from these containers must be concentrated with SPME fibers or thermal desorption tubes prior to analysis. In addition, Tedlar bags may be effective at holding VSCs in dry environments (Sulyok et al., 2001); however, in humid environments, this technique has been shown to sorb and potentially degrade VSCs (Kuster and Goldan, 1987). Drying of air using desiccates has been shown to improve results with Tedlar bags, but the results are short term due to the diffusion of humidity into the bags with storage (Nielsen and Jonsson, 2002a, b; Cariou and Guillot, 2006). Stainless-steel canisters and surfaces have also been found unsuitable material for the sampling and transferring of VSCs since exposure to these surfaces leads to the rapid loss of the most reactive compounds (Parmar et al., 1996; Kim et al., 2006).

The development of fused silica coatings onto stainless steel has reduced the surface reactivity of stainless steel and improved the storage stability and recovery of VSCs from stainless steel canisters