

# Odour emissions following land spreading of animal slurry assessed by proton-transfer-reaction mass spectrometry (PTR-MS)

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Emission of odorous compounds from field application of animal slurry is a major nuisance in rural areas where livestock waste is used as fertilizer. Technologies for reduction of odour nuisance have been proposed, but the efficiency of these in terms of odour reduction is difficult to evaluate due to major uncertainties in the measurement of odour by e.g. dynamic olfactometry. Chemical methods represent a more accurate and reproducible approach although the relationship between odorant concentrations and perceived odour is not completely resolved.

In this work, results from application of on-site direct mass spectrometry is presented and discussed. Odorants were collected in static flux chambers and odorants were measured by proton-transfer-reaction mass spectrometry (PTR-MS). The method was used in a laboratory-scale setup to assess the effect of pig slurry ozonation and subsequently in a full-scale field test for assessing the effect of soil injection of pig slurry. As a part of this work, a static chamber previously used in field trials was characterized in terms of odorant stability. Ozonation of raw pig slurry resulted in moderate emission reductions of several odorants, but H<sub>2</sub>S and 4-methylphenol were not affected and carboxylic acid emissions increased. Soil injection of untreated slurry was observed to have a significant potential for odorant emission reduction with best results obtained by a combined tine/disk injector system. A need for improvement of the static flux chamber method in order to obtain more stable concentration levels was identified.

## 1. Introduction

Although livestock manure is a source of plant nutrients odour nuisance associated with field application of manure remains a local environmental problem. Soil injection of animal slurry has previously been demonstrated to hold a potential for reduction of odor emissions compared to slurry application by trailing hoses (Hanna et al., 2000; Pahl et al., 2001). Recently, improved technology that allows for injection of slurry in growing winter cereal crops without significant crop damage has been developed (Nyord et al., 2009). Slurry treatment by e.g. solid-liquid separation or anaerobic digestion has also been proposed as a means of reducing odour emissions (Hansen et al., 2006; Hjorth et al., 2009). However, documentation of technologies for odour reduction from field-applied slurry is challenging because of the relatively large random and systematic

uncertainties associated with conventional measurements of odour by olfactometry (Clanton et al., 1999; Trabue et al., 2006). Chemical measurements of odorants have therefore been proposed as an alternative to olfactometry with the advantage of providing more reliable quantitative data. For emission studies, pre-concentration of samples for odour or odorant measurements has been achieved by a static chamber (Hansen et al., 2006; Hjorth et al., 2009) in order to obtain detectable levels. This method, however, has not been evaluated with respect to sampling time and compound recovery, partly due to the lack of sensitive time-resolved measurement methods.

In this work, time-resolved proton-transfer-reaction mass spectrometry (PTR-MS) is presented as a new tool used both in a field trial and in a laboratory-scale experiment to assess the effects of soil injection and slurry treatment by ozonation, respectively. As part of the work, a static chamber for pre-concentration of odorants has also been investigated.

## 2. Materials and Methods

### 2.1 Instrumentation

A high-sensitivity proton-transfer-reaction mass spectrometer (PTR-MS; Ionikon Analytik, Innsbruck, Austria) was used to monitor odorants. This technique utilizes an ionization technique based on protonated water ( $\text{H}_3\text{O}^+$ ) to convert neutral organic compounds into positive ions that are mass-filtered and detected in a quadrupole mass spectrometer. The technique has been reviewed in detail elsewhere (de Gouw and Warneke, 2007). Detectable compounds include known odorants from pig slurry comprising reduced sulphur compounds, volatile carboxylic acids, phenols, indoles and carbonyl compounds. Compound assignment was based on comparison with parallel analyses by gas chromatography – mass spectrometry with thermal desorption sample introduction. Air was sampled through a 6 m 1/8" Teflon tube temperature-controlled at 40°C. For the field measurements, the PTR-MS instrument was located on a truck close to the fertilized area. Sensitivity was determined by calibration based on certified gas standards or a Dynacal permeation device (VICI, Schwitzerland) as well as from calculated protonation rate constants as described by de Gouw et al. (de Gouw and Warneke, 2007).

### 2.2 Static chamber evaluation

The static chamber was made of hard PVC (height = 0.60 m, length = 2.40 m, width = 1.30 m) and was equipped with two internal ventilators (Desk Fan, FT6, Zhongshan, China). Two tests were carried out: In one, a mixture (Air Liquide) of  $\text{H}_2\text{S}$  (5.43 ppm  $\pm$  10%), methanethiol (5.17 ppm  $\pm$  10%), and dimethyl sulphide (5.33 ppm  $\pm$  10%) in  $\text{N}_2$  was injected into the chamber during two periods of 10 and 12 min, respectively. In the other, 3 l  $\text{m}^{-2}$  of pig slurry was distributed with a watering can over a grass surface before being covered by the static chamber. The temperature in the chamber was between 8 and 9°C. In both experiments the time-profiles of odour compounds were monitored by PTR-MS.

### 2.3 Field trial

The field test aimed at comparing emissions after manure application by conventional trailing hoses with emissions after application by 1) a rotating 400 mm disk injector and

2) an experimental injector consisting of two angled 400 mm discs followed by a simple tine.

Emission of odour after land application by the different application techniques was quantified by means of a static flux chamber technique using the chamber described above. The external surface of the chamber was covered by aluminium foil to restrict unequal solar heating of the chamber during sampling.

#### 2.4 Laboratory study

The experimental setup consisted of boxes packed with soil which had been adjusted to one of three moisture levels and then packed to a well-defined bulk density. Slurry was applied in triplicates by simulating trailing hose application. Polyethylene boxes of 21 liters volume were used as static chambers. Raw finisher pig slurry was treated by ozone using a LAB2B corona discharge ozone generator (Degremont Technologies, Glasgow, UK) at doses of 5 and 80 mg O<sub>3</sub> per liter manure. O<sub>3</sub> produced from pure O<sub>2</sub> was added during stirring of the manure via a stainless steel diffuser. For comparison, a volume of manure was also treated by bubbling O<sub>2</sub> gas through the liquid. Ozone treatment was carried out the day before adding manure to the soil.

### 3. Results and discussion

#### 3.1 Static chamber evaluation

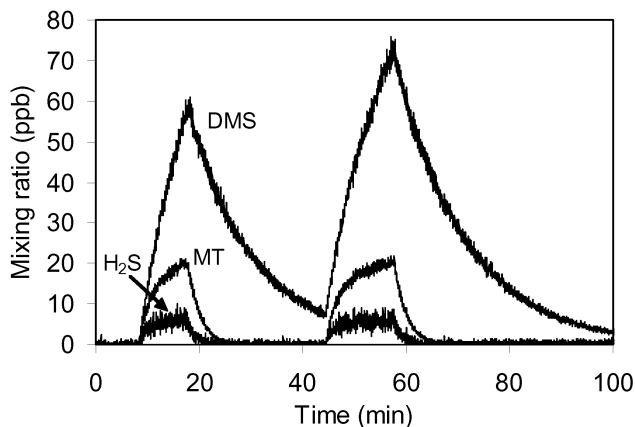


Figure 1. Results of two consecutive injections of a mixture of sulphur compounds (H<sub>2</sub>S, methanethiol, and dimethyl sulphide; each at ~5 ppm) into the emission chamber. The concentration increase and decays were measured continuously by PTR-MS. The gas mixture was turned off after 10 and 12 minutes respectively.

Selected results from testing the field static chamber are presented in Figure 1-2. From injection of a mixture of sulphur-gases at comparable concentrations it appears that very different air mixing ratios of H<sub>2</sub>S, methanethiol and dimethyl sulphide are reached. In addition, the decays of the compounds differ in that dimethyl sulphide is significantly more stable than methanethiol and H<sub>2</sub>S. Regarding the results from application of pig manure (Figure 2), a rapid increase to a high concentration of H<sub>2</sub>S was observed

followed by a decay leaving only ~10 % remaining after 20 min. For methanethiol and dimethyl sulphide the increase in concentration occurs at a slower rate and the decrease is onset at a later stage, especially for dimethyl sulphide (at ~30 min). Phenols are released more slowly from the manure into the chamber and relatively stable air concentrations are reached after 20-40 min. The results demonstrate the challenges in using time-averaged sampling for olfactometry and chemical analysis since concentrations in the static chamber are not stable. Since most applications of the static method assumes a certain pre-concentration time (15-20 minutes), the odour contribution of particularly H<sub>2</sub>S, but also methanethiol, may well be highly underestimated.

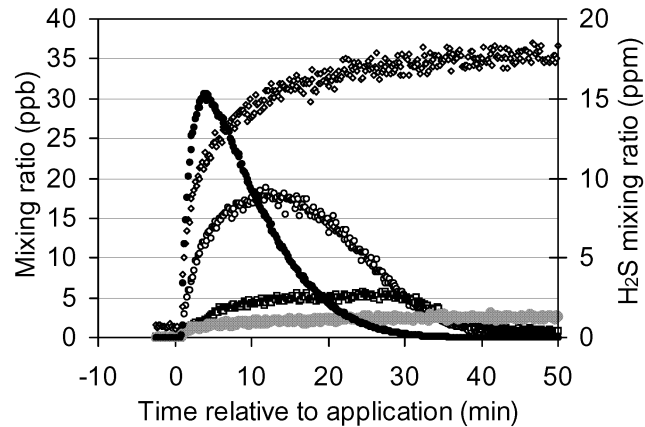


Figure 2. Results from monitoring H<sub>2</sub>S (*m/z* 35; ●), methanethiol (*m/z* 49; ○), dimethyl sulphide (*m/z* 63; □), 4-methylphenol (*m/z* 109; ◇) and 4-Ethylphenol (*m/z* 123; ●) by PTR-MS following application of pig manure and covering by a static emission chamber.

### 3.2 Field trial

Based on the above results, measuring by PTR-MS in the field trial was initiated immediately after covering the slurry-amended soil. Measurements of emissions from manure applied by trailing hoses were unfortunately influenced by surprisingly high levels of ammonia (>50 ppm) in the chamber to an extent at which it interferes with the ionization of other compounds in the instrument. Therefore, only the two injection techniques are compared as presented in Figure 3. The data shows that relatively low levels of odorants were detected compared to the results presented in Figure 2 and 3. Under the conditions of this field trial, stable concentrations of H<sub>2</sub>S were achieved.

As can be seen from Figure 3, significantly lower odorant emissions from manure applied by a combined disk/tine method can very clearly be documented. The reason is that with this technique the manure is covered with soil, whereas with the simple disk the manure is more directly exposed to air.

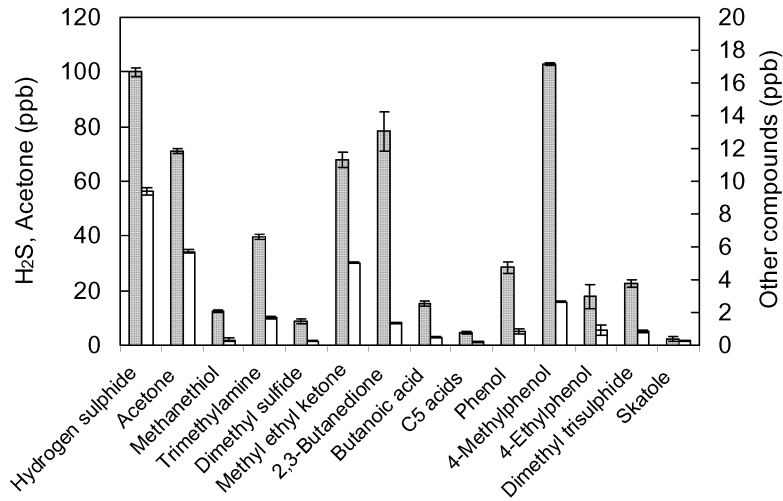


Figure 3. Concentrations of odorants measured in a static emission chamber placed above manure applied by disk injection (grey bars) and combined disk/tine injection (white bar).

### 3.3 Laboratory study

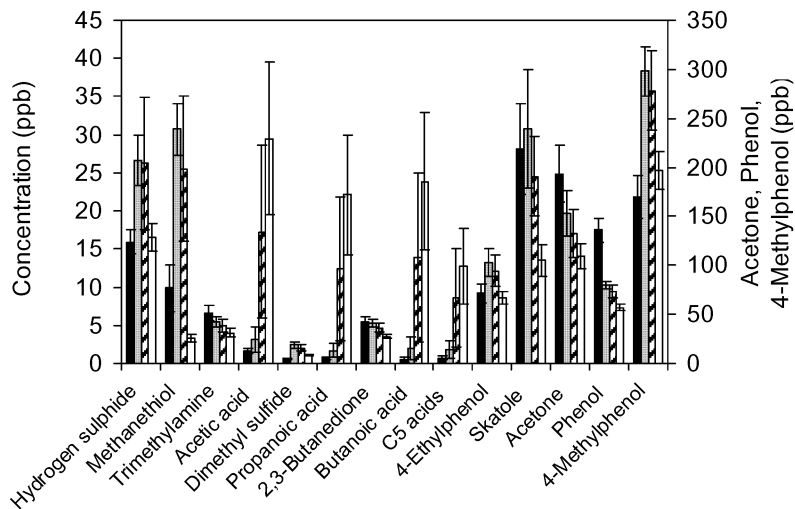


Figure 4. Concentrations of selected compounds in static chambers packed with soil as recorded 15 minutes after slurry application. Black: Untreated, Grey: Oxygenated, Diagonal stripes: Low ozone dose, White: High ozone dose. Error bars represent one standard deviation based on three chambers. The right y-axis is used for acetone, phenol and 4-methylphenol.

Comparison of ozone-treated, oxygenated and untreated manure is presented in Figure 4. It is observed that the highest dose of O<sub>3</sub> leads to reduction of the levels of several compounds; methanethiol, trimethylamine, 2,3-butanedione, 4-ethylphenol, skatole, acetone and phenol with reduction efficiencies ranging from 36-66%. 4-Methylphenol, which is presumed to be a major odorant, was not reduced. Low-dose ozonation and treatment with oxygen alone did in most cases lead to higher emissions. Furthermore, ozonation (low and high doses) was observed to lead to increased levels of carboxylic acids, presumably due to production of these as a byproduct of degradation of organic material. In these static chambers, H<sub>2</sub>S was observed to be stable.

#### 4. Conclusions

PTR-MS is a useful tool for quantitative measurements of odorous compounds from livestock waste as well as for documenting effects of emission abatement technologies. The static flux chamber used in the field did not allow for stable concentrations of sulfur compounds under certain circumstances and should be improved for future work.

Based on a field trial, it is documented that a slurry injection technique that includes covering of the applied manure with soil efficiently reduces odorant emissions. The potential of emission abatement by slurry ozonation as tested in laboratory scale was less clear since not all compound concentrations were reduced.

#### 5. References

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