Temporal Variation in Odorant Composition Following Land Application of Manure

Anders Feilberg*, Dezhao Liu, Tavs Nyord

Department of Engineering, Aarhus University, Hangøvej 2, 8200 Aarhus N, Denmark
af@eng.au.dk

Emissions of odorants following land application of livestock manure cause nuisance in the local environment for which reason odor legislation and abatement technologies are in demand. Collection of representative odor samples requires knowledge on emissions of odorants in the period following application of manure to soil or crop.

In this work, the temporal evolution of odorant emissions is investigated based on laboratory scale dynamic chambers and field scale wind tunnels. Measurements of odorants have performed using proton-transfer-reaction mass spectrometry (PTR-MS), which is a sensitive analytical technique with sufficient time resolution for characterizing the temporal evolution of odorant emissions.

It is observed that the most volatile and least water-soluble compounds, most notably H_2S, are only present in the initial few minutes following land application. In this initial stage, H_2S is assessed to contribute predominantly to odor based on its odor active value (OAV; concentration divided by odor threshold value). However, this contribution cease quickly within 10-20 minutes. The fast decay of emissions is well explained by the strong degree of partitioning of H_2S into the air phase. Sampling of this initial burst of odorant emission is very challenging due to the limited time available. At longer time scale, other odorants become more important, since they prevail and may be observed at levels above their odor threshold even on the next day following slurry application. The single compound that is estimated to contribute mostly to odor at longer time scales (based on OAV) is 4-methylphenol, but also 2,3-butanedione, trimethylamine and C5-carboxylic acids may be important.

The implications for using olfactometry to measure odor from land-applied slurry are discussed.

1. Introduction

Livestock manure slurry is increasingly used as fertilizer in agriculture (van Grinsven et al., 2012). However, application of livestock slurry to soil is also a source of odor nuisance (Hanna et al., 2000) and techniques for reducing odorant emissions (Feilberg et al., 2011;Hanna et al., 2000;Pahl et al., 2001) have been introduced. Although positive effects have been observed, there is clearly a need for further research on the effects of treatment technologies on specific odorants as well as the link between odor nuisance and composition of odorants. There is, however, a challenge in measuring emissions of odorants from manure applied to fields due to the lack of reliable sampling and measurement methods. Feilberg et al. (Feilberg et al., 2011) used a static chamber to investigate emissions of odorants and found several potential key odorants, but this techniques is only useful for relative measurements e.g. of the effects of different treatment methods. It was also observed that the static chamber had a profound impact on sulphur compounds, which were hardly detected after 15-20 minutes, despite being very abundant initially. Since static chamber techniques are often used for collecting samples for odor analysis by sensory evaluation (olfactometry) (Hansen et al., 2006), this sampling method could give very erroneous results if sulphur compounds (as expected (Feilberg et al., 2011)) contribute significantly to perceived odor. In addition to uncertainties linked to field sampling, sensory evaluation of odor is also flawed by very poor recovery in sampling bags (Hansen et al., 2011) as well as in dilution systems used for dynamic dilution olfactometry (Hansen et al., 2013). Since no solutions to this exist presently, an alternative approach for assessing odor based on key odorants (Hansen et al., 2012a) seems more viable at the moment, although

this approach needs further improvement. Analytical-chemical measurements of odorants may provide not only knowledge on key odorants, but also knowledge on the effect of slurry treatment on a molecular level. Due to the variation in volatility (e.g. H_2S vs. 4-methylphenol) and chemical stability it is likely, that the odorant/VOC composition of the emissions may vary over time, which is also indicated by the results obtained by Feilberg et al. (Feilberg et al., 2011). This may affect which key odorants are expected to cause nuisance at different periods after application and may also affect the choice of relevant abatement technologies.

As an alternative to field trials, emissions may also be investigated at laboratory scale using small model systems with an artificial air exchange (Nyord et al., 2008), which can be designed to simulate ambient conditions as far as possible (Reichman and Rolston 2002).

The aim of the present study was to test the use of dynamic flux chambers (laboratory scale) and a wind tunnel setup (both semi-field and field trial) to investigate emissions from manure slurry applied to soil with respect to the potential for measurement of key odorants by online proton-transfer-reaction mass spectrometry (PTR-MS). In addition, data on the relative magnitude and temporal trends in gaseous emissions are achieved.

2. Materials and methods

2.1 Laboratory-scale dynamic chambers
The setup used in the present work was identical to the setup used by Nyord et al. (Nyord et al., 2008). In short, soil was placed in dynamic chambers, which were rectangular PVC boxes (350 mm long, 250 mm wide, 170 mm high). The boxes were filled with 12 kg of soil to about 65% of their height, leaving a headspace of about 5.2 L. Air entered the chamber via two orifices (10 mm in diameter) placed 100 mm apart 50 mm from the top of the chamber. The air was sucked through the dynamic chambers at a flow of 13.6 L min^{-1} per chamber equal to an air exchange rate of 2.61 min^{-1}.

2.2 Field measurements with wind tunnels
The wind tunnel measurements were first carried out in a test with manually applied slurry on a grass surface and, since this proved successful, were subsequently used in a field trial in a comparison of full scale application techniques. The wind tunnels have been used previously for ammonia emission measurements (Nyord et al., 2012). The emission area of the wind tunnel is 0.85 m^2 and the average wind speed was controlled at 1 m s^{-1}. The volumetric air flow through the wind tunnel was 221 m^3 hour^{-1}.

2.3 Analytical measurements
Measurement of odorous gases was carried out by a high sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria). This online technique uses protonated water to ionize compounds with a proton affinity higher than water (Feilberg et al., 2010a). Selected m/z values (Table 1) were monitored over up to ~24 hours by PTR-MS.

The PTR-MS was run under standard drift tube conditions (2.15 mbar, 333 K) using a drift voltage of 600 V, which gives an E/N number (electric field per gas density) of 138 Townsend.

The sampling for the PTR-MS was done by a thermostatic valve system (50 C) consisting of 5 on/off valves controlled by the PTR-MS instrument. All sampling tubes were insulated and heated to 50 C.

The PTR-MS was calibrated with respect to sulfur compounds (H_2S, dimethyl sulfide and methanethiol) by means of certified reference gases at known concentrations (±10%) close to 5 ppm. The reference gases were diluted with clean air by using calibrated mass flow controllers (Sierra Instruments, Monterey, CA, USA). Humidity dependent H_2S calibration is necessary and was performed as described by Feilberg et al. (Feilberg et al., 2010b). For the remaining compounds, the sensitivity was estimated based on calculated or experimentally determined proton-transfer rate constants and a mass transmission curve measured as described previously (Feilberg et al., 2010b).

The PTR-MS was run in multiple ion detection mode (as opposed to full mass scan mode) in order to achieve the lowest detection limits and the highest time resolution. The ions were selected based on previous work on very similar systems (Feilberg et al., 2010b;Feilberg et al., 2011;Hansen et al., 2012b).

3. Results and discussion

### 3.1 Laboratory experiments using dynamic chambers

The experiments based on small dynamic chambers showed emissions of a range of compounds from the applied slurry. The dominant volatile compound was ammonia reaching concentrations of 25 ppm. In addition, H_2S and a number of volatile organic compounds were measured. The most important of these in terms of odour were identified by applying odor threshold values (OTV) to estimate odor activity values (OAV) of the individual compounds (OAV = concentration/OTV). Values of OTV were obtained from the comprehensive dataset by Nagata et al. (Nagata 2013). Key odor compounds within 5 minutes and after 180 minutes of emission under dynamic conditions are presented in Table 1.

Table 1. Key odor compounds with odor threshold values (OTV) and odor activity values (OAV) initially and 180 minutes after slurry application in a laboratory setup.

Compound	OTV (ppb)[1]	OAV$_{0-5min}$	OAV$_{180min}$
H_2S	0.7	261	ND[2]
Methanethiol	0.07	11	1
Trimethyl amine	0.03	240	6
Acetic acid	6	9	1
Butanoic acid	0.19	13	3
Pentanoic acid[3]	0.06	24	10
4-Methylphenol	0.05	126	26
2,3-Butanedione	0.15	55	10
3-Methyl-1H-indole	0.006	21	7

[1](Nagata 2013). [2]ND: Below detection limit. [3]Possibly a mixture of 2-3 isomers that cannot be distinguished by PTR-MS.

It can be seen that the initial odor is estimated to be dominated by H_2S and trimethylamine. However, since these decay relatively fast the odor contribution after 180 minutes is shifted towards a higher (relative) contribution by mainly 4-methylphenol. The results can be compared with recent data from a pig production facility, where odor was predicted by a semi-field statistical method to be caused mainly by H_2S, methanethiol, 4-methylphenol and trimethylamine (Hansen et al., 2012a). In our work, methanethiol concentration was very low, but otherwise the results are strikingly similar in terms of key odorants. 4-methylphenol has also been suggested by other researchers as a key odorant from pig production (Bulliner et al., 2006).
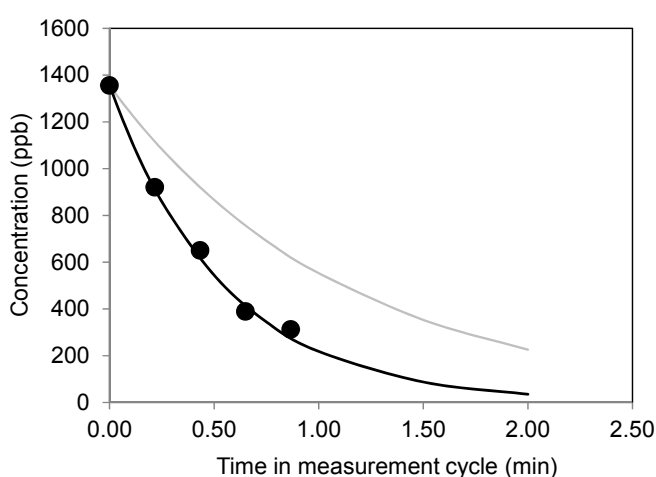
Figure 1. Example of initial H_2S decay within the first measurement cycle. The grey curve is a simulation using initial pH (7.6) and the black curve is a simulation using pH 7.2.

The initial contribution of H_2S is difficult to assess, since the emissions cease rapidly. Transient concentrations up to ~1000 ppb were measured and therefore odor may initially be completely dominated by a pulse of H_2S. However, this pulse was only detected in the first data cycle and a clear declining trend was seen within the measurement cycle (consisting of 5 consecutive measurements within one minute). In order to test if this is simply due to physical stripping of H_2S due to the high volatility of this compound, the decay was simulated by a simple expression based on pH, the Henry's law constant and the air exchange assuming instant equilibrium (no mass transfer limitation). One example of measured and simulated H_2S decay is presented in Figure 1. It can be seen that if the original pH is used, then the decay is even faster than what can be explained by physical stripping. However, this may simply be explained by a decrease in pH following soil application due to 1) a lower pH of the soil and 2) rapid evaporation of CO_2 from the soil surface. If pH is adjusted only 0.4 pH units from 7.6 (measured initially) to 7.2, then physical stripping explains well the decay.

3.2 Preliminary wind tunnel test

The preliminary wind tunnel test was carried out with manual slurry application on a grass field. Based on the experience with rapid decay of H_2S emission, great care was taken in order to measure immediately after slurry application. In this test (using cattle slurry) only two compounds were abundant at concentrations above their odor threshold values; H_2S and 4-methylphenol. The results are presented in Figure 2. As can be seen, the H_2S concentration initially reach very high concentrations (close to 1000 times higher than the odor threshold value), but in accordance with the results from the previous experiment, the concentration cease within ~10 minutes. On the contrary, 4-methylphenol reaches a more stable albeit lower concentration during the measurement period. Thus, the data indicates that 4-methylphenol may dominate the odor nuisance caused by slurry application except for the initial burst of H_2S. Due to the low odor threshold value of 4-methylphenol, the low concentrations still correspond to an OAV of 30-40 at the high air velocity of the wind tunnel. Although this was measured at a much higher air velocity compared to the laboratory setup, the concentrations are still within the same range.
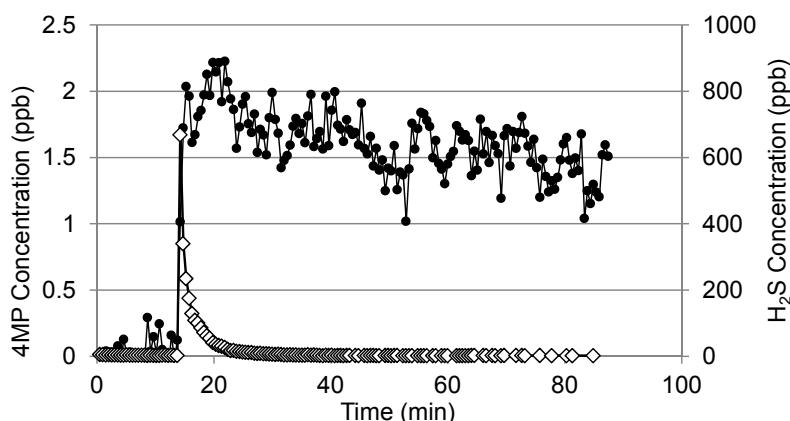

Figure 2. Concentrations of H_2S (◊) and 4-methylphenol (4MP; •)
measured in a wind tunnel following application of slurry at ~15 min.
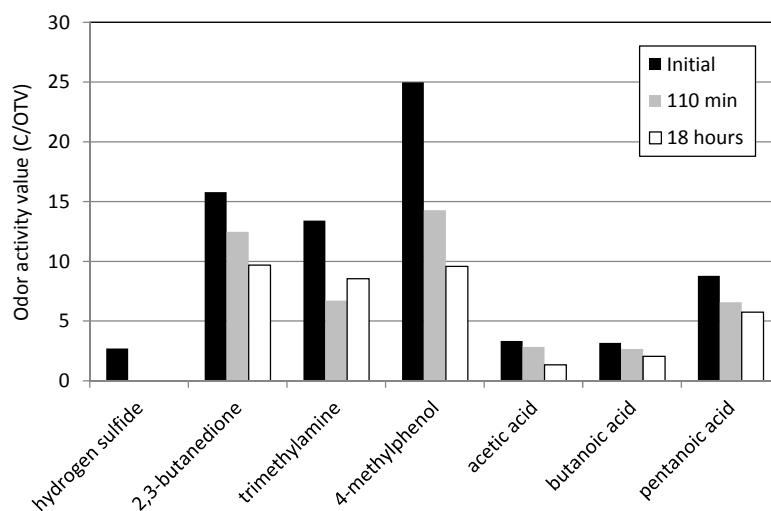
3.3 Field measurements

Following the preliminary test of the wind tunnel, an attempt was made to measure the odorant composition and temporal variation in a full scale experiment with cattle slurry applied to a field. Concentrations were monitored over a period of ~18 hours starting in the afternoon and continuing to the following morning. Selected results are presented in Table 2 as concentrations at three different time intervals. For practical reasons it was not possible to start the measurements immediately after slurry application and as a consequence the initial data was obtained after ~5 minutes. Since H_2S concentrations were very low even at the first measurement point, it is believed that the initial high H_2S emissions had already ceased when the first measurements were done. Furthermore, it appears that the concentration levels were relatively low in this experiment for unknown reasons. Still several compounds were detected in concentrations exceeding their odor threshold values, as seen in Figure 3. The odor compounds (apart

from H_2S) were still detected after ~18 hours of emission with the concentrations observed to be slightly reduced.

Table 2. Concentrations (ppb) of selected odor compounds following slurry application in the field measured initially (after 10 min), after ~110 minutes after 18 hours (day 2).

Compound	Concentration (t = 0 – 10 min)	Concentration (t = 110 min)	Concentration (t = 18 hours)
H_2S	1.9	ND	ND
2,3-Butanedione	2.4	1.9	1.5
Trimethylamine	13.4	6.7	8.6
4-Methylphenol	1.3	0.7	0.5
Acetic acid	20.0	17.1	8.0
Butanoic acid	0.6	0.5	0.4
Pentanoic acid[1]	0.5	0.4	0.4

ND: Below detection limit. [1]Possibly a mixture of 2-3 isomers that cannot be distinguished by PTR-MS.

Figure 3. Odor activity values of odor compounds present at concentrations above their odor threshold value at different times following field application of cattle slurry.

3.4 Implications for odor measurement

It is assessed that using olfactometry for quantification of odor following land application of manure will not give useful results because 1) the initial burst of H_2S is difficult to capture and 2) because the main odorants remaining after the initial 10-20 minutes are not well recovered in sampling bags and dilution systems used for olfactometry (Hansen et al., 2011; Hansen et al., 2013). Specifically, 4-methylphenol has a recovery of <10% in sampling bags used for olfactometry and trimethylamine has a similarly low recovery in the dilution system of an olfactometer. Hence, only a relatively small fraction of the original concentration of those odorants will reach the nose of panelists used for sensory measurement.

4. Conclusions

The temporal variation in odorant composition following slurry application was investigated with two different setups; laboratory scale and dynamic chamber, with the latter being applied in a semi-field test and a full scale field application. The results showed that H_2S is emitted in high amounts immediately after application of slurry, but emission of this compound cease rapidly by physical stripping in agreement with a simple simulation based on insignificant mass transfer limitation (close to instant air-slurry equilibrium). Other odorants are emitted for longer time scales and was observed in a field trial the day following the application. Thus, there is a pronounced change in odorant composition over time. The major odor

compounds apart from the initial 10-20 minutes are predicted (based on odor activity values) to be 4-methylphenol, 2,3-butanedione, trimethylamine and pentanoic acid.

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