Analyses of Odours from Concentrated Animal Feeding Operations: A Review

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Abstract

Concentrated Animal Feeding Operations (CAFOs) are widely present all over the world due to the high population demand for food and products of animal origin. However, they have generated several environmental concerns, including odour nuisance, which affects people health and quality of life. Odours from livestock are a very complex mixtures of molecules and their analytical investigation is highly demanding. Many works have been published regarding the study of odours from CAFOs, using different techniques and technologies to face the issue. Thus, the aim of this review paper is to summarize all the ways to study odours from CAFOs, starting from the sampling methods and then treating in general the principles of Dynamic Olfactometry, Gas Chromatography coupled with Mass Spectrometry and Electronic Noses. Finally, a deep literature summary of Gas Chromatography coupled with Mass Spectrometry and Electronic Noses applied to odours coming from poultry, dairy and swine feeding operations is reported. This work aims to make some order in this field and it wants to help future researchers to deal with this environmental problem, constituting a state-of-the-art in this field.

Keywords

1. Introduction

During the last decades, the global population growth has implied an increased demand of food of animal origins, such as meat, eggs and milk, with the consequent intensification of livestock production systems. A large number of concentrated animal feeding operations (CAFOs) have been recently built in many parts of the world (Cai and Koziel, 2011). Therefore, these practices have led to several environmental issues, such as increased ammonia, greenhouse gases, odours, particulate matter (PM) and volatile organic compounds (VOCs) emissions into the atmosphere (Bibbiani and Russo, 2012; National Research Council US, 2003).

Odours emitted from CAFOs are generated directly from animals, bedding and faeces (Carey et al., 2004). They are not constituted by a single compound, but rather by a complex mixture of hundreds of diluted volatile substances, which make difficult their identification, quantification and abatement. The US Environmental Protection Agency (US EPA) does not regulate odours with specific federal standards, but considers them as a nuisance, which is defined as interference with the normal use of property (Carey et al., 2004). Indeed, odorous emissions from livestock often generate conflicts between farmers and their neighbourhood (Romain et al., 2013), due to the unpleasant smell, and this causes a decline in the surrounding properties value (Cai and Koziel, 2011). Moreover, these odours have generated concerns about health and welfare of both animals and humans working inside or living nearby these facilities (Lovanh et al., 2016). Livestock malodours could induce emotional stress, anger and physical symptoms in population living nearby CAFOs (Schiffman, 1998). Thus, it is of primary importance to possess reliable analytical techniques to study odours, in order to develop appropriate abatement technologies and mitigation strategies, aimed to reach a greater environmental sustainability of livestock production. In addition, the sampling step is a critical point, which should be carefully performed to have representative samples, avoiding wrong conclusions and results after the following analyses (Bibbiani and Russo, 2012). Moreover, it must be noticed that odour composition and concentration depend on several factors, such as temperature, ventilation rate, relative humidity, age of the birds, season, dietary composition, litter type and bird stocking density (Pan and Yang, 2007), and this makes odours evaluation very demanding.

Given the complexity of the problem, this review paper summarizes the techniques to collect and analyse odorous sample, firstly from a general point of view and then regarding their application in the study of odours from poultry, dairy and swine CAFOs. In particular, Section 2 is focused on odour sampling methods, Section 3 regards instrumental and not instrumental techniques devoted to study odours and finally Section 4 concerns the application of gas chromatography coupled with mass spectrometry (GC-MS) and electronic noses in the evaluation of odours from CAFOs. The aim of the work is to make some order in the field of odour evaluation from CAFOs, resuming all the previous papers and laying the foundations for future researchers that want to deal with this problem.

2. Field air sampling

When an odour is encountered, the first thing to do is to correctly sample it. Air is sampled by means of three different techniques: polymer bags (Section 2.1); metal canisters (Section 2.2); sorbent tubes (Section 2.3) (Brattoli et al., 2011; Koziel et al., 2005). In polymer bags and in metal canisters, air is captured in its entirety (as a whole "body"), while in sorbent tubes the gaseous sample passes through a solid sorbent that adsorbs the volatile compounds (Woolfenden, 2010). A brief explanation about these sampling tools and methodologies is given below.

2.1 Polymer bags

Polymer bags are light, easy to use and low cost tools useful to sample the air in its entirety. Their filling is achieved by means of a pump and they can be made of two different polymeric materials: Tedlar (Pau et al., 1991) or Nalophan (Hansen et al., 2011). Many works have been focused on the factors that can modify the gaseous sample inside the bag and how these can affect the following analysis. Examples of factors that can lead to serious mistakes are the release of contaminants from the inner surface of the bag to the sample, chemical instability of the sample, sorption of the molecules of the sample on the inner surface of the polymer, storage time and temperature, light exposure of the bag and humidity of the air sample (Boeker et al., 2014; Capelli et al., 2014; Ghimenti et al., 2015; Ghosh et al., 2011; Hansen et al., 2011; Le et al., 2013, 2015; Szyłak-Szydłowski, 2015; Trabue et al., 2006; Van Durme and Werbrouck, 2015; Van Harreveld et al., 1999; Van Wang et al., 1996; Zarra et al., 2012).

2.2 Metal canisters

Metal canisters are pre-evacuated metal containers that do not require a pump for their filling, which is achieved by regulating a valve. These systems are robust but more expensive than polymer bags (Wang and Austin, 2006) and also in this case losses and modification of the gaseous sample could happen inside the canister (Koziel et al., 2005; S. Trabue et al., 2008).

2.3 Sorbent tubes

Sorbent tubes are glass or metal tubes packed with one or more solid sorbents, often polymeric materials or activated carbon (Woolfenden, 2010). They are portable and low cost, but they require a pump to sample the volatile compounds dispersed in the air. In addition, a thermal or solvent extraction of the adsorbed molecules is necessary for their analytical identification and, eventually, quantification (Brattoli et al., 2011). In some cases, a single solid sorbent is not able to retain all the volatile compounds present in the sample and so sorbent tubes packed with multiple sorbent materials are suggested (Smith et al., 1977).

In all these cases, some considerations must be pointed out. Firstly, a sampling system should ensure the sample integrity (Trabue et al., 2006) and the following analysis should be performed as soon as possible. In addition, pre-cleaning of the sampling device with pure air could be necessary (Laor et al., 2010). Lastly, choosing strategic points to sample air in large areas is an issue that must be carefully considered (Abdullah et al., 2012; Capelli et al., 2014).

3. Tools to study the sampled odours

After the sampling step, three methods to study odours exist: Dynamic Olfactometry (Section 3.1), Gas Chromatography coupled with Mass Spectrometry (Section 3.2) and Electronic Noses (Section 3.3).

3.1 A sensorial method: Dynamic Olfactometry

An odour is a mixture of volatile chemical compounds that humans and other animals perceive with the sense of olfaction and Dynamic Olfactometry is a technique that allows to assign to an odour its concentration, which is defined as the number of dilutions with odourless air required for an odour to be detected by 50% of a panel of human evaluators (CEN, 2003). Odour concentration is expressed in European odour units (OU_E), where one odour unit is defined by the European Standard as equivalent to the response elicited by one European reference odour mass, most commonly 123 μg n-butanol evaporated into 1 m^3 of neutral gas, with a resulting concentration of one OU_E m^{-3} (CEN, 2003).

Measurements are performed with an olfactometer, which is a dilution instrument (made of inert and odourless materials) that presents the odour under investigation, diluted with odour-free air at different ratios, to a panel of human assessors. Examiners are selected after sniffing the reference gas n-butanol (Van Harreveld et al., 1999) and they should satisfy the following requirements:

- average n-butanol odour threshold between 20 ppb and 80 ppb;

- the antilogarithm of the standard deviation of individual responses less than 2.3.

Samples are presented to the panelists from the more to the less diluted, in order to avoid getting the olfactory system used to the previous presented odour (Brattoli et al., 2011). Two operative methods exist to determine odour concentration by means of Dynamic Olfactometry (Ueno et al., 2009): the Yes or No Method and the Forced Choice Method. In the first one, the sample leaves only from one port of the olfactometer and the assessor answers yes if he/she smells an odour, no if he/she does not. In the other one, there are more than one active ports, but the odour goes out only from one of them, while odourless air leaves from the others. Evaluators say if they smell an odour from one of the ports.

Odour intensity is the perceived strength of odour sensation. It shares a logarithmic relationship with odour concentration (Misselbrook et al., 1993) and so the dilution ratios of the samples presented to panelists are chosen following a logarithmic function. For a dynamic olfactometer, the odour concentration C is given by:

$$C = (Q_0 + Q_f)/Q_f$$

where Q_0 is the flow of the odorous sample and Q_f is the flow of the odour-free air required to reach the threshold (Brattoli et al., 2011). Once each panelist has perceived an odour, the geometric mean between the concentrations of the last negative and the first positive answer is calculated and this is the odour concentration detected by each assessor. Then statistical calculations are performed to give a global result and exclude unreliable data (CEN, 2003).

In addition to odour concentration, other measurements (called Parametric Sensory Measurements) can be done to completely characterize an odour (Brattoli et al., 2011). To be more precise, these are:

- the odour character, based on specific dictionaries;
- the aforementioned odour intensity, based on specific scales;
- the hedonic tone, which quantifies how much an odour is pleasant or unpleasant.

Assessment of odours performing Dynamic Olfactometry is expensive and not objective, as it is based on the olfactory system of different human assessors. Therefore, if the panel is not trained well, the accuracy of the results could be low. Moreover, air must be sampled and then taken to the laboratory, and this involves loss of time and the impossibility to perform real-time and on-site measurements. To overcome these problems, Field Olfactometry was developed, in which panelists perform the olfactory analysis directly on-site (Brandt et al., 2011; Sucker et al., 2008). In this case, the first difficulty is to isolate the assessors from the environment that they are going to examine, in order to avoid olfaction fatigue and getting the olfactory system used to the odour under investigation. Moreover, the panelists could be influenced in their answers because fact that they look at the ambient from which the odour comes from (Capelli et al., 2013).

Dynamic Olfactometry has been applied in the evaluation of zootechnical odorous emissions (Hamilton and Arogo, 1999), for example in the analysis of odours from swine (Brambilla and Navarotto, 2010; Brose et al., 2001; Gallmann et al., 2001; Hansen et al., 2016; Hove et al., 2012; Jacobson et al., 2008; Schauberger et al., 2013), poultry (Dunlop et al., 2010; Jacobson et al., 2008; Williams, 1989) and dairy cattle (Rzeznik et al., 2014) livestock. Since this work is focused on the instrumental techniques to evaluate odours from CAFOs, the paper cited in the previous sentence will not be exhaustively summarized in the following sections, because Dynamic Olfactometry is based on the human sense of smell.

3.2 An instrumental technique: Gas Chromatography coupled with Mass Spectrometry

Gas Chromatography coupled with Mass Spectrometry, also abbreviated in Gas Chromatography-Mass Spectrometry (GC-MS), is an instrumental technique to obtain qualitative and, eventually, quantitative information about the individual volatile compounds present in a complex chemical mixture. The chromatographic column separates the species that compose the mixture thanks to their different affinity to the column package, resulting in diverse elution times (also called retention times). Once a substance ends its chromatographic run, it is analysed by the mass spectrometer hyphenated with the gas chromatograph and it is identified by its mass spectrum.

GC-MS has some advantages, such as robustness, low detection limits, high accuracy and the ability to identify single substances in a mixture. On the other hand, it lacks of portability, requires long times for each analysis and it is expensive. In addition, GC-MS does not give information about odours because they are a feature of the whole mixture (Mackie et al., 1998), which is divided during the chromatographic analysis. To better explain, single odorous compounds can reduce or strengthen the global sensorial perception when they are present with other substances, and also non-odorous substances can play a role in masking or increasing the whole perceived odour (Cain, 1975; Thomas-Danguin and Chastrette, 2002). Separating the single components using chromatography implies the loss of the global odour information. Anyway, it is useful to know all the substances that take part of an odorous mixture in order to improve abatement strategies

(Amon et al., 1997; Bibbiani and Russo, 2012; Pillai et al., 2012) and find correlations between odours and chemical composition (Blanes-Vidal et al., 2009; Zahn et al., 2001).

GC-MS can be integrated with olfactometry (GC-MS/O) to understand which are the odour-determining compounds (Bulliner et al., 2006; Laor et al., 2008; S. Zhang et al., 2010a). In this case, a splitting tube, which brings the eluate to the mass spectrometer on one side and to a sniffing port on the other side, is assembled after the chromatographic column. The dual output consists in a chromatogram and an olfactogram, which shows peaks where an odour is detected. By means of this technique, it is possible to understand which are the most odorous molecules in the mixture, although any information about the latter as a whole is lost.

3.3 Simulating the human olfactory system: the Electronic Nose technology

An electronic nose, also called e-nose, is a device that acts as the human olfactory system and thus it is able to discriminate between different odours. It firstly appeared in the Literature in 1982, when Persaud and Dodd worked on a "device” that “can reproducibly discriminate between a wide variety of odours, and its properties show that discrimination in an olfactory system could be achieved without the use of highly specific receptors” (Persaud and Dodd, 1982). Actually, the key component of an e-nose is an array of gas sensors that are not required to be highly specific to target compounds because their whole response gives the so-called “fingerprint” that characterizes each particular odour. In other words, the ensemble of the responses of non-specific or partially specific sensors is the feature that allow recognizing and classifying an odorous sample (Abdullah et al., 2012; Nicolas et al., 2000; Sohn et al., 2009). It is important to underline that an e-nose is sensible also to odourless compounds, since its response depends on interactions between molecules and sensors surfaces, whether or not they have a specific odour.

In general, an electronic nose is composed by three elements (Gardner and Bartlett, 1994; Peris and Escuder-Gilabert, 2009): a sampling system (Section 3.3.1); a sensors chamber (Section 3.3.2); a data processing and pattern recognition system (Section 3.3.3).

3.3.1 Sampling system

Generally, it consists of a tube connected with a pump, which brings the gaseous sample to the chamber in which the sensors array is located.

3.3.2 Sensors chamber

Once the sample is sucked by the delivering system, it is analysed by the array of sensors. They work modifying their physical or chemical properties after the contact with volatile compounds and this variation can be measured in order to obtain information about the sample.

Different materials are utilized in the construction of sensors for electronic noses (Gebicki, 2016; Wilson and Baietto, 2009) and the most used are:

- Metal Oxide Semiconductors (MOS) (Fine et al., 2010; Govardhan and Nirmala Grace, 2016; James et al., 2005; Korotcenkov, 2007), which change conductivity/resistance in the presence of gaseous species. They can be n-type or p-type semiconductors but, in both cases, atmospheric oxygen adsorbs onto the MOS surface, scavenging electrons from the material. If a reducing gas faces an n-type MOS sensor surface, it reacts with the adsorbed oxygen, which releases back the electrons to the semiconductor, increasing/lowering its conductivity/resistance. The same principle is also valid for an oxidizing volatile molecule interacting with a p-type semiconductor surface, where the presence of the gaseous analyte increases the hole concentration of the MOS sensor;
- Conductive Polymers (CP) (Gardner and Bartlett, 1995; James et al., 2005), which are materials to develop conductimetric sensors as MOS. They can be intrinsically or composite CPs (Gebicki, 2016). In the first case, the adsorption of the gaseous species into the polymer directly involves a change in its conductivity, which can be measured. In the case of composite conductive polymers, the sensitive layer is composed by a non-conductive polymer matrix in which conductive molecules are dissolved. When a gaseous species approaches the layer, it is adsorbed inside it, which becomes geometrically larger. The result is that the conductive molecules increase their distances, thus increasing the measurable resistance of the sensitive layer;
- Quartz Crystal Microbalances (QCM) (Escuderos et al., 2011; Si et al., 2007), which are classified as piezoelectric sensors. A change in the mass of the microbalance, due to the adsorption of the analysed gas, causes a change in the oscillation frequency that is applied to the sensor, and this variation can be measured.

In addition to the most used conductimetric and piezoelectric sensors, there are other types of sensors that are used in the sensors array fabrication. These are thermal, electrochemical and optical sensors, classified on the basis of their working principle (Brattoli et al., 2011; Capelli et al., 2014). The sensors array can be formed by the same type of sensors or can be hybrid (Holmberg et al., 1995; Ulmer et al., 2000) (composed by sensors that work with different principles).

3.3.3 Data processing and pattern recognition system

Before the recognition and the classification of an odour into the appropriate class, a preliminary data analysis is often performed (Capelli et al., 2014). The most used technique is the Principal Component Analysis (PCA) (Abdi and Williams, 2010; Møller et al., 2005), which is a data reduction technique in which the dimensionality of the whole initial dataset is reduced to a smaller one, still preserving the information of the initial dataset. The redundancy of the information is eliminated. Other examples of preliminary data analysis are the Hierarchical Cluster Analysis (HCA) (Milligan and Cooper, 1987) and the Polar Plot Analysis (Brezmes et al., 1997).

Then, it is necessary to assign each sample to the more similar olfactory class, obtained previously by the training of the e-nose (Capelli et al., 2014; Shaffer et al., 1999). The most known classification techniques are K-Nearest Neighbors (KNN) (Ciosek and Wróblewski, 2006), Discriminant Function Analysis (DFA) (Gardner et al., 1992), Partial Least Squares (PLS) (Ciosek and Wróblewski, 2006), Artificial Neural Networks (ANN) (Haugen and Kvaal, 1998) and Fuzzy Logic (Scott et al., 2006).

The use of electronic noses for air quality monitoring involves many advantages, such as real-time, continuous and in-situ measurements, low cost analysis and possibility of remote control. A limit is the dependence of the results on the environmental conditions (humidity level, temperature, wind speed), which could lead to wrong evaluations. In order to take into account these parameters, many e-noses are fabricated coupling sensors that monitor these external conditions (Brattoli et al., 2011; Capelli et al., 2014). Another possibility is to sample the air with the aforementioned methods and then take the samples to the laboratory for e-nose analysis. Doing so, the opportunity for a real-time and on-site monitoring is lost, but the readings are less affected by environmental factors.

The electronic nose technology has been applied in many fields, such as food (Deisingh et al., 2004; Peris and Escuder-Gilabert, 2009), beverage (Berna, 2010; Di Natale et al., 1996; Gardner et al., 1992), environmental analyses (Capelli et al., 2014) and biomedical applications (Casalinuovo et al., 2006; Gardner et al., 2000). A suggestion is to develop and train e-nose instruments dedicated to specific purposes, choosing carefully the most suited combination of gas sensors and thus optimizing the performances (Bourgeois et al., 2003).

4. Application of GC-MS and E-Noses in the monitoring of odours from concentrated animal feeding operations

In this section, papers that have dealt with the evaluation of odours from poultry, dairy and swine feeding operations using GC-MS and e-nose instrumental techniques are summarized.

4.1 Poultry

Some papers have dealt with the analysis of odours from poultry buildings by means of GC-MS technique. Their contents and results are resumed in Table 1. Trabue et al. (S. Trabue et al., 2008) sampled air from a commercial broiler house in order to quantify volatile sulphur compounds (VSCs). They sampled with sampling canisters coated with fused silica in order to minimize losses of reactive VSCs, and temperature and relative humidity (RH) of the sampled air were equal to 0 °C and 76%, respectively. The gas chromatograph was equipped with two detectors: a mass spectrometer and a pulsed flame photometer. The latter made the VSCs quantification possible without the use of internal standards because the response factor for each VSC was equimolar (average response factor of $3.86 * 10^7$ (ng S)$^{-1}$). In another work (S. L. Trabue et al., 2008), the same authors studied different sorbent materials for the sampling and chose CP-X (Carbopack C:Carbopack X in 1:2 packing ratio) for field application because of the great recoveries and the little amount of sorbed water. They found that acetic acid was the most abundant compound and that 4-methyl phenol was the only substance detected above its odour threshold value. Van Huffel et al. (Van Huffel et al., 2012) analysed air from pig stables and poultry houses by means of thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) and selected ion flow tube-mass spectrometry (SIFT-MS). They explained the relatively large standard deviations of target compounds concentrations stating that the environmental conditions were not constant in time and space. They found that ethanoic acid was the most abundant molecule (more than 40% on mass basis of the total concentration), followed by 2-butanone and phenol for broilers and dimethyl sulfide and dimethyl disulfide for laying hens. Overall, volatile organic compounds (VOCs) were more concentrated in swine stables than in poultry houses. Murphy et al. (Murphy et al., 2014) reported that eight out of a total of 47 non-methane volatile organic compounds (NMVOCs) identified in samples from five broiler sheds containing chickens of similar ages were predictors of the perceived odour. These NMVOCs were dimethyl sulfide, dimethyl trisulfide, 2,3-butanedione, 3-methyl butanal, 1-butanol, 3-methyl-1-butanol, acetoin and 2-butanone in a concentration range equal to BDL (below detection limit)-1.7, 0.01-26, 3-324, BDL-43, BDL-6, BDL-25, 15-16000 and 0.6-290, respectively. Yang et al. (Yang et al., 2014) analysed extracts from total suspended particulate (TSP) and PM_{10} collected nearby CAFOs, in particular swine and poultry. They identified 57 compounds, grouped in five categories: carbonyls (acetones and aldehydes), alcohols, acids, phenols and nitrogen-containing compounds. In a large study about microbiological and chemical contamination of settled dust at poultry farms, Skóra et al. (Skóra et al., 2016) analysed air samples by means of GC-MS technique and observed an increase in ammonia, carbon dioxide, acetaldehyde and acetic acid concentrations during broiler production cycles.

As far as the Authors know, only four studies dealt with the use of e-nose technology for air monitoring in poultry sheds. Pan and Yang (Pan and Yang, 2007) used an e-nose constituted of 14 gas sensors, a temperature sensor and a humidity sensor in order to develop a useful tool for odour management in livestock and poultry farms. They designed and implemented "Odour Expert", a software that helps the farmers in making decisions about what to do to reduce odour intensity. The researchers tested the system in 14 livestock and poultry farms located in Ontario, comparing the results with those from a panel of human assessors. They showed that the use of the e-nose increased the accuracy of the measurements. In another work, Pan et al. (Pan et al., 2007) used the same electronic nose to understand which factors (animal species, distance to the odour source, wind speed, temperature, cloud cover, atmospheric stability) have an influence on odour nature and strength in two poultry farms, six dairy farms and six pig farms. Sohn et al. (Sohn et al., 2008) developed a model able to predict odour concentration in a broiler shed by means of an e-nose composed by 24 MOS sensors located in three different chambers. They also applied the instrument in the continuous air monitoring over a broiler production cycle, demonstrating that it measured different odour concentrations corresponding to the incidence of different events in the shed, such as variations in bird stocking density and rainfall. Finally, Abdullah et al. (Abdullah et al., 2012) built a malodour mapping of a chicken farm using the electronic nose technology and showed that their tool discriminates among different sampling locations and malodour concentrations in the farm.

4.2 Dairy

For what concern the application of GC-MS in the monitoring of odours from dairy buildings (Table 2), Rabaud et al. (Rabaud et al., 2003) used thermal desorption GC-MS with concurrent olfactometry to analyse volatile organic compounds emitted from an industrial dairy located in Northern California. They sampled by means of sorbent tubes packed with 100 mg of Tenax TA and Carboxen GR configured in series, covering the tubes with ice gel-packs in order to minimize solar heating and optimize the adsorption of analytes in the solid phase. They found 35 compounds, belonging to the chemical classes of volatile fatty acids (VFAs), esters, alcohols, aldehydes, ketones, halogenates, amines and hydrocarbons. They also found that VFAs and esters exhibited the greatest olfactory impact and that the temperature and the relative humidity did not affect significantly the results, although these factors were relatively stable during the study. Filipy et al. (Filipy et al., 2006) identified VOCs as alcohols, aldehydes, ketones, esters, ethers, aromatic hydrocarbons, halogenated hydrocarbons, terpenes, other hydrocarbons, amines, other nitrogen containing compounds and sulphur-containing compounds at a lactating cow open stall, thermally desorbing them from Carbotrap B/Carbosieve S-III cartridges or U-shaped tubes containing glass beads with Pyrex glass wool plugs before the chromatographic run. Concentrations of duplicate samples varied up to 27% and results were dependent on meteorological conditions as wind speed, wind direction and temperature. They also stated that no volatile fatty acids were identified because of the column type used in GC-MS experiments and that many chromatographic peaks were not attributed to any molecules of the mass spectrometer library. In a work of Lu et al. (Lu et al., 2008), the authors made the air inside a dairy passing through a cartridge packed with a mixture of polyurethane form, charcoal, XAD and silica gel. Then, they extracted the adsorbed compounds with two solvents (dichloromethane and methanol) and injected 0.5 μL of the liquid into the GC-MS. They found the compounds reported in Table 2. Zhang et al. (S. Zhang et al., 2010b) analysed odour-causing compounds from a dairy site, sampling with sorbent tubes made of 304-grade stainless steel packed with 65 mg of Tenax and quantifying with thermal desorption multidimensional gas chromatography-mass spectrometry/olfactometry. They found 11 volatile compounds of which they also evaluated odour intensity and hedonic tone after the chromatographic separation. The same analytical technique was used by Cai et al. (Cai and Koziel, 2011) to determine odorous gases from two dairy barns, one located in Wisconsin and the other in Indiana. The authors concluded that some compounds (acetic acid, propanoic acid, 2-methyl propanoic acid, butyric acid, 3-methyl butanoic acid and 4-methyl phenol in Wisconsin, guaiacol, 1-(2-aminophenyl)-ethanone and indole in Indiana) showed a seasonal significant difference in the emission rate, and acetic, propanoic, 2-methyl propanoic, butyric and 3-methyl butanoic acids were significantly different between the two sites. The contents of these works are summarized in Table 2. Also electronic noses have been applied in the monitoring of volatile compounds from dairy livestock. As said before, Pan et al. (Pan et al., 2007) applied an e-nose prototype to compare its results with odour evaluations performed by a panel that measured at two poultry, six dairy and six pig farms located in southern Ontario.

They stated that the gas sensors values were in agreement with human assessors' evaluations. Furthermore, Chang et al. (Chang and Heinemann, 2015) trained an e-nose in which 32 polymer sensors were present in order to predict human assessments of odours from a dairy farm.

4.3 Swine

Many studies that have tried to resolve odours from swine buildings by the use of gas chromatography-mass spectrometry have been conducted (Table 3). Schiffman et al. (Schiffman et al., 2001) analysed air from swine facilities in North Carolina and found acids, alcohols, aldehydes, amides, amines, aromatics, esters, ethers, fixed gases, halogenated hydrocarbons, hydrocarbons, ketones, nitriles, other nitrogen-containing compounds, phenols, sulphur-containing compounds, steroids, and other compounds. The authors stated that most of these compounds were present at concentrations below the respective odour thresholds and that many chromatographic peaks were not sufficiently high to allow the identification of the corresponding molecule. They quantified the volatile chemical compounds coming from a cleaned swine house using the average of the response factors of the following 14 selected molecules, which should represent the chemical classes of the molecules typically found in the atmosphere of the swine house: thiophene, acetic acid, 2-pentanone, methyl disulfide, propanoic acid, 1-pentanethiol, *n*-butanoic acid, 2-heptanone, methyl sulfoxide, *n*-pentanoic acid, methyl sulfone, 2-nonanone, 1-nonanethiol, and *n*-nonanoic acid. The most abundant compounds were butanoic acid, acetic acid, 3-methyl butanoic acid, 4-methyl phenol, propanoic acid, 2-methyl propanoic acid, 2-methyl butanoic acid, vinyl acetate, 4-ethyl phenol, phenol, and acetaldehyde. Razote et al. (Razote et al., 2002) optimized and tested a dynamic air sampling system in conjunction with solid phase microextraction (SPME) technique to sample and then analysed by GC-MS compounds present in the air of a swine house in Manhattan city. Takai et al. (Takai et al., 2005) studied how temperature, management and categories of pigs influence the emission of five key odorants, adsorbing them onto SPME fibers followed by GC-MS analysis. In a work of the same year, Blunden et al. (Blunden et al., 2005) sampled air from five swine CAFOs located in the eastern part of North Carolina and found more than 100 compounds, including paraffins, olefins, aromatics, monoterpenes, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides. Identification with retention times and quantification were performed using GC coupled with a Flame Ionization Detector (FID) and GC-MS was employed to confirm the correct identification of the molecules present in the samples. The authors calibrated the GC-FID instrument using 0.25 ppm propane in air (± 1.2%) National Institute of Standards and Technology Standard Reference Material (NIST SRM) and then calculated compounds' concentrations in parts per billion carbon (ppbC) using the averaged area count per ppbC response factor of the propane standard. Acetaldehyde, methanol, ethanol and acetone were found to be the most concentrated compounds in all the facilities. Cai et al. (Cai et al., 2006) placed three tapered element oscillating microbalances (TEOMs) inside a 1000-head swine finish barn in central Iowa to capture particulate matter (PM) and then VOCs adsorbed/absorbed to dust were allowed to equilibrated in a vial headspace and extracted with SPME fibers. They found that Carboxen/Polydimethylsiloxane (PDMS) adsorbent material was the SPME fiber that gave the best performances. Analyses of VOCs were done with a GC-MS/O instrument and 50 compounds, included in alkanes (4), alcohols (4), aldehydes (8), ketones (7), acids (8), amines and nitrogen heterocycles (8), sulfides and thiols (3), aromatics (7) and furans (1) chemical classes, were identified. Cai et al. (Cai et al., 2010) collected odorous samples every two weeks (for almost one year) from two dairy and two swine barns using sorbent tubes containing Tenax TA and analysing the adsorbed compounds by thermal desorption-GC-MS/O. Concentrations ranged between 1.1 and 121 $\mu g\ m^{-3}$ for volatile fatty acids and 0.03 and 42 $\mu g\ m^{-3}$ for phenolics and indolics. In the same year, Zhang et al. (S. Zhang et al., 2010b) found 14 VOCs at a swine site, sampling air with sorbent tubes packed with Tenax TA and then performing the analysis with GC-MS/O. Andersen et al. (Andersen et al., 2014) measured the concentrations of 17 odorants in a pig house both in the gas phase and in particles, using TD-GC-MS with the optimal desorption temperature of 290 °C. They stated that the high observed standard deviations for compounds concentrations were due to daily variations and differences in sampling time. They found that carboxylic acids were the most abundant molecules in the particle phase, probably because of the acid dissociation in the solid matter.

As in the cases of poultry and dairy, also the odours from swine feeding operations have been studied using the e-nose technology. Gralapp et al. (Gralapp et al., 2001) used an AromaScan A32S electronic nose, containing an array of 32 conducting-polymer sensors, to analyse air collected in Tedlar bags from two swine feeding rooms at an Iowa State University facility. Results from the e-nose were well correlated to GC-MS analysis of the same samples, but not with those from olfactometric measurements. Gallmann et al. (Gallmann et al., 2004) studied how the climatic and biological changes in pig husbandry influence odour emissions, using an e-nose composed by 10 metal oxide chemosensors. In another work, Lorwongtragool et al. (Lorwongtragool et al., 2010) developed an electronic nose prototype to assess malodours in swine buildings and, after testing it, they gave suggestions on feeding menu, buildings' cleaning schedule and emission control program.

Finally, an e-nose constituted of 6 metal oxide sensors was employed by Romain et al. (Romain et al., 2013) to continuously monitor odours from an experimental pig farm in Liège. After an appropriate calibration against olfactometric measurements, the e-nose proved to be reliable.

5. Use of VOC's to detect pathology in animals

The odour from farmed animals is influenced by their health status and, in particular, enteric problems are characterised by peculiar odour properties (Sohn et al., 2008).

Several studies have explored the possibility to diagnose pathologies in livestock and in humans via identification of the Volatile Organic Compounds (VOCs) produced by pathogens, host-pathogen interactions and biochemical pathways (Ellis et al., 2014).

VOCs analysis has been explored as a method to diagnose bovine respiratory disease, brucellosis and bovine tuberculosis in cattle. Exploring volatile organic compounds (VOCs) as non-invasive biomarkers of diseases or infections is a research area of growing interest, in both human and veterinary medicine (Purkhart et al., 2011) and in particular, the investigation of faecal VOCs may be the best non-invasive and early way of diagnosing livestock diseases.

6. Conclusions

Odours from livestock farming are a very demanding analytical challenge due to their chemical complexity and the low concentrations of the single compounds. It is extremely important to study them in order to understand their origin and develop efficient abatement technologies. As presented in this review paper, a reference technique to deal with this issue does not exist, but there are different ways to approach the problem. Dynamic Olfactometry, Gas Chromatography coupled with Mass Spectrometry and Electronic Noses have different working principles and outputs, so the combined use of them could maximize the information obtained about odours originated from CAFOs.

Apart from the techniques used to detect them, the VOC's seem to be the new frontier of diagnostics both in human and in livestock; in fact, the VOCs emitted from different areas of the living body can be considered as individual 'fingerprints' and pathological processes (such as infection and endogenous metabolic disorders), can influence the odour fingerprints by producing new VOCs or by changing the ratio of VOCs that are produced normally. One of the main advantage of these techniques is that it is a non-invasive diagnostic tool that does not requires any manipulation of the animals. For these reasons, exploring volatile organic compounds (VOCs) is a research area of growing interest in both human and veterinary medicine.

In this context, electronic noses, considering their low cost, their simplicity of use and the possibility to remotely control their output from different analytical locations, appear to be the best solution to solve the above-mentioned challenge. However, these devices (particularly those characterized by inexpensive systems) are currently based on a sensor array, composed by 5-10 sensors, each of which capable of detecting a very general class of compounds. Therefore, they are not appropriately designed for specifically detecting the compounds related to a specific disease. More research has to be done in order to find the typical VOCs responsible of the odour released by unhealthy human or animal individuals, and to connect each odour to a typical compound. This challenge can be tackled using all the techniques presented in this review, particularly those allowing to be extremely selective and sensitive. Once the correlation between disease-compound-odour has been found, very specific sensors could be designed, each of which tailored for specific targets and selected applications. The use of affinity-based recognition, perm-selective membranes, molecularly imprinted polymers (MIP), host-guest systems could allow to reach the sought selectivity in these sensors.

Conflicts of interest

Conflicts of interest: none

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Tables

Authors and year	Sample and Location	Sampling material/technique	Number of detected molecules	Reference
Trabue et al. (2008)	Air of a commercial broiler house	Fused silica lined canisters	7 sulfur-containing odorants	(S. Trabue et al., 2008)
Trabue et al. (2008)	Air of a broiler facility	Sorbent tubes containing CP-X (Carbopack C:Carbopack X in 1:2 packing ratio)	11 molecules	(S. L. Trabue et al., 2008)
Van Huffel et al. (2012)	Air of broiler chickens or laying hens facilities in Merelbeke, Belgium	Nalophan bags followed by loading in sorbent tubes containing Tenax TA + Carbotrap (50:50)	20 molecules	(Van Huffel et al., 2012)
Murphy et al. (2014)	Air of five broiler houses in Queensland, Australia	Sorbent tubes containing Tenax	47 chemical odorants	(Murphy et al., 2014)
Yang et al. (2014)	Air of six poultry buildings in the U.S. Midwest	Harvard impactors and UIUC isokinetic TSP samplers	57 non-sulfur-containing odorants	(Yang et al., 2014)
Skóra et al. (2016)	Air of one broiler and two laying hens farms in Kuyavia-Pomerania and Lodz districts, Poland	Tedlar bags	20 molecules	(Skóra et al., 2016)

Table 1. Summary of papers that have dealt with the application of GC-MS technique to poultry farms.

Authors and year	Sample and Location	Sampling material/technique	Number of detected molecules	Reference
Rabaud et al. (2003)	Air of an industrial dairy in Yuba County, Northern California	Sorbent tubes containing 100 mg of Tenax TA and Carboxen GR	35 compounds	(Rabaud et al., 2003)
Filipy et al. (2006)	Air of an open stall housing lactating cows at the Washington State University Knott Dairy Farm	Sorbent tubes containing Carbotrap B and Carbosieve S-III or U-shaped glass tubes containing glass beads with Pyrex glass wool plugs	82 compounds	(Filipy et al., 2006)
Lu et al. (2008)	Air of a dairy in Central Ohio	Sorbent tubes containing polyurethane form, charcoal, XAD and silica gel	12 compounds	(Lu et al., 2008)
Zhang et al. (2010)	Air of a dairy site	Sorbent tubes containing 65 mg of Tenax TA	11 compounds	(Shicheng Zhang et al., 2010)
Cai et al. (2011)	Air of two dairy barns, one in Wisconsin and the other in Indiana	Sorbent tubes containing 65 mg of Tenax TA	18 compounds	(Cai and Koziel, 2011)

Table 2. Summary of papers that have dealt with the application of GC-MS technique to dairy farms.

Authors and year	Sample and Location	Sampling material/technique	Number of detected molecules	Reference
Schiffman et al. (2001)	Air of swine houses in North Carolina	Sorbent tubes containing Tenax or deodorized cotton	203 VOCs found in Tenax and 112 in cotton	(Schiffman et al., 2001)
Razote et al. (2002)	Air of a swine house at the Kansas State University Swine Teaching and Research Unit, Manhattan	SPME fibers with a dynamic air sampling system	90 compounds from building exhaust fan, 80 inside the building and 60 from manure pit fan	(Razote et al., 2002)
Takai et al. (2005)	Air of four swine herds	SPME fibers	5 compounds	(Takai et al., 2005)
Blunden et al. (2005)	Air of five swine facilities in Eastern North Carolina	6-L electropolished stainless steel SUMMA canisters	More than 100 compounds	(Blunden et al., 2005)
Cai et al. (2006)	Air of a swine finish barn in central Iowa	Tapered element oscillating microbalance (TEOM) 1400a analysers to sample particulate matter (PM) and then Carboxen/Polydimethylsiloxane (PDMS) SPME fibers to adsorb VOCs from the headspace of PM	50 VOCs grouped into nine chemical classes	(Cai et al., 2006)
Cai et al. (2010)	Air of a swine finisher barn in Indiana and swine gestation/farrowing barns in Iowa	Sorbent tubes containing 65 mg of Tenax	15 odorous gases	(Cai et al., 2010)
Zhang et al. (2010)	Air of a swine site	Sorbent tubes containing 65 mg of Tenax TA	14 compounds	(Shicheng Zhang et al., 2010)
Andersen et al. (2014)	Air of a pig house at the research centre in Foulum, Aarhus University, Denmark	PTFE coated glass fibre filters and sorbent tubes containing Tenax TA and Carbograph 5TD	16 compounds	(Andersen et al., 2014)

Table 3. Summary of papers that have dealt with the application of GC-MS technique to swine farms.