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Biological and Chemical Atmospheric Emissions of the Biogas Industry

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Actions of French governments on waste, resource and energy management force to focus on waste treatment and recovery process. Among these processes, anaerobic digestor offers significant advantages compared to other forms of waste treatment. It permits an organic waste treatment and a double valorization. The organic waste treatment enables the production of a digestate and a combustible gas fraction called biogas. The digestate, is an improved fertilizer, and can be enhanced by spreading or composting. Biogas can be valorized to produce heat or electricity. From this activity sector, energy production is expected to increase from 1,478 GWh in 2005 to 13,701 GWh in 2020 (Club Biogas ATEE, 2011).
Anaerobic digestion is widely studied to understand its mechanisms at microbial level and to improve biogas production and process stability. However, health risk for workers in these facilities and for surrounding residents is very poorly documented. Gaseous and particulate emissions are also incompletely defined. Information on odor concentrations and biogas chemical /biological composition has been investigated. Nevertheless, no data on emissions from inputs storage locations or digestate was currently available.
The EMAMET project aims to improve our understanding concerning the biogas production sector. Sources of gaseous and bioaerosol emissions will be researched and characterized on the whole production chain. The chemical composition of gaseous emissions will be completed by odor concentration determination. Biological emissions will be determined by molecular methods. From this information, specific biological and/or chemical indicators of this activity will be defined. In addition, 2D and 3D emission modeling will used to determine the influence zone of the biogas production implantation. To confirm this influence area a research of biological and microbial indicators around a pilot site will be realized. These data can help to assess health and environmental risks for workers and surrounding populations. This information is necessary to develop relevant sensors for control and monitoring of such emerging energetic processes.

1. Context

The French plan for waste management indicates several actions such as the reduction of 15% of waste incinerated or stored the increase of waste valorization to decrease the pressures on resources. Along with these decisions, the government has set a baseline to achieve by 2020 the target of 23% renewable energy in total final energy consumption set by Directive EC/2009/28. The evolution of waste management leads to a resurgence of interest for treatment plant and implementation of valorization treatment. Among these treatments, methanation is interesting because it allows the waste treatment and a double valorization. Treatment of fermentable organic waste leads, on the one hand the production of digestate, which can be used in agriculture as a nutrient fertilizer and/or organic amendment, and secondly the production of a combustible gaseous fraction, biogas, which can be used for producing heat or electricity. Biogas is generated by microbial activity and corresponds to a gas mixture saturated with water at the outlet of the digester. Methane content ranged from 50% to 70%, carbon dioxide from 20% to 50% and there are also some gases traces (NH_3, N_2, H_2S).

The number of biogas facility increases in France, between 197 operational plants, in 2011 to 338 plant in 2013 (SINOE waste, 2015) Depending on the waste treated, different types of the following units can be distinguished: at the farm, territorial (receiving waste from different sources, including agricultural), WWTP, Industrial… The majority of facilities are "on the farm" (43%). Ninety one biogas plants are found in industry, and 66 in treatment plants. These three sectors account for about 90% of biogas plants in France (SINOE waste, 2015).

On a biogas production site, several areas can be defined. The biogas industry is composed of at least five areas: 1 / the input storage area, 2 / inputs preparation area in dedicated and confined buildings, 3 / methanation reactor, 4 / Phase separation zone of digestate, 5 / storage area for digestate and biogas. Moreover, a post digester could be present in case of leakage from the digester. A gas treatment process may also be present on the site and allow the reduction of odorous annoyance.

Chemical compounds and particles can be emitted by each zone. Indeed, the process requires the mix, the handling and tracking of waste and digestate between different areas of a site. Movement applied in these actions causes various emissions. In addition, biogas can be emitted through leaks on the networks or by incident during maintenance operations. People exposed to theses emissions are the workers, but also the population around such plants.

Airborne particles (called bioaresols) can consist of dust but also of all or part of living organisms (fungal, bacterial, viral, plant and animal particles). The effects of the particles depend on their size. The largest are stopped in the nose and throat. The very small particle size penetrates deep into the respiratory tract to the bronchioles. Thus, they can lead to major health and environmental impacts. Indeed, the particle deposition can affect humans, animals and plants either directly (by inhalation, contact or absorption), or indirect ingestion (ingestion of contaminated foodstuffs) and then induce infection or non-infectious diseases (allergy, asthma, chronic obstructive pulmonary disease - COPD) due to living organisms (infections) or microorganisms fragments such as endotoxin or β-glucan (toxic, inflammatory) respectively.

Chemical compounds emissions can cause environmental and health impacts. Methane (main biogas component) is recognized as a powerful greenhouse gas, 21 times higher than CO_2 in terms of global warming potential, and represents 7% of greenhouse gas emissions in France. At very high concentrations, methane can cause suffocation. In addition, biogas can contain traces of odorous compounds such as hydrogen sulfide (H_2S), the emission of which can also take place at the storage area, and induces odor annoyance. The acute toxicity can be observed from 100ppm by irritation of the mucous membranes, 500ppm exposure causes a rapid loss of consciousness followed by a coma accompanied by respiratory disorder.

In theory, the use of anaerobic digestion could cause environmental and health hazards (toxic, infectious, inflammatory) and odorous annoyance via air emissions. These effects are generally found in all biological processes. Although the environmental and health impact of biological process is increasingly studied, the biogas sector remains very little studied to date. Considering the development of this sector, it is urgent to investigate and increase knowledge of the atmospheric emissions of this plant and their potential impacts.

2. State of art

The biogas industry can produce biogas from the degradation of organic matter by a specialized microbial community. Waste and effluents that can be treated by anaerobic digestion are organic and come from different sectors: industry (food, chemicals and paper mills), agriculture and livestock, sewage, or household garbage. The characteristics (dry matter (DM), chemical oxygen demand (COD),...) of such wastes and effluents vary according to their origins. Because of this diversity, and to increase the efficiency of the anaerobic process, effluents often undergo pre-treatments before to be treated in the digester (crushing, screening, cleaning, preheating, homogenization, chemical treatment / biological). The biogas chemical composition varies depending on the nature and origin of the waste or the treated effluent. It is saturated with water, as wet product. It contains mainly methane (between 50 and 70%), carbon dioxide (CO_2) but also traces of H_2S (0 to 5,000 ppm), nitrogen (N_2), ammonia (NH_3) and other compounds. The simultaneous presence of H_2S and water makes such biogas highly corrosive.

Sources of potential gas and particulate emissions can be located throughout the biogas production site. The waste inputs are stored and handled, resulting in the emission of dust containing in particular microorganisms. During the storage step, aerobic and anaerobic degradation reactions may occur resulting in the emission of various compounds into the atmosphere. The digestate from the storage phase can also cause the emission of volatile compounds and microorganisms.

Concerning the VOC emissions of the biogas industry, few references are found in the scientific literature. Most of the references from anaerobic environment are related to landfills or laboratory scale reactors. No information is available concerning inputs of storage facilities, or the efficiency of the air treatment process. Information on the biogas composition is available. Some assessment of the odors level on anaerobic digestion (Orzi et al., 2011), post digestion step (Tepe et al., 2009), digestate storage (Verma et al., 2006, Wilson et al., 2006), liquid fraction storage and after soil application (Hjorth, et al. 2009) are available. However, it is important to note that odor annoyance is considered as the main problem of this activity. Preliminary work has been carried out by Olentica to characterize the odors levels from the biogas sector at the industrial scale. These measures showed levels of odors up to 2000 odor unit per cubic meter (UO_E/m^3) on the storage of fermentable organic waste and even higher during the composting step. In addition, odor can be perceived at five kilometers around the emission sources.

The gases flow along the production chain is also poorly documented. Only leak information on biogas network is found. According to the sources, fugitive emissions by 0-15% should be considered (Martin, 2008; U.S.-E.P.A., 2008).

The microflora involved in anaerobic digestion has been widely studied qualitatively and quantitatively (Godon et al., 1997, Levén et al. 2007, Krober et al., 2009). Thus, density and structure of microbial community in this ecosystem is well known. Microflora biogas or condensate from biogas has also been studies using classical (Vinnerås et al., 2006, Traversi et al., 2015) and molecular microbiology (Krause et al., 2008, Kröber et al., 2009, Moletta et al. 2007, 2010). Microbial composition of biogas is different of the microflora of digestate (Moletta et al. 2007, 2010). Microbial densities have been estimated between 10 to 100 Colony Forming Units (CFU)/m^3 (Vinnerås et al., 2006), prokarya and eukaryota are respectively between 6.10^5 to 2.10^7 CFU/m^3 and 1.10^4 to 2.10^5 CFU/m^3 (Moletta et al., 2007).

The microorganisms identified by Vinnerås et al. (2006) in biogas included opportunistic pathogens (such as *Klebsiella pneumonea*). Yeasts and fungi have also been detected in the biogas. They may be the origin of allergies. Moletta et al., 2007, focused on the molecular composition of the microbial community present in biogas. They showed that the groups were aerosolized specifically (*Staphylococcus* spp., and *Propionibacterium acnes*): their densities are higher in biogas than in the digestate and other groups (synergists for example) are underrepresented in the biogas. However, up to date, pathogens have not been specifically investigated in the biogas.

The bacterial community appears as the best represented microorganisms (Krause et al., 2008). Bioaerosol bacterial is composed by *Firmicutes, Bacteroides, Actinobacteria*, β- and γ- *Proteobacteria (*Moletta et al., 2007, Krause et al., 2008). Within the domain *Archaea,* most 16S-rDNA sequences are close to *Methanomicrobiales* and notably to *Methanocellus (*Moletta *et al.*, 2007, Krause et al., 2008). Only Vinneras et al. 2006 were interested in fungi population and found three groups *Fusarium*, *Mucor* and yeast.

The presence in the digestate of pathogenic organisms has been demonstrated. In 37% of digestate samples from 87 biogas plants, the presence of strict or opportunistic pathogens has been detected (ADEME, 2011). Bagge et al., 2005, showed the presence of pathogenic microorganisms (*Salmonella*, *Listeria*, *Campylobacter*) in the digester outlet, but also bacteria having the ability to produce spores (*Clostridium* spp., and *Bacillus spp*.). Compared with a mesophilic biogas, improved sanitation is achieved by thermophilic anaerobic digestion (Carballa et al., 2009). However, a re-contamination and a re-growth of bacteria in digestate was frequently noted (Bagge et al., *2005*). The agronomic quality of digestate was also studied (ADEME, 2011).

Thus, emissions of microorganisms, pathogenic or not, can take place in the digester, but also throughout the methanation facility: waste storage, storage of digestate. The occurrence of pathogens and chemical emissions, to our knowledge, has never been qualitatively or quantitatively characterized at these locations.

Health risk related to bioaerosols concerns not only infection but also toxicity of, inflammation linked to dead microorganisms or fragments of microorganisms.

Data on health risk of this sector are incomplete. Vinnerås et al., 2006, and Traversi et al*.,* 2015 have concluded that occupational risk is linked to individual plant. To our knowledge, no published study has focused on the global health impact of the biogas industry.

3. General presentation of EMAMET Project

Anaerobic digestion seems to be an appropriate response to current issues of waste disposal and recycling in France. This pathway allows the processing of fermentable organic waste which corresponds in part to the waste from agricultural, industrial, household waste and sewage sludge. Energy recovery of biogas produced by anaerobic digestion is done either in the form of cogeneration (electricity and heat) or by direct injection of purified gas into the natural gas network.

In this context, the main issues to which this project will try to answer are:

• What are the sources of chemical and biological contamination (storage area, leaks on the network, biogas storage area and digestate ...)?

• What are the concentration and compositions of chemical compounds and microbial populations emitted during the anaerobic digestion?

• Can specific indicator of methanation activity be defined to monitor the health impact of this sector?

• Are the emissions from this sector a risk to public health?

To answer these questions, the EMAMET project has been elaborated. It is divided in 5 technical tasks.

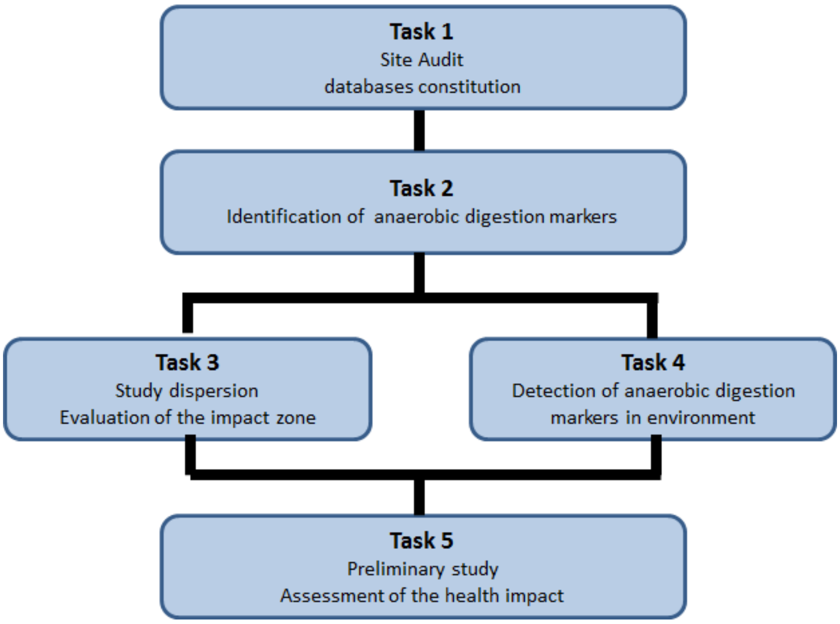

Figure 1: EMAMET project

3.1 Task 1 : Diagnostic of anaerobic digestor plant

In order to be representative of the diversity of biogas sectors, the 3 sites will be used during the project belonging to different categories: on the farm, an industrial anaerobic digestion site, a sewage treatment plant.

In the first step, an audit of each plant will be performed to determine the necessary number of measurements. A sample will be performed on each sector of the industry, and on unsuspected sources such as leaks. Air contains chemical compounds and microflora which constitute background noise. This noise must be characterized to determine emissions attributable specifically to the process of anaerobic digestion. Blank samples will be made upstream of the winds.

Emissions from different sources will be characterized in terms of their physical and chemical composition using adapted analytical tools (on fields and on the laboratory). Chemicals compounds will be evaluated on field by analyzers (PID, FID), especially to detect leaks. Some samples will be realized by using a lung box. For area sources, sampling will be conducted using a flow chamber. A fixed sampling flow rate will be used, allowing the calculation of the pollutant flow (g/h) requisite for dispersion modeling. The use of the same sampling flow rate during all determinations, allows comparing area source pollutant emissions regardless of weather conditions.

In the laboratory, the concentration of several gases will be determined. Concentrations of methane and carbon dioxide will be measured by gas chromatograph (Clarus 580, Perkin-Elmer) equipped with a thermal conductivity detector. Sulfur compounds are analysed by gas chromatography coupled with a flame photometric detector (Chromatotec/ Chroma S). Volatile Organic Compounds (VOCs) composition of air samples will be characterized with a Thermodesorption (Turbomatrix, Perkin Elmer) / gas chromatography / mass spectrometry (GC Ultra Trace / MS DSQ 2, Thermo Scientific) system. Air samples will therefore be obtained by pre-concentration on adsorbent tubes.

A characterization of odor levels will be achieved according to the NF EN 13725 using a dynamic dilution olfactometer (ODILE, Odotech Inc). The jury will be composed of 6 qualified panelists. The odor acceptability will be measured according to a specific protocol developed by the company OLENTICA (Chaignaud, 2014).

The biological composition of air emission will also be characterized. Samples will be taken either on the same sources (channeled sources) or close to the surface sources. On field, microbial density will be studied by ATP measurement (GL Biocontrol Company method), and a granulometric analysis of the particles range from 0.5 and 25 µm will be performed using a Particle Counter (TSI).

In the laboratory, a quantitative and qualitative study will be conducted by molecular biology methods after sampling using a Coriolis µ biocollector (Bertin Technologies). Densities of microorganisms groups such as bacteria, fungi, archaea will be determined using quantitative PCR. Identification of microorganisms belonging to each of these groups will be made by high throughput sequencing.

During sampling, various additional parameters will be measured such as temperature, humidity, direction and wind speed with an ultrasonic anemometer (81000 Meteorological instrument model, Young). These will be useful in the dispersion modeling.

3.2 Task 2: Identification of anaerobic digestion markers

The goal is to define indicator of anaerobic digestion plant. A comparative analysis of our results and review of the literature will be undertaken. Data from the literature concerning atmospheric emission of biogas production site (digestor and landfills) and from the sector emissions and biological processes (composting, waste processing ...) will be considered to define chemical and biological indicators characteristics of the biogas sector.

The tracer will have:

- to be present during each analysis on the biogas industry
- to be described in other research studies on methanation sectors
- not to be found in low concentration at the site of various sectors of the anaerobic digestion.

3.3 Task 3: Evaluation of impact area

The dispersion of chemical and biological pollutants around the site under normal weather conditions and in some damaging scenarios will be modelling by using the ARIA Impact software (2D / 3D software). A 2D dispersion simulation based on results achieved in task 1 and on weather file of one or three years will be realized. Then, the 2D model may be supplemented by a 3D simulation, especially when biogas plants will be located in hilly areas. The most disadvantageous weather conditions and most likely will be examined. This task will allow us to define the impacted area by chemical and biological programs depending on weather conditions. This area is the zone of influence of the biogas industry.

3.4 Task 4: Detection of anaerobic digestion markers in environment

Chemical and biological indicators determined during the previous task will be sought in the environment around the anaerobic site. The sample location and detection of activity markers will be compared with results of dispersion studies (Task 3), which will refine the knowledge of the site's area of influence.

3.5 Task 5: Assessment of the health impact

The goal of this task is an analysis of potential direct and indirect health risks (acute and chronic) for workers and neighbours of biogas plants. This analysis will be performed independently on each site and will take into account the existing urban and environmental ecosystem

For each type of facility, a mapping of chemical compounds found will be carried out. Their nature, prevalence, concentration and dissemination will initially define which substances are exposed to workers and populations. Identification of chemicals will assess the risk of each substance-related emission (from theoretical toxicological data) and hazardous substances classification will be achieved. Thus, a calculation of a risk quotient can be achieved leading to a first health risk assessment. This risk analysis will be carried out according to the following 4 steps: (1) identification of hazards (fire, explosion, pollution, and chemicals), (2) presentation of dose-effect relationships for potential active substances (toxicity) (3) evaluation of the exposure (based on measurements and models), (4) characterization of health risk (calculation of risk quotient, *iso*-risk curves).

4. Conclusions

Currently, there is an increased willingness on the part of worldwide governments to adopt more ecological methods of energy production, to reduce our impact on resources and to better manage our waste. Production of biogas from anthropogenic waste could be a solution. However, health impact from biogas industry is largely unknown. Studies have been focused on the biogas product and not on the plant. The "EMAMET" project aims to provide data to establish a preliminary health risk studies in this sector. The biological and chemical composition of atmospheric emissions will be determined on three biogas plants.

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