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University of Veterinary Medicine
Research Institute of Veterinary Medicine
Hlinkova 1/A
040 01 Košice
Slovak Republic

CHEMICAL INDICATORS THAT DETERMINE OLFACTORY RESPONSE FROM PIG AND CHICKEN MANURE

***Hobbs,P.J.* [1], *Misselbrook,T.H.* [1], *Noble R.* [2], *& Persaud K.C.* [3],**

[1]*Institute of Grassland and Environmental Research, North Wyke, Okehampton, Devon, EX20 2SB.*
[2]*Horticultural Research Institute, Wellesbourne, Warwick, CV35 9EF.*
[3]*Department of Instrumentation and Analytical Science, UMIST, Manchester, M60 1QD.*

ABSTRACT

Determination of a human olfactory response to livestock odours by instrumental means has been sought to simplify on-site measurement and reduce cost. A new approach has been developed using volatile components to identify the olfactory response from different manure types. The chemical concentration of the odorants was determined in the headspace of pig manure. The headspace of chicken manure composted with straw was determined using thermal desorption -gas chromatography- mass spectrometry with the intention of finding marker compounds indicative of the olfactory response. The major odorous compounds were identified as those significantly greater than their odour threshold values. An equation for each manure odour was determined and able to predict the odour concentration. For odour from pig manure the predictive compounds, that are also odorants, were H_2S, 4-methyl phenol and acetic acid. H_2S, dimethyl sulphide, butanoic acid, methanethiol and trimethylamine were the significant odorants emitted from chicken manure. For composting chicken manure the odour response was proportional to the sum of the combined concentrations of H_2S + DMS. Synthetic odour mixtures were produced in the concentration ranges of the selected odorants for each manure type. Models were developed to explain variations of olfactory response using a trained odour panel. Sensitivity tests surprisingly revealed that 4-methyl phenol could reduce the olfactory response in certain circumstances for pig manure odours. Multiple linear regression and interpolative neural network approaches were used and the merits of both are discussed. Direct and rapid measurement of the sulphides on the chicken manure composting site was possible using gas detector tubes. There was a close correlation between the odour concentration of the odour samples and, measured on-site with gas detector tubes.

Keywords. Odour, olfactometry, GC-MS, odour analysis, livestock manure, modelling,

INTRODUCTION

Measurement of odours by either olfactometry or chemical analysis of volatile compounds has proved difficult because they are often near or at at their threshold of odour detection and these concentrations are in the parts per billion range ppb(v) (10^{-9}). Interpretation of an instrumental measurement as a sensory response requires knowledge of the chemical composition of an odour that requires advanced analysis. Concentrating the odorants is necessary at these low concentrations followed by thermal desorption into a chromatography coupled with mass spectrometry system to identify and quantify emissions from manure[1]. They have been recognised as containing mostly sulphides, ammonia, volatile fatty acids, phenols and indoles. Fifteen odorants have been identified as major components contributing to the odour of livestock wastes[2], but at different concentrations for different livestock wastes. This was confirmed by the production of synthetic odour samples(unpublished).

In this experiment, we aimed to determine the olfactory response from mixtures of odorants commonly found in pig[3] and chicken manure[2]. Secondly synthetic mixtures were used to demonstrate that the correct approach to develop the models. The applicability of the models was evaluated using data obtained from both chicken and pig manure odours.

EXPERIMENTAL

The concentration of each of the major odorants were identified by GC-MS for pig and chicken manure sources.
To build an interpretive model a mathamatically design was necessary. A second order uniform precision rotatable central composite design was used which essentially determines the most effective way to model the response as OC in terms of the best accuracy and precision[4].
A range of concentrations of hydrogen sulphide, 4-methyl phenol (fmp), ammonia and acetic acid were produced in tedlar sample bags to develop a model for the pig manure odour. Olfactory analysis was performed with an odour panel containing 8 people, selected according to recognised European criteria to determine the odour concentration. Odour concentration is the dilution factor necessary for a sample to achieve threshold odour concentration which is statistically percieved by 50% of the odour panel.
Multiple linear regression (MLR) was used to generate a model of the four odorant concentrations as explanatory variables for OC. A newly produced radial basis function neural network (RBFNN) was employed to allow complex functional forms to be modeled. Validation of the models was performed using odours from each of the manure types.

RESULTS

Odour from composted chicken manure

Odorants from the composted chicken manure that were found to exceed their detection thresholds by the greatest order of magnitude were, in decreasing order: H_2S, DMS, butanoic acid, methanethiol and trimethylamine[5]. Concentrations of NH_3 were generally above the detection threshold in most of the samples but did not affect OC. There was considerable variation in the relative difference between stages of composting in terms of

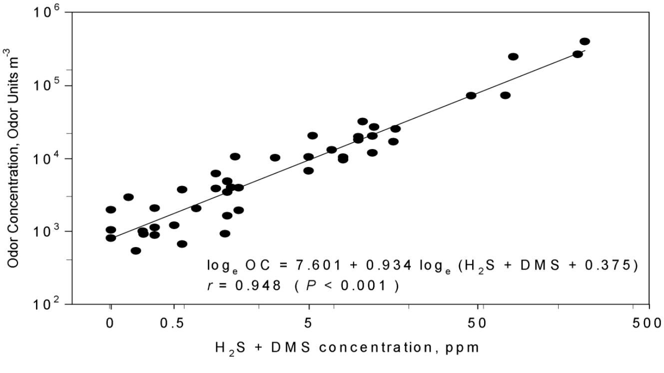

Fig. 1 Relationship between the combined on-site hydrogen sulphide and dimethyl sulphide concentrations and the 24-h odor concentration of mushroom composting odor samples. Each point is the mean of two sample determinations.

OC and H_2S, DMS and NH_3 concentrations. In this case the model was derived directly from the samples and was best described as shown in Figure 1.
Measuring H2S and DMS accounted for 45% (p=0.05) of the variance in OC from poultry manure compost after the exclusion of 2 outlier points. Neural network analysis identified 16 hidden nodes from the 24 data points and accounted for 75% of the variance for four odorant concentrations.

Odour from pig manure
H_2S and FMP concentrations accounted for the majority of the 74.1% variance of the model. Acetic acid and ammonia concentrations had a marginal and insignificant influence respectively. The model with standard errors for each variable is expressed in the equation

$$OC= 950 + 2630.[H_2S] -25617.[fmp] +179.[acetic]$$

This compared to 77% for the multiple linear regression analysis using H_2S, fmp and acetic acid concentrations. Neural network analysis identified 16 hidden nodes from the 24 data points and accounted for 88% of the variance for four odorant concentrations.

Figure 2 testing the pig manure odour

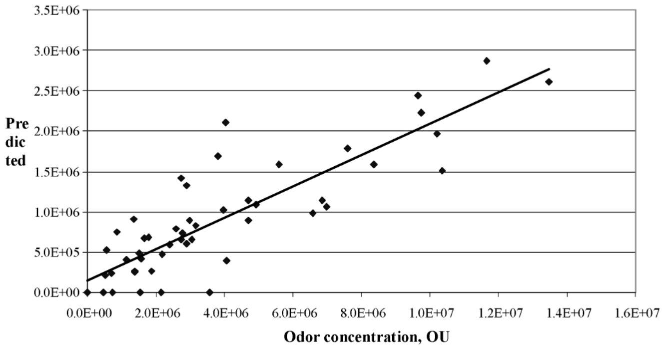

Figure 2 shows the applicability of the model to samples where the odour concentrations and chemical concentrations were measured. 76% of the variance was accounted for, however the odour concentrations were 20% less than predicted indicating other odour components were contributing to the olfactory response[6].

DISCUSSION

There are some general phenomena that describe the olfactory response from pig and chicken manure. H_2S was a primary odorant and necessary to modelling the relationship to olfactory response. Ammonia was below its odour threshold concentration and had no effect on the OC of the odorant mixture nor in the description of the olfactory reponse.
For the pig manure odours 4-methyl phenol gave a negative OC effect with increasing concentration, which was not identified statistically as a crossover effect within the model. The multiple linear regression model utilises H2S, 4-methyl phenol and acetic

acid. The concentration of the individual odorants did not follow an additive, geometric or average olfactory prediction. Radial basis function neural network software was able to improve upon multiple regression model to describe the OC with changing odorant concentrations. The one major limitation was that the the neural network model was only successful for OC values within the range of the model that is the range of the training database. However if we can limit the number of nodes used in the neural network we could approach a more normalised model that would be close to principal component analysis.

Only composted chicken manure was investigated where the major components were identified as hydrogen and dimethyl sulphides, methanethiol, butanoic acid and trimethylamine. However the model only included H_2S and dimethyl sulphide, where there was a close correlation between the OC of composting odour samples and the model adding H_2S + DMS.

CONCLUSION

The multiple linear regression approach was able to model the OC from pig manure odours and composted chicken manure. Our approach demonstrated that we have selected the appropriate volatile components that are also odorants to predict the OC for both types of manure.

The neural network approach operated well within the bounds of the training data presented to the process, however if the concentration of samples presented to the model to predict the odour concentration were outside of the range of the training data there was no correlation between the model and the olfactory concentration measured.

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