MULTI-METHOD MONITORING OF ODOR EMISSIONS IN AGRICULTURAL BIOGAS FACILITIES

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ABSTRACT

The production of farm-based biogas and electricity is an area of alternative-energy interest to many livestock producers. However, it is still insignificant in comparison to the maximum potential of farms all over the world. Market penetration should involve better confidence in the technique and better understanding of its possible assets and limits. For instance, is the environmental impact of biomethanation positive or negative? What are the possible ways to avoid or to control process imbalances?
In the context of a European project, the research group attempted to tackle those questions under the angle of gas emission and more particularly of odor annoyance.

A multi-method approach was applied to monitor biogas and odor emissions, both at the laboratory level on pilot plants and at real scale in 4 agricultural biogas facilities, in Belgium, Luxembourg, France and Germany.
Results show that digested material is generally less odorant than crude manure or slurry, while preserving all the amendment and fertilizing qualities of the original material. Possible annoyance of agricultural biogas facilities in the surroundings remains limited and can be solved through simple techniques.

Keywords

Dynamic olfactometry; field inspection; anaerobic digestion; electronic nose

INTRODUCTION

The production of biogas from biomass is not a new concept, but the wish to better understand and to control this energy production path is becoming a recent challenge at the international level. Managers of biogas facilities are confronted with a huge variety of substrates of heterogeneous composition and the use of such products in bioreactors, without knowing their characteristics, can lead to serious process disturbances (Ward et al., 2008). There is no straightforward solution to early detect them. Hence, one of the major shortfalls in biogas production in the agricultural sector is the lack of reliable

sensory equipment to monitor key process and environmental parameters aiming at giving better confidence in the technique.
Keeping this aim in mind, sensory equipment focusing on the gas phase of anaerobic reactors should provide possible monitoring online tools while avoiding difficult sampling from highly heterogeneous sludge of high solid content.
And on the environmental point of view, the study of possible odor annoyance caused by agricultural biogas facilities should contribute to a better understanding of their possible assets and limits.

This paper presents a part of a study conducted in the context of a European project (2009-2012), with various partners, coming from different fields: agriculture, biology, environment, instrumentation … The present part concerns the attempt to tackle the question under the angles of gas emission and of odor annoyance.

METHODS AND OBJECTIVES

It is well known that odor is generally a complex gas mixture influenced by various factors and that the resulting annoyance can be measured by a range of available techniques, each of them having its particular interest (Romain et al., 2008). Therefore, a multi-method approach was applied to monitor biogas and odor emissions, both at the laboratory level on pilot plants and at real scale in 4 agricultural biogas facilities, in Belgium, Luxembourg, France and Germany.

The used methods are

- GC-MS to characterize the composition of gas emissions from farm bioreactors,
- dynamic olfactometry (Odile olfactometer, Odotech, Canada with 6 assessors) to assess the concentration of odor in the ambience of the farm and the odor flux of surface sources, through a dynamic flux chamber (EPA-type, Odotech, Canada),
- field inspection and back-calculation with an atmospheric dispersion model (Tropos Impact-Odotech) to estimate the global odor emission rate from the whole facility (Nicolas et al., 2006),
- portable olfactometer (Nasal Ranger™) measurements to validate field inspection results (McGinley and McGinley, 2004),
- self-made electronic noses, equipped with 6 tin-oxide sensors (Figaro™) to monitor biogas reactor headspace with the aim of detecting process imbalances.

Measurements were made at the lab scale in 12 anaerobic semi-continuous reactors loaded with different substrates (sucrose, maize oil and sugar beet pulp) and in 4 pilot-scale anaerobic reactors fed with sugar beet pulp and exposed to punctual process disturbances. Real-size agricultural facilities were located in the 4 countries of the "Great Region" comprising Germany's Saarland and Rheinland-Pfalz, France's Lorraine, Belgium's Wallonia and Luxembourg. Each facility produces from 800 000 m^3 to 2.5 million m^3 of biogas per year generating from 550 to 4450 MWh electricity and from 850 to 5600 MWh heat.
The objectives of the different measurements were

- estimating the odor impact of farms equipped for biogas production with respect to classical farms,
- comparing the odor concentrations in the ambience of different places inside biogas production facilities,
- comparing the odor fluxes generated by various materials, before and after bio-digestion,
- assessing the odor annoyance in the surroundings of facilities,
- comparing the odor emission after application of raw slurry or anaerobically digested slurry on grasslands via broadcast or subsurface deposition,
- detecting process disturbances in the gas phase of anaerobic digesters.

RESULTS AND DISCUSSION

As a general finding, the comparison of agricultural biogas facilities with traditional farms is not easy, due to the high variability between different plants of the same type. Moreover, in both farm types, odor sources are about identical: barns, manure storage, slurry, maize silage … And finally, in biogas plants, the odor annoyance is never due to the biogas itself, because it is produced and transported in closed and airtight circuits.

Preliminary chemical analyses of trace compounds of gas emissions from farm bioreactors show a variety of VOC's including for example ketones, alcohols and terpenes (e.g. alpha- and beta-pinene, limonene and p-cymene). Concerning ketones, 2-butanone was found in significant quantities in all samples. Some biogas samples contained a lot of sulphur compounds, such as thiols, sulphur dioxide or di- and tri-sulfides.
However, though qualitative gas composition was relatively similar from one sample to another, the relative abundances of volatiles are highly dependent of the material loading the reactor.
As observed in other studies (Rasi et al., 2007), most concentrated compounds were terpenes. Their presence is mainly due to the use of vegetable feedstock in on-farm biogas plants. When the sampling point was located after the filtering and cooling device, just at the entry of the cogeneration engine, it was observed that most of the trace VOC's were significantly reduced.

Various compounds in gas phase of the bioreactors are intermediates of the biological process that occurs in the liquid phase: alcohols, ketones, sulphur compounds. Some other compounds are directly emitted from feedstock of reactors, such as terpenes.
However, the high variability of the relative abundances of trace compounds in different biogas samples makes difficult an objective comparison of biogas production plants emissions on the sole basis of GCMS analyses.

No volatile fatty acids (VFA) were detected in any biogas sample. This could be due to the basic pH of the liquid phase (higher than 7.2), where VFA were present under the dissociated and non-volatile form. Another reason was probably the bad performance for C2-C4 molecules of Tenax adsorbent used in trapping cartridges.
Anyway, the analyses of the substrate (liquid or solid phase) exhibited a huge variation of the volatile fatty acid contents between the raw slurry/manure and the digestate (Ubeda et al., 2010). For the studied cases, the VFA reduction efficiency of anaerobic digestion lay between 77 and 96% for the liquid/solid phase.
As shown in figure 1, this VFA reduction was accompanied by a significant reduction of the odor concentration in air samples collected over the material.

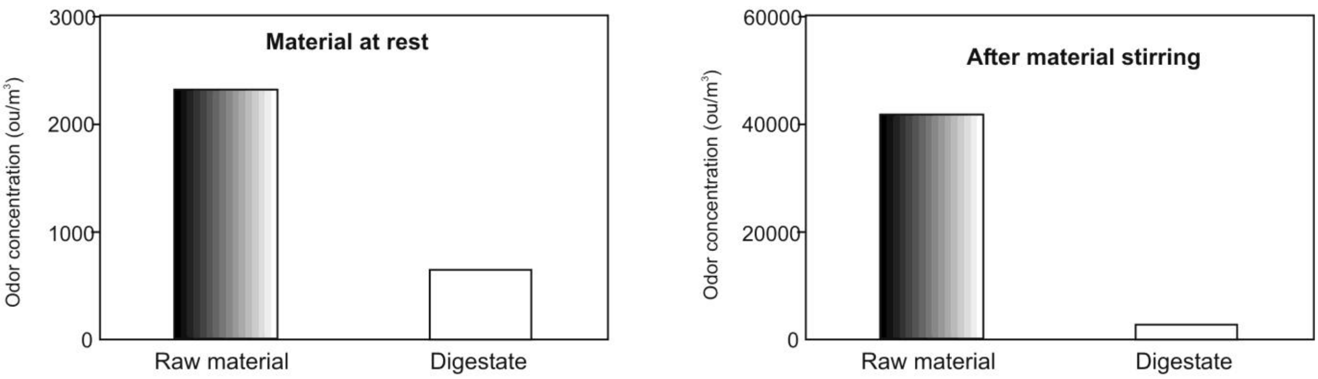

Figure 1 : Average values of odor concentration in headspace above raw material and anaerobically digested material, either at rest or after stirring.

VFA are actually often used as chemical indicators of the odor strength of livestock manure (Ni et al, 2012). Concerning the anaerobic digestion process, VFA are intermediate products resulting of the hydrolysis of organic material, but there are later converted into methane and carbon dioxide. And so, their concentration in digestate is relatively low. The concentration of other odorants, such as phenols, p-cresol, indole or skatole, could also be reduced during the biomethanation process.

In the conditions of material at rest, the odor concentration after digestion exhibited a three-fold decrease with respect to the raw material (slurry). When the material is stirred, this odor concentration difference could even reach a factor of 20. Such finding confirms the results of scientific literature (Hjorth et al., 2009). It is thus clear that anaerobic digestion reduces significantly the odor of the material which will later be spread on meadows.

More generally, the measurement of odor flux emitted by different materials confirms the trend that digested material is less odorant. Liquid digestate in tank emits about 1 $ou/m^2.s$; the odor flux of raw slurry can reach 70 $ou/m^2.s$; but the highest emission is observed for the storage of by-products of food industry, which are frequently used as co-substrates (up to 500 $ou/m^2.s$).

Similar tendency is observed in the ambience, with highest odor around raw material storage tanks, but which is only awkward when the material is handled. Table 1 shows typical odor concentrations measured for different locations in pilot farms.

Location	***Pilot farm***	***Odor concentration (ou_E/m^3)***
Cow barn	Palzem	634
Slurry pit	Beckerich	70 230
		283 698
		98 867
		10 935
		6 575
Storage of mixed solid waste (maize, chocolate fabrication by-products, manure)	Faascht	6 640
		86 980
		630
Liquid by-products of food industry	Faascht	533 700
Digestate storage tank	Beckerich	8 493
		5 368
		185
		83
	Faascht	2500
		450
Digestate drying	Faascht	1 371
		914
		602
		729

Table 1 : Odor concentration measured at different locations in pilot farms

On the basis of such spot measurements, it is difficult to estimate the fraction of the odor emitted by the anaerobic digestion process with respect to the one generated by the material usually present in an ordinary farm. Major odor fluxes are observed above the zones of storage of the raw material, prior methanation. However, most of these zones are covered and odor remains confined. Moreover, the odor flux depends on the material type, on its handling, on the period and on the location. In any case, by-products of food industry always produce highest odor emission rates.

Concerning the measurements in the vicinity of pilot farms, field inspection and back calculation were performed 8 times during spring and summer 2009 and 2010.

Table 2 presents the results. The maximum odor perception distance never exceeded 600 m and was always on this side of the first resident. The estimated odor emission rate was highly variable from site to site, but also for different days in the same site. The highest variability was observed for the farm of Faascht (Belgium), for which the maximum odor emission rate was due to the digestate drying, but for a short period of time during the whole year. At Beckerich plant (Luxemburg), the odor came mostly from the manure and maize silage as well as from the slurry, during its discharge in the pit. In this particular case, the odor is only attributed to the anaerobic digestion process, since there is no cow barn.
For the Palzem farm (Germany), only the maize silage odor emerged from the normal odor of the farm.

Pilot farm	**Odor emission rate (ou/s)**	**Maximum odor perception distance (m)**
Faascht	79 384	600
Faascht	10 725	250
Faascht	23 553	430
Beckerich	7 306	300
Beckerich	43 752	500
Beckerich	10 942	300
Palzem	24 197	300
Palzem	18 593	500

Table 2 : Results of field inspection and back calculation for 3 pilot farms

Considering those measurements, the average global odor emission rate from a typical facility could be estimated at about 20 000 ou/s, but with a high variability. As a benchmark, the odor emission rate estimated from landfill or composting areas with the same methodology and similar topography and climate conditions lies around 60 000 to 120 000 ou/s.

During field inspection, some measurements were made with the portable olfactometer Nasal Ranger^{TM}. They do not provide additional information with respect to the simple odor plume estimation, but they could be used for validation purpose. During the traditional plume measurement, observers note actually the odor perception limit, corresponding to the concentration of 1 ou/m^3. Nasal Ranger is able to measure also concentrations above the perception threshold. It was shown that these measurements were in good agreement with odor plumes simulated by the atmospheric dispersion model (bi-gaussian model Tropos Impact).

Figure 2 shows a series of measurements performed at Beckerich site in July 2009. The odor emission rate as adjusted by the back-calculation procedure was used to simulate, with Tropos Impact, the isopleths corresponding to different odor concentration values (black curves and values as banner-style labels). In parallel, the concentrations measured at different locations by the portable olfactometer are presented as white text pointing towards the measurement locations. Both series of values are matching together.

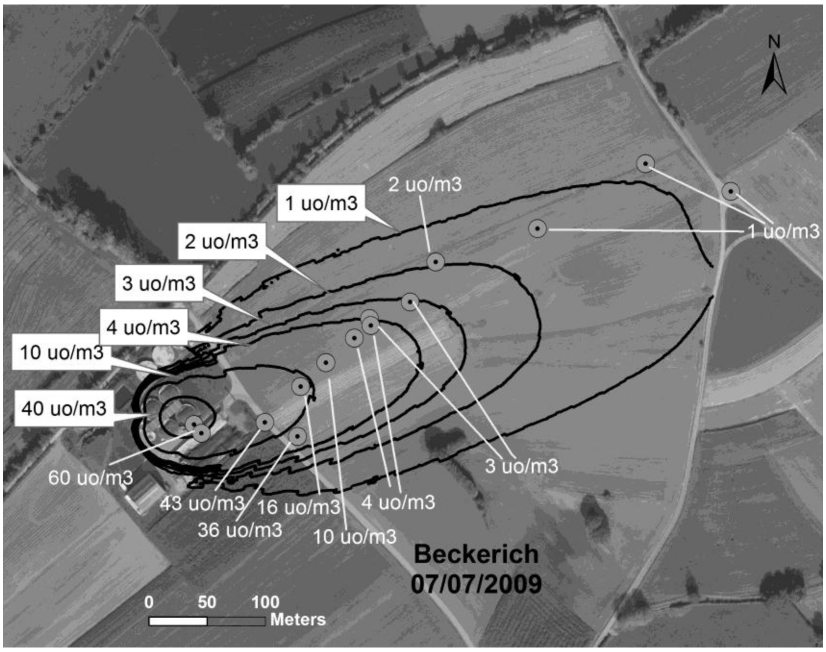

Figure 2 : Comparison of odor concentration isopleths and values measured by Nasal Ranger^{TM} field olfactometer.

Regarding the odor after the application of material on grasslands, odor samples were collected at different times after material application. A dynamic flux chamber (EPA-type Odotech Canada) was employed and the odor emission flux was determined after olfactometric measurement. Figure 3 shows clearly lower odor flux and quicker decreasing for application of digestate, but it was also shown that the application technique (broadcast or subsurface deposition) had greater influence on the emitted odor than the applied material type.

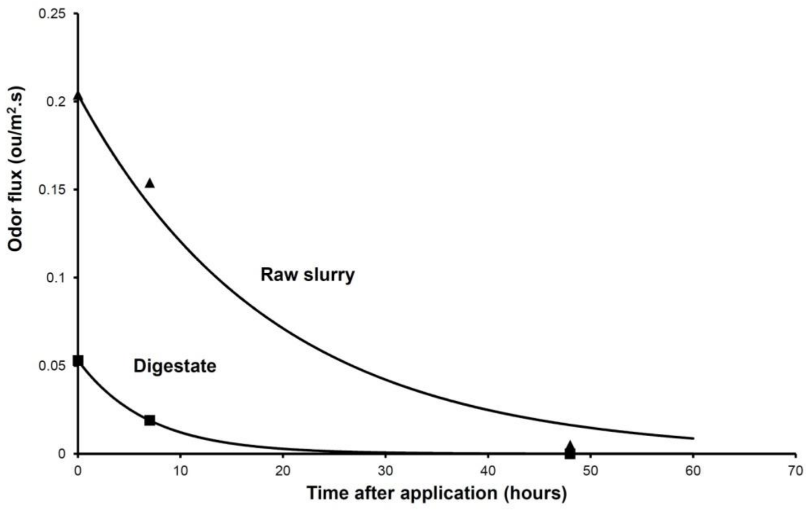

Figure 3 : Temporal decreasing of odor fluxes after application of raw slurry or digestate on grasslands.

Finally, the monitoring of biogas with electronic nose, both at the laboratory level and in real plants, demonstrates good potential of this technique to detect process disturbances such as ammonia inhibition or acidosis. It should constitute a powerful real-time tool for the plant manager to detect and prevent organic overload of the reactors (Adam et al., 2012). Different experiments were conducted either on mini-reactors in the lab, or on pilot-scale reactors, or in real farms. Figure 4 presents a typical result deduced from the monitoring of a pilot-scale reactor where different typical anaerobic digestion problems (ammonia inhibition, acidosis) were deliberately induced. A Principal Component Analysis was applied on the 6 sensor signals of the electronic nose and the variation of the scores for the two first factors (after suitable rotation), representing more than 84% of the total variance, is displayed on a time scale.

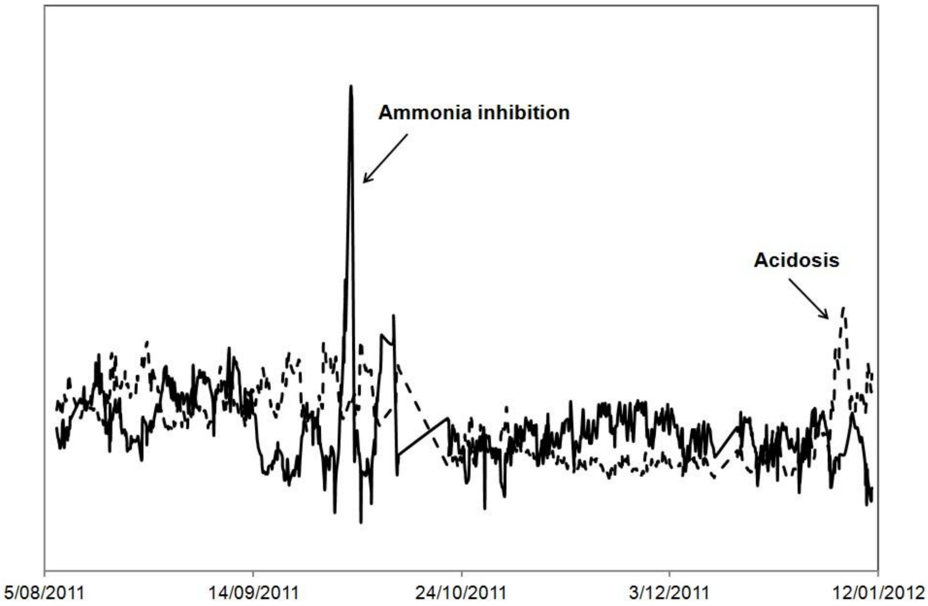

Figure 4 : Evolution of two indicators of process disturbance in the gas phase of anaerobic digesters based on PCA.

In this case, the first factor (solid line) is an indicator of ammonia inhibition and the second one (dashed line) an indicator of acidosis. So, with the same electronic nose, it is possible to follow two types of process disturbance in the gas phase of anaerobic digesters.

CONCLUSION

For a complete study of gas emissions of complex facilities, such as farms with biogas production, a tool box comprising complementary odor measurement techniques proves to be necessary. Each technique has its own niche and provides its own contribution to the global diagnosis.
In the present study, dynamic olfactometry was used to compare odor concentrations in the ambience of different locations inside production facilities. When the odor sample was collected through a dynamic flux chamber, it allowed estimating the odor fluxes generated by various materials, before and after biodigestion or after application on grasslands.
Field inspection technique and back-calculation coupled with field olfactometer measurements were used to assess the global odor emission rate of facilities, from which the odor annoyance in the surroundings can be deduced.
And finally, electronic nose was applied to detect process disturbances in the gas phase of anaerobic digesters.

For this particular study, it was shown that the odor generated by farms equipped for biogas production is not really higher than the one emitted from classical farms. Possible additional odor could be produced by higher volumes of material storage, prior methanation. However, after its anaerobic digestion, the odor of the material is significantly weakened. In all studied cases, the odor impact of such farms remained moderate and could be reduced by simple solutions, such as confinement of stored material.
Lastly, possible process disturbances could be early detected from the monitoring of the gas phase.

ACKNOWLEDGEMENTS

Authors gratefully acknowledge the financial support of the European Regional Development Fund through the INTERREG IVa programme.

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