1 **Analyses of Odours from Concentrated Animal Feeding Operations: A Review**

2 P. Guffanti[a], V. Pifferi[b], L. Falciola[b], V. Ferrante[a]

3 [a]Department of Environmental Science and Policy, Università degli Studi di Milano, Via Celoria 10,
4 Milan, Italy

5 [b]Department of Chemistry, Università degli Studi di Milano, Via Golgi 19, Milan, Italy

6 **Corresponding Author**: P. Guffanti

7 address: Via Celoria 10, 20133, Milan, Italy

8 e-mail: paolo.guffanti@unimi.it phone number: +39 02503 18041

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10 **Abstract**

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

24 **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

88 Sorbent tubes are glass or metal tubes packed with one or more solid sorbents, often polymeric

89 materials or activated carbon (Woolfenden, 2010). They are portable and low cost, but they require

90 a pump to sample the volatile compounds dispersed in the air. In addition, a thermal or solvent

91 extraction of the adsorbed molecules is necessary for their analytical identification and, eventually,

92 quantification (Brattoli et al., 2011). In some cases, a single solid sorbent is not able to retain all the

93 volatile compounds present in the sample and so sorbent tubes packed with multiple sorbent

94 materials are suggested (Smith et al., 1977).

95 In all these cases, some considerations must be pointed out. Firstly, a sampling system should

96 ensure the sample integrity (Trabue et al., 2006) and the following analysis should be performed as

97 soon as possible. In addition, pre-cleaning of the sampling device with pure air could be necessary

98 (Laor et al., 2010). Lastly, choosing strategic points to sample air in large areas is an issue that must

99 be carefully considered (Abdullah et al., 2012; Capelli et al., 2014).

100 **3. Tools to study the sampled odours**

101 After the sampling step, three methods to study odours exist: Dynamic Olfactometry (Section 3.1),

102 Gas Chromatography coupled with Mass Spectrometry (Section 3.2) and Electronic Noses (Section

103 3.3).

104 **3.1 A sensorial method: Dynamic Olfactometry**

105 An odour is a mixture of volatile chemical compounds that humans and other animals perceive with

106 the sense of olfaction and Dynamic Olfactometry is a technique that allows to assign to an odour its

107 concentration, which is defined as the number of dilutions with odourless air required for an odour

108 to be detected by 50% of a panel of human evaluators (CEN, 2003). Odour concentration is

109 expressed in European odour units (OU_E), where one odour unit is defined by the European Standard

110 as equivalent to the response elicited by one European reference odour mass, most commonly 123

111 μg n-butanol evaporated into 1 m^3 of neutral gas, with a resulting concentration of one OU_E m^{-3}

112 (CEN, 2003).

113 Measurements are performed with an olfactometer, which is a dilution instrument (made of inert

114 and odourless materials) that presents the odour under investigation, diluted with odour-free air at

115 different ratios, to a panel of human assessors. Examiners are selected after sniffing the reference

116 gas n-butanol (Van Harreveld et al., 1999) and they should satisfy the following requirements:

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

118   • the antilogarithm of the standard deviation of individual responses less than 2.3.

119   Samples are presented to the panelists from the more to the less diluted, in order to avoid getting
120   the olfactory system used to the previous presented odour (Brattoli et al., 2011). Two operative
121   methods exist to determine odour concentration by means of Dynamic Olfactometry (Ueno et al.,
122   2009): the Yes or No Method and the Forced Choice Method. In the first one, the sample leaves only
123   from one port of the olfactometer and the assessor answers yes if he/she smells an odour, no if
124   he/she does not. In the other one, there are more than one active ports, but the odour goes out
125   only from one of them, while odourless air leaves from the others. Evaluators say if they smell an
126   odour from one of the ports.

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

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

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

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

140   • the odour character, based on specific dictionaries;

141   • the aforementioned odour intensity, based on specific scales;

142   • the hedonic tone, which quantifies how much an odour is pleasant or unpleasant.

143   Assessment of odours performing Dynamic Olfactometry is expensive and not objective, as it is
144   based on the olfactory system of different human assessors. Therefore, if the panel is not trained
145   well, the accuracy of the results could be low. Moreover, air must be sampled and then taken to the
146   laboratory, and this involves loss of time and the impossibility to perform real-time and on-site
147   measurements. To overcome these problems, Field Olfactometry was developed, in which panelists

148 perform the olfactory analysis directly on-site (Brandt et al., 2011; Sucker et al., 2008). In this case,

149 the first difficulty is to isolate the assessors from the environment that they are going to examine,

150 in order to avoid olfaction fatigue and getting the olfactory system used to the odour under

151 investigation. Moreover, the panelists could be influenced in their answers because fact that they

152 look at the ambient from which the odour comes from (Capelli et al., 2013).

153 Dynamic Olfactometry has been applied in the evaluation of zootechnical odorous emissions

154 (Hamilton and Arogo, 1999), for example in the analysis of odours from swine (Brambilla and

155 Navarotto, 2010; Brose et al., 2001; Gallmann et al., 2001; Hansen et al., 2016; Hove et al., 2012;

156 Jacobson et al., 2008; Schauberger et al., 2013), poultry (Dunlop et al., 2010; Jacobson et al., 2008;

157 Williams, 1989) and dairy cattle (Rzeznik et al., 2014) livestock. Since this work is focused on the

158 instrumental techniques to evaluate odours from CAFOs, the paper cited in the previous sentence

159 will not be exhaustively summarized in the following sections, because Dynamic Olfactometry is

160 based on the human sense of smell.

161 **3.2 An instrumental technique: Gas Chromatography coupled with Mass Spectrometry**

162 Gas Chromatography coupled with Mass Spectrometry, also abbreviated in Gas Chromatography-

163 Mass Spectrometry (GC-MS), is an instrumental technique to obtain qualitative and, eventually,

164 quantitative information about the individual volatile compounds present in a complex chemical

165 mixture. The chromatographic column separates the species that compose the mixture thanks to

166 their different affinity to the column package, resulting in diverse elution times (also called retention

167 times). Once a substance ends its chromatographic run, it is analysed by the mass spectrometer

168 hyphenated with the gas chromatograph and it is identified by its mass spectrum.

169 GC-MS has some advantages, such as robustness, low detection limits, high accuracy and the ability

170 to identify single substances in a mixture. On the other hand, it lacks of portability, requires long

171 times for each analysis and it is expensive. In addition, GC-MS does not give information about

172 odours because they are a feature of the whole mixture (Mackie et al., 1998), which is divided during

173 the chromatographic analysis. To better explain, single odorous compounds can reduce or

174 strengthen the global sensorial perception when they are present with other substances, and also

175 non-odorous substances can play a role in masking or increasing the whole perceived odour (Cain,

176 1975; Thomas-Danguin and Chastrette, 2002). Separating the single components using

177 chromatography implies the loss of the global odour information. Anyway, it is useful to know all

178 the substances that take part of an odorous mixture in order to improve abatement strategies

179 (Amon et al., 1997; Bibbiani and Russo, 2012; Pillai et al., 2012) and find correlations between

180 odours and chemical composition (Blanes-Vidal et al., 2009; Zahn et al., 2001).

181 GC-MS can be integrated with olfactometry (GC-MS/O) to understand which are the odour-

182 determining compounds (Bulliner et al., 2006; Laor et al., 2008; S. Zhang et al., 2010a). In this case,

183 a splitting tube, which brings the eluate to the mass spectrometer on one side and to a sniffing port

184 on the other side, is assembled after the chromatographic column. The dual output consists in a

185 chromatogram and an olfactogram, which shows peaks where an odour is detected. By means of

186 this technique, it is possible to understand which are the most odorous molecules in the mixture,

187 although any information about the latter as a whole is lost.

188 **3.3 Simulating the human olfactory system: the Electronic Nose technology**

189 An electronic nose, also called e-nose, is a device that acts as the human olfactory system and thus

190 it is able to discriminate between different odours. It firstly appeared in the Literature in 1982, when

191 Persaud and Dodd worked on a "device" that "can reproducibly discriminate between a wide variety

192 of odours, and its properties show that discrimination in an olfactory system could be achieved

193 without the use of highly specific receptors" (Persaud and Dodd, 1982). Actually, the key component

194 of an e-nose is an array of gas sensors that are not required to be highly specific to target compounds

195 because their whole response gives the so-called "fingerprint" that characterizes each particular

196 odour. In other words, the ensemble of the responses of non-specific or partially specific sensors is

197 the feature that allow recognizing and classifying an odorous sample (Abdullah et al., 2012; Nicolas

198 et al., 2000; Sohn et al., 2009). It is important to underline that an e-nose is sensible also to odourless

199 compounds, since its response depends on interactions between molecules and sensors surfaces,

200 whether or not they have a specific odour.

201 In general, an electronic nose is composed by three elements (Gardner and Bartlett, 1994; Peris and

202 Escuder-Gilabert, 2009): a sampling system (Section 3.3.1); a sensors chamber (Section 3.3.2); a data

203 processing and pattern recognition system (Section 3.3.3).

204 **3.3.1 Sampling system**

205 Generally, it consists of a tube connected with a pump, which brings the gaseous sample to the

206 chamber in which the sensors array is located.

207 **3.3.2 Sensors chamber**

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

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

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

235   In addition to the most used conductimetric and piezoelectric sensors, there are other types of
236   sensors that are used in the sensors array fabrication. These are thermal, electrochemical and
237   optical sensors, classified on the basis of their working principle (Brattoli et al., 2011; Capelli et al.,

238   2014). The sensors array can be formed by the same type of sensors or can be hybrid (Holmberg et
239   al., 1995; Ulmer et al., 2000) (composed by sensors that work with different principles).

3.3.3 Data processing and pattern recognition system

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

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

253   The use of electronic noses for air quality monitoring involves many advantages, such as real-time,
254   continuous and in-situ measurements, low cost analysis and possibility of remote control. A limit is
255   the dependence of the results on the environmental conditions (humidity level, temperature, wind
256   speed), which could lead to wrong evaluations. In order to take into account these parameters,
257   many e-noses are fabricated coupling sensors that monitor these external conditions (Brattoli et al.,
258   2011; Capelli et al., 2014). Another possibility is to sample the air with the aforementioned methods
259   and then take the samples to the laboratory for e-nose analysis. Doing so, the opportunity for a real-
260   time and on-site monitoring is lost, but the readings are less affected by environmental factors.

261   The electronic nose technology has been applied in many fields, such as food (Deisingh et al., 2004;
262   Peris and Escuder-Gilabert, 2009), beverage (Berna, 2010; Di Natale et al., 1996; Gardner et al.,
263   1992), environmental analyses (Capelli et al., 2014) and biomedical applications (Casalinuovo et al.,
264   2006; Gardner et al., 2000). A suggestion is to develop and train e-nose instruments dedicated to
265   specific purposes, choosing carefully the most suited combination of gas sensors and thus
266   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

329 optimize the adsorption of analytes in the solid phase. They found 35 compounds, belonging to the

330 chemical classes of volatile fatty acids (VFAs), esters, alcohols, aldehydes, ketones, halogenates,

331 amines and hydrocarbons. They also found that VFAs and esters exhibited the greatest olfactory

332 impact and that the temperature and the relative humidity did not affect significantly the results,

333 although these factors were relatively stable during the study. Filipy et al. (Filipy et al., 2006)

334 identified VOCs as alcohols, aldehydes, ketones, esters, ethers, aromatic hydrocarbons,

335 halogenated hydrocarbons, terpenes, other hydrocarbons, amines, other nitrogen containing

336 compounds and sulphur-containing compounds at a lactating cow open stall, thermally desorbing

337 them from Carbotrap B/Carbosieve S-III cartridges or U-shaped tubes containing glass beads with

338 Pyrex glass wool plugs before the chromatographic run. Concentrations of duplicate samples varied

339 up to 27% and results were dependent on meteorological conditions as wind speed, wind direction

340 and temperature. They also stated that no volatile fatty acids were identified because of the column

341 type used in GC-MS experiments and that many chromatographic peaks were not attributed to any

342 molecules of the mass spectrometer library. In a work of Lu et al. (Lu et al., 2008), the authors made

343 the air inside a dairy passing through a cartridge packed with a mixture of polyurethane form,

344 charcoal, XAD and silica gel. Then, they extracted the adsorbed compounds with two solvents

345 (dichloromethane and methanol) and injected 0.5 μL of the liquid into the GC-MS. They found the

346 compounds reported in Table 2. Zhang et al. (S. Zhang et al., 2010b) analysed odour-causing

347 compounds from a dairy site, sampling with sorbent tubes made of 304-grade stainless steel packed

348 with 65 mg of Tenax and quantifying with thermal desorption multidimensional gas

349 chromatography-mass spectrometry/olfactometry. They found 11 volatile compounds of which

350 they also evaluated odour intensity and hedonic tone after the chromatographic separation. The

351 same analytical technique was used by Cai et al. (Cai and Koziel, 2011) to determine odorous gases

352 from two dairy barns, one located in Wisconsin and the other in Indiana. The authors concluded

353 that some compounds (acetic acid, propanoic acid, 2-methyl propanoic acid, butyric acid, 3-methyl

354 butanoic acid and 4-methyl phenol in Wisconsin, guaiacol, 1-(2-aminophenyl)-ethanone and indole

355 in Indiana) showed a seasonal significant difference in the emission rate, and acetic, propanoic, 2-

356 methyl propanoic, butyric and 3-methyl butanoic acids were significantly different between the two

357 sites. The contents of these works are summarized in Table 2. Also electronic noses have been

358 applied in the monitoring of volatile compounds from dairy livestock. As said before, Pan et al. (Pan

359 et al., 2007) applied an e-nose prototype to compare its results with odour evaluations performed

360 by a panel that measured at two poultry, six dairy and six pig farms located in southern Ontario.

361 They stated that the gas sensors values were in agreement with human assessors' evaluations.

362 Furthermore, Chang et al. (Chang and Heinemann, 2015) trained an e-nose in which 32 polymer

363 sensors were present in order to predict human assessments of odours from a dairy farm.

364 **4.3 Swine**

365 Many studies that have tried to resolve odours from swine buildings by the use of gas

366 chromatography-mass spectrometry have been conducted (Table 3). Schiffman et al. (Schiffman et

367 al., 2001) analysed air from swine facilities in North Carolina and found acids, alcohols, aldehydes,

368 amides, amines, aromatics, esters, ethers, fixed gases, halogenated hydrocarbons, hydrocarbons,

369 ketones, nitriles, other nitrogen-containing compounds, phenols, sulphur-containing compounds,

370 steroids, and other compounds. The authors stated that most of these compounds were present at

371 concentrations below the respective odour thresholds and that many chromatographic peaks were

372 not sufficiently high to allow the identification of the corresponding molecule. They quantified the

373 volatile chemical compounds coming from a cleaned swine house using the average of the response

374 factors of the following 14 selected molecules, which should represent the chemical classes of the

375 molecules typically found in the atmosphere of the swine house: thiophene, acetic acid, 2-

376 pentanone, methyl disulfide, propanoic acid, 1-pentanethiol, *n*-butanoic acid, 2-heptanone, methyl

377 sulfoxide, *n*-pentanoic acid, methyl sulfone, 2-nonanone, 1-nonanethiol, and *n*-nonanoic acid. The

378 most abundant compounds were butanoic acid, acetic acid, 3-methyl butanoic acid, 4-methyl

379 phenol, propanoic acid, 2-methyl propanoic acid, 2-methyl butanoic acid, vinyl acetate, 4-ethyl

380 phenol, phenol, and acetaldehyde. Razote et al. (Razote et al., 2002) optimized and tested a dynamic

381 air sampling system in conjunction with solid phase microextraction (SPME) technique to sample

382 and then analysed by GC-MS compounds present in the air of a swine house in Manhattan city. Takai

383 et al. (Takai et al., 2005) studied how temperature, management and categories of pigs influence

384 the emission of five key odorants, adsorbing them onto SPME fibers followed by GC-MS analysis. In

385 a work of the same year, Blunden et al. (Blunden et al., 2005) sampled air from five swine CAFOs

386 located in the eastern part of North Carolina and found more than 100 compounds, including

387 paraffins, olefins, aromatics, monoterpenes, ethers, alcohols, aldehydes, ketones, halogenated

388 hydrocarbons, phenols, and sulfides. Identification with retention times and quantification were

389 performed using GC coupled with a Flame Ionization Detector (FID) and GC-MS was employed to

390 confirm the correct identification of the molecules present in the samples. The authors calibrated

391 the GC-FID instrument using 0.25 ppm propane in air (± 1.2%) National Institute of Standards and

392 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 μg m^{-3} for volatile fatty acids and 0.03 and 42 μg 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.

425   Finally, an e-nose constituted of 6 metal oxide sensors was employed by Romain et al. (Romain et

426   al., 2013) to continuously monitor odours from an experimental pig farm in Liège. After an

427   appropriate calibration against olfactometric measurements, the e-nose proved to be reliable.

428   **5**. **Use of VOC's to detect pathology in animals**

429   The odour from farmed animals is influenced by their health status and, in particular, enteric problems are

430   characterised by peculiar odour properties (Sohn et al., 2008).

431   Several studies have explored the possibility to diagnose pathologies in livestock and in humans via

432   identification of the Volatile Organic Compounds (VOCs) produced by pathogens, host-pathogen interactions

433   and biochemical pathways (Ellis et al., 2014).

434   VOCs analysis has been explored as a method to diagnose bovine respiratory disease, brucellosis and bovine

435   tuberculosis in cattle. Exploring volatile organic compounds (VOCs) as non-invasive biomarkers of diseases

436   or infections is a research area of growing interest, in both human and veterinary medicine (Purkhart et al.,

437   2011) and in particular, the investigation of faecal VOCs may be the best non-invasive and early way of

438   diagnosing livestock diseases.

439

440   **6. Conclusions**

441   Odours from livestock farming are a very demanding analytical challenge due to their chemical

442   complexity and the low concentrations of the single compounds. It is extremely important to study

443   them in order to understand their origin and develop efficient abatement technologies. As

444   presented in this review paper, a reference technique to deal with this issue does not exist, but

445   there are different ways to approach the problem. Dynamic Olfactometry, Gas Chromatography

446   coupled with Mass Spectrometry and Electronic Noses have different working principles and

447   outputs, so the combined use of them could maximize the information obtained about odours

448   originated from CAFOs.

449   Apart from the techniques used to detect them, the VOC's seem to be the new frontier of

450   diagnostics both in human and in livestock; in fact, the VOCs emitted from different areas of the

451   living body can be considered as individual 'fingerprints' and pathological processes (such as

452   infection and endogenous metabolic disorders), can influence the odour fingerprints by producing

453   new VOCs or by changing the ratio of VOCs that are produced normally. One of the main advantage

454   of these techniques is that it is a non-invasive diagnostic tool that does not requires any

455   manipulation of the animals. For these reasons, exploring volatile organic compounds (VOCs) is a

456   research area of growing interest in both human and veterinary medicine.

457   In this context, electronic noses, considering their low cost, their simplicity of use and the possibility

458   to remotely control their output from different analytical locations, appear to be the best solution

459   to solve the above-mentioned challenge. However, these devices (particularly those characterized

460   by inexpensive systems) are currently based on a sensor array, composed by 5-10 sensors, each of

461   which capable of detecting a very general class of compounds. Therefore, they are not appropriately

462   designed for specifically detecting the compounds related to a specific disease. More research has

463   to be done in order to find the typical VOCs responsible of the odour released by unhealthy human

464   or animal individuals, and to connect each odour to a typical compound. This challenge can be

465   tackled using all the techniques presented in this review, particularly those allowing to be extremely

466   selective and sensitive. Once the correlation between disease-compound-odour has been found,

467   very specific sensors could be designed, each of which tailored for specific targets and selected

468   applications. The use of affinity-based recognition, perm-selective membranes, molecularly

469   imprinted polymers (MIP), host-guest systems could allow to reach the sought selectivity in these

470   sensors.

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474   **Conflicts of interest**

479   **References**

480   (CEN), C. for E.N., 2003. EN 13725: Air quality - Determination of odour concentration by dynamic

481   olfactometry Brussels.

482   Abdi, H., Williams, L.J., 2010. Principal component analysis. Wiley Interdiscip. Rev. Comput. Stat. 2,

483   433–459. doi:10.1002/wics.101

484   Abdullah, A.H., Adom, A.H., Ammar Zakaria, Saad, F.S.A., Kamarudin, L.M., 2012. Chicken Farm
485   Malodour Monitoring Using Portable Electronic Nose System. Chem. Eng. Trans. 30, 55–60.
486   doi:10.3303/CET1230010

487   Amon, M., Dobeic, M., Sneath, R.W., Phillips, V.R., Misselbrook, T.H., Pain, B.F., 1997. A farm-scale
488   study on the use of clinoptilolite zeolite and De-Odorase® for reducing odour and ammonia
489   emissions from broiler houses. Bioresour. Technol. 61, 229–237.

490   Andersen, K.B., Glasius, M., Feilberg, A., 2014. Gas–particle partitioning of odorants in a pig house
491   measured by thermal desorption GC/MS. Environ. Sci. Process. Impacts 16, 1059.
492   doi:10.1039/c3em00444a

493   Berna, A., 2010. Metal oxide sensors for electronic noses and their application to food analysis.
494   Sensors 10, 3882–3910. doi:10.3390/s100403882

495   Bibbiani, C., Russo, C., 2012. Odour emission from intensive livestock production system:
496   Approaches for emission abatement and evaluation of their effectiveness. Large Anim. Rev.
497   18, 135–138.

498   Blanes-Vidal, V., Hansen, M.N., Adamsen, A.P.S., Feilberg, A., Petersen, S.O., Jensen, B.B., 2009.
499   Characterization of odor released during handling of swine slurry: Part I. Relationship
500   between odorants and perceived odor concentrations. Atmsopheric Environ. 43, 2997–3005.

501   Blunden, J., Aneja, V.P., Lonneman, W.A., 2005. Characterization of non-methane volatile organic
502   compounds at swine facilities in eastern North Carolina. Atmos. Environ. 39, 6707–6718.
503   doi:10.1016/j.atmosenv.2005.03.053

504   Boeker, P., Leppert, J., Lammers, P.S., 2014. Comparison of odorant losses at the ppb-level from
505   sampling bags of nalophanTM and tedlarTM and from adsorption tubes. Chem. Eng. Trans.
506   40, 157–162.

507   Bourgeois, W., Romain, A.-C., Nicolas, J., Stuetz, R.M., 2003. The use of sensor arrays for
508   environmental monitoring: Interests and limitations. J. Environ. Monit. 5, 852–860.

509   Brambilla, M., Navarotto, P., 2010. Sensorial analysis of pig barns odour emissions. Chem. Eng.
510   Trans. 23, 243–248.

511   Brandt, R.C., Elliott, H.A., Adviento-Borbe, M.A.A., Wheeler, E.F., Kleinman, P.J.A., Beegle, D.B.,
512   2011. Field olfactometry assessment of dairy manure land application methods. J. Environ.
513   Qual. 40, 431–437.

514   Brattoli, M., de Gennaro, G., de Pinto, V., Loiotile, A.D., Lovascio, S., Penza, M., 2011. Odour
515   detection methods: Olfactometry and chemical sensors. Sensors 11, 5290–5322.
516   doi:10.3390/s110505290

517   Brezmes, J., Ferreras, B., Llobet, E., Vilanova, X., Correig, X., 1997. Neural network based electronic
518   nose for the classification of aromatic species. Anal. Chim. Acta 348, 503–509.

519   Brose, G., Gallmann, E., Hartung, E., Jungbluth, T., 2001. Detection of the dynamics of odour
520   emissions from pig farms using dynamic olfactometry and an electronic odour sensor. Water
521   Sci. Technol. 44, 59–64.

522   Bulliner, E.A., Koziel, J.A., Cai, L., Wright, D., 2006. Characterization of Livestock Odors Using Steel
523   Plates, Solid-Phase Microextraction, and Multidimensional Gas Chromatography–Mass
524   Spectrometry–Olfactometry. J. Air Waste Manage. Assoc. 56, 1391–1403.
525   doi:10.1080/10473289.2006.10464547

526   Cai, L., Koziel, J.A., 2011. Odorous chemical emissions from livestock operations in United States.
527   Remote Sensing, Environ. Transp. Eng. (RSETE), 24-26 June 2011 532–535.

528   Cai, L., Koziel, J.A., Lo, Y.C., Hoff, S.J., 2006. Characterization of volatile organic compounds and
529   odorants associated with swine barn particulate matter using solid-phase microextraction
530   and gas chromatography-mass spectrometry-olfactometry. J. Chromatogr. A 1102, 60–72.
531   doi:10.1016/j.chroma.2005.10.040

532   Cai, L., Zhang, S., Koziel, J.A., Sun, G., Heathcote, K.Y., Hoff, S.J., Parker, D.B., Caraway, E.A.,
533   Jacobson, L.D., Akdeniz, N., Hetchler, B.P., Cortus, E.L., Bereznicki, S.D., Heber, A.J., 2010.
534   Odor and odorous chemical emissions from animal builidngs: Part 3 - chemical emissions.
535   ASABE - Int. Symp. Air Qual. Waste Manag. Agric. 2010 294–302.

536   Cain, W.S., 1975. Odor intensity: mixtures and masking. Chem. Senses Flavor 1, 339–352.

537   Capelli, L., Sironi, S., Del Rosso, R., 2014. Electronic noses for environmental monitoring
538   applications. Sensors (Basel). 14, 19979–20007. doi:10.3390/s141119979

539   Capelli, L., Sironi, S., Del Rosso, R., Guillot, J.M., 2013. Measuring odours in the environment vs.

540   dispersion modelling: A review. Atmos. Environ. 79, 731–743.

541   doi:10.1016/j.atmosenv.2013.07.029

542 Carey, J.B., Lacey, R.E., Mukhtar, S., 2004. A review of literature concerning odors, ammonia, and

543   dust from broiler production facilities: 2. Flock and house management factors. J. Appl. Poult.

544   Res. 13, 509–513. doi:10.1093/japr/13.3.509

545 Casalinuovo, I.A., Di Pierro, D., Coletta, M., Di Francesco, P., 2006. Application of Electronic Noses

546   for Disease Diagnosis and Food Spoilage Detection. Sensors 6, 1428–1439.

547   doi:10.3390/s6111428

548 Chang, F., Heinemann, P., 2015. Prediction of human assessments of odor using electronic nose

549   and artifical network. Am. Soc. Agric. Biol. Eng. Annu. Int. Meet. 26-29 July 2015.

550 Ciosek, P., Wróblewski, W., 2006. The analysis of sensor array data with various pattern

551   recognition techniques. Sensors Actuactors, B Chem. 114, 85–93.

552 Deisingh, A.K., Stone, D.C., Thompson, M., 2004. Applications of electronic noses and tongues in

553   food analysis. Int. J. Food Sci. Technol. 39, 587–604. doi:10.1111/j.1365-2621.2004.00821.x

554 Di Natale, C., Davide, F.A.M., D'Amico, A., Nelli, P., Groppelli, S., Sberveglieri, C., 1996. An

555   electronic nose for the recognition of the vineyard of a red wine. Sensors Actuactors, B Chem.

556   33, 83–88.

557 Dunlop, M., Gallagher, E., Sohn, J.H., 2010. Odour emissions from tunnel-ventilated broiler sheds:

558   Case study of nine Queensland farms. Anim. Prod. Sci. 50, 546–551.

559 Ellis, C., Stahl, R., Nol, P., Waters, W., Palmer, M., 2014. A Pilot Study Exploring the Use of Breath

560   Analysis to Differentiate Healthy Cattle from Cattle. PlosOne 9(2), 1-12

561 Escuderos, M.E., Sánchez, S., Jiménez, A., 2011. Quartz Crystal Microbalance (QCM) sensor arrays

562   selection for olive oil sensory evaluation. Food Chem. 124, 857–862.

563 Filipy, J., Rumburg, B., Mount, G., Westberg, H., Lamb, B., 2006. Identification and quantification of

564   volatile organic compounds from a dairy. Atmos. Environ. 40, 1480–1494.

565   doi:10.1016/j.atmosenv.2005.10.048

566 Fine, G.F., Cavanagh, L.M., Afonja, A., Binions, R., 2010. Metal oxide semi-conductor gas sensors in

567   environmental monitoring. Sensors 10, 5469–5502. doi:10.3390/s100605469

568   Gallmann, E., Brose, G., Hartung, E., Jungbluth, T., 2001. Influence of different pig housing systems
569   on odor emissions. Water Sci. Technol. 44, 237–244.

570   Gallmann, E., Hartung, E., Brose, G., Jungbluth, T., 2004. Determination of the dynamics of the
571   odour release from a pig house, using an electronic odour sensor. Water Sci. Technol. 50,
572   101–108.

573   Gardner, J.W., Bartlett, P.N., 1995. Application of conducting polymer technology in microsystems.
574   Sensors Actuactors A. Phys. 51, 57–66.

575   Gardner, J.W., Bartlett, P.N., 1994. Brief history of electronic noses. Sensors Actuactors, B Chem.
576   B18, 211–220.

577   Gardner, J.W., Shin, H.W., Hines, E.L., 2000. Electronic nose system to diagnose illness. Sensors
578   Actuators, B Chem. 70, 19–24. doi:10.1016/S0925-4005(00)00548-7

579   Gardner, J.W., Shurmer, H.V., Tan, T.T., 1992. Application of an electronic nose to the
580   discrimination of coffees. Sensors Actuators, B Chem. 6, 71–75.

581   Gebicki, J., 2016. Application of electrochemical sensors and sensor matrixes for measurement of
582   odorous chemical compounds. TrAC - Trends Anal. Chem. 77, 1–13.
583   doi:10.1016/j.trac.2015.10.005

584   Ghimenti, S., Lomonaco, T., Bellagambi, F.G., Tabucchi, S., Onor, M., Trivella, M.G., Ceccarini, A.,
585   Fuoco, R., Di Francesco, F., 2015. Comparison of sampling bags for the analysis of volatile
586   organic compounds in breath. J. Breath Res. 9.

587   Ghosh, S., Kim, K.-H., Sohn, J.R., 2011. Some Insights into Analytical Bias Involved in the
588   Application of Grab Sampling for Volatile Organic Compounds: A Case Study against Used
589   Tedlar Bags. Sci. World J. 11, 2160–2177. doi:10.1100/2011/529532

590   Govardhan, K., Nirmala Grace, A., 2016. Metal/metal oxide doped semiconductor based metal
591   oxide gas sensors - A review. Sens. Lett. 14, 741–750.

592   Gralapp, A.K., Powers, W.J., Bundy, D.S., 2001. Comparison of olfactometry, gas chromatography,
593   and electronic nose technology for measurement of indoor air from swine facilities. Trans.
594   Am. Soc. Agric. Eng. 44, 1283–1290.

595   Hamilton, D.W., Arogo, J., 1999. Understanding Farmstead Odors: An Annotated Review. Prof.

596   Anim. Sci. 15, 203–210.

597   Hansen, M.J., Adamsen, A.P.S., Feilberg, A., Jonassen, K.E.N., 2011. Stability of odorants from pig

598   production in sampling bags for olfactometry. J. Environ. Qual. 40, 1096–1102.

599   Hansen, M.J., Jonassen, K.E.N., L??kke, M.M., Adamsen, A.P.S., Feilberg, A., 2016. Multivariate

600   prediction of odor from pig production based on in-situ measurement of odorants. Atmos.

601   Environ. 135, 50–58. doi:10.1016/j.atmosenv.2016.03.060

602   Haugen, J.-E., Kvaal, K., 1998. Electronic nose and artificial neural network. Meat Sci. 49, S273–

603   286.

604   Holmberg, M., Winquist, F., Lundström, I., Gardner, J.W., Hines, E.L., 1995. Identification of paper

605   quality using a hybrid electronic nose. Sensors Actuactors, B Chem. 27, 246–249.

606   Hove, N., Van Langenhove, H., Demeyer, P., 2012. Development of an olfactometric measuring

607   facility according to cen en 13725 and to generate up to date odour concentrations from

608   animal houses in flanders. Chem. Eng. Trans. 30, 97–102.

609   Jacobson, L.D., Hetchler, B.P., Schmidt, D.R., Nicolai, R.E., Heber, A.J., Ni, J.-Q., Hoff, S.J., Koziel, J.

610   a, Zhang, Y., Beasley, D.B., Parker, D.B., 2008. Quality assured measurements of animal

611   building emissions: odor concentrations. J. Air Waste Manag. Assoc. 58, 806–811.

612   doi:10.3155/1047-3289.58.6.806

613   James, D., Scott, S.M., Ali, Z., O'Hare, W.T., 2005. Chemical sensors for electronic nose systems.

614   Microchim. Acta 149, 1–17. doi:10.1007/s00604-004-0291-6

615   Korotcenkov, G., 2007. Metal oxides for solid-state gas sensors: What determines our choice?

616   Mater. Sci. Eng. B Solid State Mater. Adv. Technol. 139, 1–23.

617   Koziel, J. a, Spinhirne, J.P., Lloyd, J.D., Parker, D.B., Wright, D.W., Kuhrt, F.W., 2005. Evaluation of

618   sample recovery of malodorous livestock gases from air sampling bags, solid-phase

619   microextraction fibers, Tenax TA sorbent tubes, and sampling canisters. J. Air Waste Manag.

620   Assoc. 55, 1147–1157. doi:10.1080/10473289.2005.10464711

621   Laor, Y., Koziel, J.A., Cai, L., Ravid, U., 2008. Chemical sensory characterization of dairy manure

622   odor using headspace solid-phase microextraction and multidimensional gas chromatography

623   mass spectrometry-olfactometry. J. Air Waste Manag. Assoc. 58, 1187–1197.

624   Laor, Y., Ozer, Y., Ravid, U., Hanan, A., Orenstein, P., 2010. Methodological aspects of sample

625   collection for dynamic olfactometry. Chem. Eng. Trans. 23, 55–60.

626   Le, H., Sivret, E.C., Parcsi, G., Stuetz, R.M., 2013. Stability of Volatile Sulfur Compounds (VSCS) in

627   sampling bags - Impact of temperature. Water Sci. Technol. 68, 1880–1887.

628   Le, H.V., Sivret, E.C., Parcsi, G., Stuetz, R.M., 2015. Impact of storage conditions on the stability of

629   volatile sulfur compounds in sampling bags. J. Environ. Qual. 44, 1523–1529.

630   Lorwongtragool, P., Wongchoosuk, C., Kerdcharoen, T., 2010. Portable artificial nose system for

631   assessing air quality in swine buildings. 2010 ECTI Int. Conf. Electr. Eng. Comput.

632   Telecommun. Inf. Technol. 532–535.

633   Lovanh, N., Loughrin, J., Silva, P., 2016. The effect of aged litter materials on polyatomic ion

634   concentrations in fractionated suspended particulate matter from a broiler house. J. Air

635   Waste Manage. Assoc. 66, 707–714. doi:10.1080/10962247.2016.1170737

636   Lu, M., Lamichhane, P., Liang, F., Imerman, E., Chai, M., 2008. Identification of odor causing

637   compounds in a commercial dairy farm. Water, Air, Soil Pollut. Focus 8, 359–367.

638   doi:10.1007/s11267-007-9150-x

639   Mackie, R.I., Stroot, P.G., Varel, V.H., 1998. Biochemical Identification and Biological Origin of Key

640   Odor Components in Livestock Waste. J. Anim. Sci. 76, 1331–1342. doi:/1998.7651331x

641   Milligan, G.W., Cooper, M.C., 1987. Methodology Review: Clustering Methods. Appl. Psychol.

642   Meas. 11, 329–354.

643   Misselbrook, T.H., Clarkson, C.R., Pain, B.F., 1993. Relationship Between Concentration and

644   Intensity of Odours for Pig Slurry and Broiler Houses. J. Agric. Eng. Res. 55, 163–169.

645   Møller, S.F., Von Frese, J., Bro, R., 2005. Robust methods for multivariate data analysis. J.

646   Chemom. 19, 549–563. doi:10.1002/cem.962

647   Murphy, K.R., Parcsi, G., Stuetz, R.M., 2014. Non-methane volatile organic compounds predict

648   odor emitted from five tunnel ventilated broiler sheds. Chemosphere 95, 423–432.

649   doi:10.1016/j.chemosphere.2013.09.076

650   Nicolas, J., Romain, A.-C., Wiertz, V., Maternova, J., André, P., 2000. Using the classification model

651   of an electronic nose to assign unknown malodours to environmental sources and to monitor

652   them continuously. Sensors Actuactors, B Chem. 69, 366–371.

653 Pan, L., Yang, S.X., 2007. A new intelligent electronic nose system for measuring and analysing

654   livestock and poultry farm odours. Environ. Monit. Assess. 135, 399–408.

655   doi:10.1007/s10661-007-9659-5

656 Pan, L., Yang, S.X., DeBruyn, J., 2007. Factor Analysis of Downwind Odours from Livestock Farms.

657   Biosyst. Eng. 96, 387–397. doi:10.1016/j.biosystemseng.2006.10.017

658 Pau, J.C., Knoll, J.E., Midgett, M.R., 1991. A Tedlar Bag Sampling System for Toxic Organic

659   Compounds in Source Emission Sampling and Analysis. J. Air Waste Manage. Assoc. 41, 1095–

660   1097. doi:10.1080/10473289.1991.10466905

661 Peled, N., Ionescu, R., Nol, P., Barash, O., McCollum, M., VerCauteren, K., Koslow, M., Stahl, R.,

662   Rhyan, J. and Haick, H. 2012. Detection of volatile organic compounds in cattle naturally

663   infected with Mycobacterium bovis. Sensors and Actuators B 171–172, 588–594. doi:

664   10.1016/j.snb.2012.05.038

665 Peris, M., Escuder-Gilabert, L., 2009. A 21st century technique for food control: Electronic noses.

666   Anal. Chim. Acta 638, 1–15.

667 Persaud, K., Dodd, G., 1982. Analysis of discrimination mechanisms in the mammalian olfactory

668   system using a model nose. Nature 299, 352–355.

669 Pillai, S.M., Parcsi, G., Wang, X., Stuetz, R.M., 2012. Odour abatement of poultry litter using odour

670   control products. Chem. Eng. Trans. 30, 247–252.

671 Purkhart, R., Köhler, H., Liebler-Tenorio, E., Meyer, M., Becher, G., Kikowatz, A., Reinhold, P., 2011.

672   Chronic intestinal Mycobacteria infection: discrimination via VOC analysis in exhaled breath

673   and headspace of feces using differential ion mobility spectrometry. Journal of breath

674   research 5, 027103 (10pp) doi: 10.1088/1752-7155/5/2/02710.

675 Rabaud, N.E., Ebeler, S.E., Ashbaugh, L.L., Flocchini, R.G., 2003. Characterization and quantification

676   of odorous and non-odorous volatile organic compounds near a commercial dairy in

677   California. Atmos. Environ. 37, 933–940. doi:10.1016/S1352-2310(02)00970-6

678 Razote, E., Jeon, I., Maghirang, R., 2002. Dynamic Air Sampling of Volatile Organic Compounds

679   Using Solid Phase Microextraction 37, 365–378. doi:10.1081/PFC-120004477

680   Romain, A.C., Nicolas, J., Cobut, P., Delva, J., Nicks, B., Philippe, F.X., 2013. Continuous odour
681   measurement from fattening pig units. Atmos. Environ. 77, 935–942.
682   doi:10.1016/j.atmosenv.2013.06.030

683   Rzeznik, W., Mielcarek, P., Jugowar, J.L., 2014. The emission of odor from livestock buildings of
684   dairy cattle in Poland. Appl. Eng. Agric. 30, 961–970.

685   Schauberger, G., Lim, T.T., Ni, J.Q., Bundy, D.S., Haymore, B.L., Diehl, C.A., Duggirala, R.K., Heber,
686   A.J., 2013. Empirical model of odor emission from deep-pit swine finishing barns to derive a
687   standardized odor emission factor. Atmos. Environ. 66, 84–90.
688   doi:10.1016/j.atmosenv.2012.05.046

689   Schiffman, S.S., 1998. Livestock odors: implications for human health and well-being. J Anim Sci 76,
690   1343–1355.

691   Schiffman, S.S., Bennett, J.L., Raymer, J.H., 2001. Quantification of odors and odorants from swine
692   operations in North Carolina. Agric. For. Meteorol. 108, 213–240. doi:10.1016/S0168-
693   1923(01)00239-8

694   Scott, S.M., James, D., Ali, Z., 2006. Data analysis for electronic nose systems. Microchim. Acta 156,
695   183–207. doi:10.1007/s00604-006-0623-9

696   Shaffer, R.E., Rose-Pehrsson, S.L., McGill, R.A., 1999. A comparison study of chemical sensor array
697   pattern recognition algorithms. Anal. Chim. Acta 384, 305–317.

698   Shirasu, M., Touhara, K., 2011. The scent of disease: volatile organic compounds of the human
699   body related to disease and disorder. The Journal of Biochemistry 150, 257-266.
700   10.1093/jb/mvr090

701   Shirasu, M., Touhara, K., 2011. The scent of disease: volatile organic compounds of the human
702   body related to disease and disorder. The Journal of Biochemistry 150, 257-266.
703   10.1093/jb/mvr090

704   Si, P., Mortenses, J., Komolov, A., Denborg, J., Møller, P.J., 2007. Polymer coated quartz crystal
705   microbalance sensors for detection of volatile organic compounds in gas mixtures. Anal.
706   Chim. Acta 597, 223–230.

707   Skóra, J., Matusiak, K., Wojewódzki, P., Nowak, A., Sulyok, M., Ligocka, A., Okrasa, M., Hermann, J.,
708   Gutarowska, B., 2016. Evaluation of microbiological and chemical contaminants in poultry

709 farms. Int. J. Environ. Res. Public Health 13, 1–16. doi:10.3390/ijerph13020192

710 Smith, M.S., Francis, A.J., Duxbury, J.M., 1977. Collection and analysis of organic gases from

711 natural ecosystems: application to poultry manure. Environ. Sci. Technol. 11, 51–55.

712 doi:10.1021/es60124a005

713 Sohn, J.H., Hudson, N., Gallagher, E., Dunlop, M., Zeller, L., Atzeni, M., 2008. Implementation of an

714 electronic nose for continuous odour monitoring in a poultry shed. Sensors Actuators, B

715 Chem. 133, 60–69. doi:10.1016/j.snb.2008.01.053

716 Sohn, J.H., Pioggia, G., Craig, I.P., Stuetz, R.M., Atzeni, M.G., 2009. Identifying major contributing

717 sources to odour annoyance using a non-specific gas sensor array. Biosyst. Eng. 102, 305–312.

718 Sucker, K., Both, R., Bischoff, M., Guski, R., Winneke, G., 2008. Odor frequency and odor

719 annoyance. Part I: Assessment of frequency, intensity and hedonic tone of environmental

720 odors in the field. Int. Arch. Occup. Environ. Health 81, 671–682. doi:10.1007/s00420-007-

721 0259-z

722 Szyłak-Szydłowski, M., 2015. Odour Samples Degradation During Detention in Tedlar® Bags. Water,

723 Air, Soil Pollut. 226, 227. doi:10.1007/s11270-015-2495-2

724 Takai, H., Dahl, P.J., Tegersen, F., Johnsen, J., Maahn, M., Segaard, H., 2005. Analysis of odorous

725 compounds in swine buildings and their relationship to thermal environment, management

726 and categories of pigs. Livest. Environ. VII - Proc. Seventh Int. Symp. 334–340.

727 Thomas-Danguin, T., Chastrette, M., 2002. Odour intensity of binary mixtures of odorous

728 compounds. Comptes Rendus - Biol. 325, 767–772.

729 Trabue, S., Scoggin, K., Mitloehner, F., Li, H., Burns, R., Xin, H., 2008. Field sampling method for

730 quantifying volatile sulfur compounds from animal feeding operations. Atmos. Environ. 42,

731 3332–3341. doi:10.1016/j.atmosenv.2007.03.016

732 Trabue, S.L., Anhalt, J.C., Zahn, J.A., 2006. Bias of tedlar bags in the measurement of agricultural

733 odorants. J. Environ. Qual. 35, 1668–1677.

734 Trabue, S.L., Scoggin, K.D., Li, H., Burns, R., Xin, H., 2008. Field sampling method for quantifying

735 odorants in humid environments. Environ. Sci. Technol. 42, 3745–3750.

736 doi:10.1021/es7031407

737   Ueno, H., Amano, S., Merecka, B., Kosmider, J., 2009. Difference in the odor concentrations

738   measured by the triangle odor bag method and dynamic olfactometry. Water Sci. Technol.

739   59, 1339–1342.

740   Ulmer, H., Mitrovics, J., Weimar, U., Göpel, W., 2000. Sensor arrays with only one or several

741   transducer principles? The advantage of hybrid modular systems. Sensors Actuactors, B

742   Chem. 65, 79–81.

743   US, N.R.C., 2003. Ad hoc commitee on air emissions from animal feeding operations (2003). Air

744   emissions from animal feeding operations: current knowledge, future needs 50–56; 169–176.

745   Van Durme, J., Werbrouck, B., 2015. Phase ratio variation approach for the study of partitioning

746   behavior of volatile organic compounds in polymer sample bags: Nalophan case study.

747   Environ. Sci. Pollut. Res. 22, 11067–11075. doi:10.1007/s11356-015-4320-2

748   Van Harreveld, a P., Heeres, P., Harssema, H., 1999. A review of 20 years of standardization of

749   odor concentration measurement by dynamic olfactometry in Europe. J. Air Waste Manag.

750   Assoc. 49, 705–715. doi:10.1080/10473289.1999.11499900

751   Van Huffel, K., Heynderickx, P.M., Dewulf, J., Van Langenhove, H., 2012. Measurement of odorants

752   in livestock buildings: Sift-ms and td-gc-ms. Chem. Eng. Trans. 30, 67–72.

753   doi:10.3303/CET1230012

754   Van Wang, Raihala, T.S., Jackman, A.P., John, R.S.T., 1996. Use of Tedlar bags in VOC testing and

755   storage: Evidence of significant VOC losses. Environ. Sci. Technol. 30, 3115–3117.

756   doi:10.1021/es950582y

757   Wang, D.K.W., Austin, C.C., 2006. Determination of complex mixtures of volatile organic

758   compounds in ambient air: Canister methodology. Anal. Bioanal. Chem. 386, 1099–1120.

759   doi:10.1007/s00216-006-0466-6

760   Williams, A.G., 1989. Dust and odour relationships in broiler house air. J. Agric. Eng. Res. 44, 175–

761   190.

762   Wilson, a. ., Baietto, M., 2009. Applications and advances in electronic-nose technologies. Sensors

763   9, 5099–5148. doi:10.3390/s90705099

764   Woolfenden, E., 2010. Sorbent-based sampling methods for volatile and semi-volatile organic

765   compounds in air: Part 1: Sorbent-based air monitoring options. J. Chromatogr. A 1217,

766   2674–2684.

767 Yang, X., Lorjaroenphon, Y., Cadwallader, K.R., Wang, X., Zhang, Y., Lee, J., 2014. Analysis of
768   particle-borne odorants emitted from concentrated animal feeding operations. Sci. Total
769   Environ. 490, 322–333. doi:10.1016/j.scitotenv.2014.05.026

770 Zahn, J.A., DiSpirito, A.A., Do, Y.S., Brooks, B.E., Cooper, E.E., Hatfield, J.L., 2001. Correlation of
771   human olfactory responses to airborne concentrations of malodorous volatile organic
772   compounds emitted from swine effluents. J. Environ. Qual. 30, 624–634.

773 Zarra, T., Reiser, M., Naddeo, V., Belgiorno, V., Kranert, M., 2012. A comparative and critical
774   evaluation of different sampling materials in the measurement of odour concentration by
775   dynamic olfactometry. Chem. Eng. Trans. 30, 307–312.

776 Zhang, S., Cai, L., Koziel, J.A., Hoff, S.J., Heathcote, K.Y., Jacobson, L.D., Akdeniz, N., Hetchler, B.P.,
777   Parker, D.B., Caraway, E.A., Heber, A.J., Bereznicki, S.D., 2010a. Odor and odorous chemical
778   emissions from animal buildings: Part 5 -correlations between odor intensities and chemical
779   concentrations (GC-MS/O). ASABE - Int. Symp. Air Qual. Waste Manag. Agric. 2010 279–285.

780 Zhang, S., Cai, L., Koziel, J.A., Hoff, S.J., Schmidt, D.R., Clanton, C.J., Jacobson, L.D., Parker, D.B.,
781   Heber, A.J., 2010b. Field air sampling and simultaneous chemical and sensory analysis of
782   livestock odorants with sorbent tubes and GC-MS/olfactometry. Sensors Actuactors, B Chem.
783   146, 427–432.

784 Zhang, S., Cai, L., Koziel, J.A., Hoff, S.J., Schmidt, D.R., Clanton, C.J., Jacobson, L.D., Parker, D.B.,
785   Heber, A.J., 2010. Field air sampling and simultaneous chemical and sensory analysis of
786   livestock odorants with sorbent tubes and GC-MS/olfactometry. Sensors Actuators, B Chem.
787   146, 427–432. doi:10.1016/j.snb.2009.11.028

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790 **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)

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

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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)

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

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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)

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