Chemical and odorous atmospheric emissions from the methanisation process: Impact of raw materials and operating conditions

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A&WMA 112th Annual Conference & Exhibition
Quebec City, QC
June 25-28, 2019

INTRODUCTION

Methanisation seems to be a relevant response to the current problems of waste treatment and recovery in France such as fermentable organic waste. The energy recovery of the biogas produced by methanisation is performed either by cogeneration (electricity and heat production) or by direct injection of the purified gas into the natural gas network.
That's why in Europe, the diversification of energy production sources leads to an increase in biogas plants. However, the implementation of a biogas plant may generate many concerns with the neighborhood in term of odor annoyance and health risk. Many studies deal with chemical composition of biogas [1–6] . They characterized major compounds (CH_4, CO_2, O_2, N_2 and H_2O) and trace compounds as several oxygenated and sulfurous molecules contained in the biogas directly but not the emissions of all related activities of handling inputs and digestates.
To evaluate the nuisance potential (with respect to nearby people), the characterization of on-site odors and VOCs emissions is firstly required. The objective of this work is to characterize the emissions of the most significant sources in terms of odors and VOCs[7,8].

Plant description

In this study, chemical and odorous emissions from three biogas units using three different kinds of substrate have been monitored. Table 1 shows the main characteristics by evaluated site type.
Table 1. Characteristics of the investigated sites.

Site	Biogas production (m^3)	Waste
Farm	691,708	Liquid and solid manure
Territory	6,052,000	Liquid and solid manure, agri-food wastes
WWTP	1,559,000	Wastewater sludge

These three sectors represent about 90% of the digester units currently installed in France.
Thus, on the supply chain, the established sampling points are identical for monitoring chemical, biological and odorous emissions.

In this article, we focused on the emissions of some specific activities identified as particularly impacted by punctual actions (mixing, input delivery, etc).

Materials and methods

Gas Sampling
In this study, gas samples were collected in lab-made 40L Nalophan® bags according to the methodology defined in European standard EN 13725. Olfactometric and chemical analyses were conducted on the same sample to minimize time dependency of VOCs emissions.
Olfactometric analyses
Odor concentration are measured according to EN 13725 standard using an ODILE olfactometer (ODOTECH Inc, Canada) and a six panelists jury.

VOCs analyses
Different analyses were conducted on each sample to obtain a more precise characterization of VOCs emissions. Analyses were performed to evaluate the total VOCs concentration using a photoionization detector (ppb RAE, RAE Systems, USA). The concentrations of sulfurous compounds were measured with a GC-FPD (Chromatotec, France). Then, identification and quantification of VOCs were obtained utilizing a TD-GC-MS analysis (Turbomatrix, Perkin Elmer (USA) coupled to a Thermo Scientific GC-MS (USA)).

RESULTS

At each site, measurements were carried out with and without specific actions potentially affecting odor emissions. A brief presentation of the results is presented in the following paragraphs.

Farm
In the farm, only the mixing of liquid digestate tank generated an increase of odor emissions as shown in table 2.

Table 2. Characterization of emissions in the liquid digestate tank.

Activity	**Liquid digestate tank**	
	Without mixing	With mixing
Odor concentration (OU_E/m^3)	2,195	5,656
Total VOCs concentration (ppb isobutene eq.)	2,500	1,900

The odor concentration was doubled during agitation of the digestate tank while introducing the liquid digestate from the reactor located approximately 2m- above the liquid digestate tank. Nevertheless this increase did not result in a similar increase in the total VOCs concentration. Considering the VOCs identified in both samples, a modification of the composition is noted by the emergence of sulfurous compounds and a decrease in alkane and aromatic compounds. This shift of composition could explain the decrease in total VOCs concentration measured by PID because aromatics have a response factor higher than sulfurous compounds.

Territory plant
In this biogas plant, two activities have been identified as potentially contributions to the emission variations over time: solid manure storage (old or fresh) and the input preparation with or without a recent delivery of agri-food wastes. Results are summarized in table 3.

Table 3. Characterization of odorous emissions sources in the territory plant.

Activity	Solid manure arrival		Input preparation	
	Old	Fresh	Without recent delivery	With recent delivery
Odor concentration (OU_E/m^3)	706	7,741	3,706	18,867
Total VOCs concentration (ppb isobutene eq.)	8,700	23,000	640	20,500

As seen in table 3, a significant increase in odor concentration (ten-fold) was observed when fresh solid manure is delivered to the plant. Total VOCs concentration emitted from fresh solid manure are also higher (factor 2.5) than those measured from old solid manure sample. For the old solid manure sample, we identified a large amount of terpenes (15.5 mg/m^3 toluene equivalent), ketones (5.6 mg/m^3 toluene equivalent) and alcohols (3 mg/m^3 toluene equivalent). Arrival of fresh solid manure resulted in a compositional change of emissions, with an increase in ketones to 8.7 mg/m^3 toluene equivalent and additional detection of sulfurous compound (especially H_2S (65 µg/m^3) and methanethiol (1,281 µg/m^3). Odors from these sulfurous compounds are commonly recognized as unpleasant with odor detection thresholds of 0.6 µg/m^3 and 0.1 µg/m^3 respectively[9].
The same pattern is measured with the delivery of agri-food wastes in preparation tank. Odorous emissions and total VOCs concentrations increased to 18,867 UO_E/m^3 and 20,500 ppb isobutene equivalent respectively. This result appears to be due to alcohol emissions, mainly ethanol (104.9 mg/m^3 toluene equivalent) and esters (31.5 mg/m^3 toluene equivalent).

WWTP
In the waste water treatment plant, two specific activities generated noted modifications of odorous concentrations (the presence of sludge in the preparation room and the loading of solid digestates in trucks). Table 4 presents a summary of the measured concentrations.

Table 4. Characterization of odorous emissions sources in the waste water treatment plant.

Activity	Input preparation area		Solid digestate disposal	
	Without sludge	With sludge	No truck loading	Truck loading
Odor concentration (OU_E/m^3)	30	1,446	174	7,908
Total VOCs concentration (ppb isobutene eq.)	450	690	200	6,000

In the input preparation area, the arrival of sludge resulted in an increased odor concentration to 1,446 OU_E/m^3 which, in turn, resulted in a rise of total VOCs concentration especially hydrogen sulfide (48 µg/m^3) and methanethiol (118 µg/m^3). Due to the low odor detection threshold of these compounds (0.6 µg/m^3 and 0.1 µg/m^3 respectively[9]), they play a key role in odor intensity and persistency.

Truck loadings with solid digestate lead to an odor concentration of 7,908 OU_E/m^3. This level can be explained by the sulfurous compounds emissions (H_2S, 104 µg/m^3; methanethiol 1,747 µg/m^3; dimethylsulfide, 3,307 µg/m^3; dimethyldisulfide, 123 µg/m^3). The odor detection threshold for dimethylsulfide and dimethyldisulfide are evaluated in literature at 7.5 and 8.4 µg/m^3, respectively. The presence of these compounds is a reasonable explanation for the increased odor concentration measured relative to the occurrence of the specific activities on site.

SUMMARY

This study highlights the impact of some potentially important and specific activities (truck loading and unloading, preparation of the inputs) that contribute to the emission of VOCs and, therefore, odor emissions in the environment of biogas generation plant. For an overview of the odorous impact on the environment based on site type, it is, therefore, important to consider all these factors, some of which may result in brief but significant odor annoyance. The ability to control these emissions is very important to gain acceptance of these plants by surrounding neighborhoods.

ACKNOWLEDGEMENTS

This work was supported by the French Agency for Environmental and Energy Management (ADEME; grant agreement 1506C0053)

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