Science of the Total Environment 621 (2018) 168–176

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Anaerobic digestion coupled with digestate injection reduced odour emissions from soil during manure distribution

Orzi V., Riva C., Scaglia B., D'Imporzano G., Tambone F., Adani F. *

Gruppo Ricicla – DiSAA, Università degli Studi di Milano, Soil and Env. Lab, Via Celoria 2, 20133 Milano, Italy

HIGHLIGHTS

- Anaerobic digestion reduces odours impact because of degradation of organic matter.
- Anaerobic digestion (AD) coupled with manure injection reduced odour emissions.
- Specific Odour Emission Rate (SOER) well correlated with electronic nose fingerprint
- Electronic nose can replace SOER in measuring odour impact.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 1 September 2017
Received in revised form 17 October 2017
Accepted 21 November 2017
Available online xxxx

Editor: P. Kassomenos

Keywords:
Digestate
Electronic nose
Field experiments
Manure spreading
Odours
Olfactometry

ABSTRACT

This work aimed to measure the odour impact of untreated cow and pig slurries and treated (digestate and liquid fraction of digestate) manures when they were used on soil at a field scale, while also testing different spreading methods, i.e. surface vs. injection. Five experiments were performed in 2012–2016 on different farms. Odours were quantitatively (specific odour emission rate – SOER) ($OU_E\ m^{-2}\ h^{-1}$) measured by using dynamic olfactometry and qualitatively, i.e. to obtain an "odour fingerprint", by using an electronic nose (EN).

Anaerobic digestion was effective in allowing the reduction of potential odour emission from digestates, so that when they were dosed on soil, odours emitted were much lower than those from soils on which untreated slurries were used. Slurries/digestate injection reduced much more odour emitted by soils so that SOER tended to become more similar to that of the control (untreated soil) although the odours were slightly greater.

Odour fingerprint data indicated that there was a direct correlation between SOER and odour fingerprints. This was due to the ability of EN to detect ammonia, S-compounds and methane that were (the first two mainly), also, responsible for odours. Very good regression was found for Log SOER and EN by using a Partial Least Square (PLS) approach ($R^2 = 0.73$; $R^2_{cv} = 0.66$; $P < 0.01$) for matrices used to fertilize soils in lab tests. Unfortunately, regression was not so good when odour data from field experiments on soil were used, so that EN cannot be proposed to replace olfactometry. EN fingerprints for control (Blank) and injected organic matrices were virtually identical, due to the creation of cavities in the soil during the injection that decreased the treated surface. Anaerobic digestion and subsequent digestate injection allowed us to reduce odour impact, avoiding annoyance to local inhabitants.

* Corresponding author.
E-mail address: Fabrizio.adani@unimi.it (F. Adani).

https://doi.org/10.1016/j.scitotenv.2017.11.249
0048-9697/

1. Introduction

Odour emissions constitute a problem when they affect public health because of the diffusion of diseases and nuisance to the surrounding population (Orzi et al., 2015). Land application of manure can be a major source of odour emission in rural communities (Parker et al., 2013). Manures emit odours, Volatile Organic Compounds (VOC) and non-VOCs (ammonia, hydrogen sulphide) that represent a concern for inhabitants close to field application sites (Parker et al., 2013).

In Europe, new legislation on environmental protection will require methods to reduce both ammonia and odour emission due to the spreading on the land of animal slurries (Pahl et al., 2001). Among different methods proposed to reduce emissions, slurry treatment through anaerobic digestion (Feilberg et al., 2015) and the direct injection of digestate into the soil have been proposed as successful practices (Riva et al., 2016).

Anaerobic digestion (AD) is a biological process that degrades organic matter contained in biomass under anaerobic conditions to produce biogas, a methane-rich gas, and a biologically stable high-value fertilizer product (Tambone et al., 2010), the digestate: this latter is used as a fertilizer at farm level (Riva et al., 2016). The degradation process, reducing the easily available organic matter through microorganisms' activities, also reduces the potential for producing odours by the digestate (Orzi et al., 2010).

Slurry spreading by injection is a method that uses devices capable of delivering the slurry directly into the subsoil, reducing the impact of odours during spreading (Pahl et al., 2001; Riva et al., 2016). Therefore coupling anaerobic digestion with digestate injection should reduce a lot of the odours' impact and so population annoyance and environmental problems, as well.

The increasing number of complaints about odours due to slurry spreading on the land had stimulated interest in odour measurement techniques to identify and verify suitable and reliable odour abatement techniques (Stuetz et al., 1999; Feilberg et al., 2015). Current methods to measure odours refer to the use of panels of odour assessors to determine human detection thresholds, i.e. dynamic dilution olfactometry (Stuetz et al., 1999). This measurement is time consuming, labour intensive, and it is carried out in specially designed odour laboratories that are often remote from the sampling sites (Misselbrook et al., 1997). Dynamic dilution olfactometry gives only a quantitative response to odours and it says nothing about the nature of odours. The evaluators are also subjected to inhalation of organic molecules of unknown origin and which may sometimes be toxic.

The availability of commercial electronic nose (EN) systems for odour detection and measurement may offer an alternative method for odours' assessment. These systems consists of an array of electronic chemical sensors specific for one or for a group of chemical molecules (Misselbrook et al., 1997), that can be used to produce a unique odour profile or "fingerprint" by successive elaboration of sensor signals through applying statistical/neural network algorithms (Stuetz et al., 1999). Therefore, electronic noses are useful to identify odours' fingerprints, giving, also, information about their chemical nature. On the other hand, EN does not allow us to obtain quantitative responses for the odours emitted, so that it cannot be used as a field method to measure the odours' impact.

Orzi et al. (2010) were able, by performing an experiment measuring odours emitted during anaerobic digestion, to find a very good linear regression between data on odours measured by using EN and data coming from the olfactometry methodology. Some authors proposed that after a correct calibration, the EN could replace olfactometry as a tool for odour impact measurement (Defoer et al., 2002).

In order to study at full scale the effect of both anaerobic digestion and different digestate spreading methods on odour impacts, in the years 2012–2016 a series of experiments was conducted at open field farm level within different research projects. In particular, digestates and the liquid fraction of digestates were used at field scale as fertilizers, substituting for mineral fertilizers (urea). While doing so, soils treated with digestates were compared with untreated soils and soils treated with urea and undigested slurries. The large amounts of full-scale data obtained throughout four years of research activity at five experimental sites have been brought together in this paper and critically discussed.

2. Material and methods

2.1. Experimental fields

A four-year field study was conducted in 2012–2013 and in 2015–2016 on five experimental agricultural fields cropped with corn silage in farms on which active anaerobic digestion plants were present. All the farms were located in the Lombardy Region (Italy).

Different fertilizer matrices, i.e. pig and cow slurries, digestate and the liquid fraction of digestate (organic fertilizers) were characterized for their potential odour emissions when considered both on their own in lab studies and later when they were applied to soils. Mineral fertilizers (urea) and untreated soil (Blank) were considered as well. Organic fertilizers (sometimes referred to as "matrices") were applied to the soil by both surface and injection methods. During spreading, odour emissions were sampled and analysed through the Dynamic Olfactometry, Electronic Nose (EN) and GC/MS methods.

Details of the experimental fields are as follows: *i.* Field A (in 2012) was a silty-clay irrigated (surface basin irrigation) soil of 7.4 Ha; plot area was 5300 m^2. The experimental design adopted was that of a "randomized block" with four treatments characterized by different fertilization regimes repeated twice (Table 1). In the same table (Table 1) it was reported, also, the total amount of nitrogen applied for each treatments, that was determined taking into consideration crops requirement. Pig slurries, used in the mix with energy crops in the AD, was also included as untreated biomass to be compared during the campaign with the biologically AD treated samples used to fertilize crops. The seedbed was prepared by minimum tillage and plant density was 8 plants m^{-2}. *ii.* Field B (in 2013) was a silty-clay irrigated soil (surface basin irrigation) of 7.5 Ha; plot area was 4500 m^2. The experimental design adopted was that of a "randomized block" with four treatments characterized by different fertilization regimes repeated twice (Table 1). Slurry, used in the mix with energy crops in the AD, was also considered as untreated biomass to be compared during the campaign with the biologically AD treated samples used to fertilize crops. The seedbed was prepared by soil ploughing and harrowing, and the plant density was 7.5 plants m^{-2}. *iii.* Field C (in 2012–2013) was a silty-clay soil irrigated by drip (first year) and by surface basin irrigation (second year) of 5.5 Ha; the experimental design adopted was that of a "randomized block" with four treatments characterized by different fertilization regimes repeated twice for eight plots of about 4000 m^2 each (Riva et al., 2016). Cattle slurry, used in the mix with energy crops in the AD, was also included as untreated biomass to be compared during the two treatments with the biologically AD treated samples used to fertilize crops (Table 1). The seedbed was prepared by soil ploughing and harrowing, and the plant density was 8 (first year) and 9.5 (second year) plants m^{-2}. *iv.* Field D (in 2015–2016) was a loamy irrigated (surface basin irrigation) soil of 7.5 Ha; plot area was 3.75 Ha each. The seedbed was prepared by a minimum tillage method and the density was 8 plants m^{-2}. *v.* Field E (in 2015–2016) was a clay-loam irrigated soil (surface basin irrigation) of 10 Ha; plot area was 5 Ha each. The seedbed was prepared by a strip till method and the plant density was 8 plants m^{-2}.

The experimental design aimed to study the odour impacts measured during the use of digestate or the derived liquid fraction at pre-sowing and top dressing fertilization, taking into consideration different organic fertilizers and spreading methodology. Doing so comparison with odours impact coming from the use of untreated animal slurry (both pig and cow slurry), urea and no fertilizer use (the control, i.e. Blank) was considered as well. Experimental design considered, also, the comparison of

Table 1
Experimental plan design.

Field A	Treatment	Pre-sowing (120 kg N ha^{-1}) – PS	Application modality	Topdressing - TD	Application modality
	T1	Blank – no fertilization	n.a.[a]	–	–
	T2	Digestate from pig slurry	Surface	–	–
	T3	Urea	Surface	–	–
	T4	Digestate from pig slurry	Injected	–	–
	T5	Pig slurry	Surface	–	–
Field B	Treatment	Pre-sowing (191 kg N ha^{-1})	Application modality	Topdressing (116 kg N ha^{-1})	Application modality
	T1	Blank – no fertilization	n.a.[a]	Blank – no fertilization	n.a.[a]
	T2	S.l.f.[b] of digestate from pig slurry	Surface	S.l.f.[b] of digestate from pig slurry	Injected
	T3	Urea	Surface	Urea	Surface
	T4	S.l.f.[b] of digestate from pig slurry	Injected	S.l.f.[b] of digestate from pig slurry	Injected
	T5	Pig slurry	Surface	Pig slurry	Surface
Field C_1	Treatment	Pre-sowing (130 kg N ha^{-1})	Application modality	Topdressing (200 kg N ha^{-1})	Application modality
	T1	Blank – no fertilization	n.a.[a]	Blank – no fertilization	n.a.[a]
	T2	Digestate from cow slurry	Surface	Digestate from cow slurry	Injected
	T3	Urea	Surface	Urea	Surface
	T4	Digestate from cow slurry	Injected	S.l.f.[b] of digestate from cow slurry	Injected
	T5	–	–	Cow slurry	Surface
Field C_2	Treatment	Pre-sowing (180 kg N ha^{-1})	Application modality	Topdressing (160 kg N ha^{-1})	Application modality
	T1	Blank –no fertilization	n.a[a]	Blank – no fertilization	n.a[a]
	T2	S.l.f.[b] of digestate from cow slurry	Surface	S.l.f.[b] of digestate from cow slurry	Injected
	T3	Urea	Surface	Urea	Surface
	T4	S.l.f.[b] of digestate from cow slurry	Injected	S.l.f.[b] of digestate from cow slurry	Injected
	T5	–	–	Cow slurry	Surface
Field D_1	Treatment	Pre-sowing (239 kg N ha^{-1})	Application modality	Topdressing 143 kg N ha^{-1})	Application modality
	T1	Blank –no fertilization	n.a[a]	Blank – no fertilization	n.a[a]
	T2	Pig slurry	Surface	Urea	Surface
	T3	S.l.f.[b] of digestate from pig slurry	Injected	S.l.f.[b] of digestate from pig slurry	Injected
Field D_2	Treatment	Pre-sowing (205 kg N ha^{-1})	Application modality	Topdressing	Application modality
	T1	Blank –no fertilization	n.a[a]	–	–
	T2	Pig slurry	Surface	–	–
	T3	S.l.f.[b] of digestate from pig slurry	Injected	–	–
Field E_1	Treatment	Pre-sowing (175 kg N ha^{-1})	Application modality	Topdressing (145 kg N ha^{-1})	Application modality
	T1	Blank –no fertilization	n.a[a]	Blank –no fertilization	n.a[a]
	T2	Digestate from cow slurry	Surface	Urea	Surface
	T3	Digestate from cow slurry	Injection	S.l.f.[b] of digestate from cow slurry	Injected
Field E_2	Treatment	Pre-sowing (269 kg N ha^{-1})	Application modality	Topdressing (144 kg N ha^{-1})	Application modality
	T1	Blank –no fertilization	n.a[a]	Blank –no fertilization	n.a[a]
	T2	Digestate from cow slurry	Surface	Urea	Surface
	T3	Digestate from cow slurry	Injection	Digestate from cow slurry	Injection

[a] No application.
[b] Separate liquid fraction.

different methods for dosing organic matrices, i.e. injection vs. superficial spreading.

Organic fertilizers and urea were dosed taking into consideration plant needs and N efficiency. A detailed representation of the experimental design is shown in Table 1.

2.2. Organic fertilizers sampling and chemical characterization

During field trials, representative samples of different organic fertilizers, i.e. digestates, separate liquid fraction of digestates and pig/cow slurries, were sampled by using a 500 mL jar with a telescopic bar. Samples collected were then stored in 6 L PTFE bottles without headspace and brought to the laboratory for chemical characterization and odour determination, and worked within 2 h. Total solids (TS) and volatile solids (VS) were determined following standard procedures (APHA, 1998). Total N-Kjeldahl (TKN) and ammonia (TAN) were analysed on fresh samples according to the analytical method established for wastewater sludge (APHA, 1998); pH was determined according to standard procedures (US Department of Agriculture and US Composting Council, 2002). Total P and K contents were determined by inductively coupled plasma mass spectrometry (Varian, Fort Collins, USA). Standard samples (National Institute of Standards and Technology, Gaithersburg, MD, USA) and blanks were run with all samples to ensure precision in the analyses. P and K detection was preceded by acid digestion (EPA, 1998) of the fertilized samples. All analyses were performed in triplicate.

2.3. Air sampling and odours analyses

From each of the fertilizers' matrices (both organic and inorganic), the odours emitted (potential odour) were measured by using standardized methodology under lab conditions, using a flux chamber system (Orzi et al., 2010; Riva et al., 2016). In brief, 5 kg of sample were put in a tray container and covered with the chamber (surface of 0.196 m^2 for field A, B, C and of 0.160 m^2 for field D, E) and continuously flushed with air (0.35 $m^3\ h^{-1}$ for field A, B, C and 0.38 $m^3\ h^{-1}$ for field D, E). The flux chamber was then continuously flushed for 10 min with odourless air. Then the output gas from the chamber was taken from the outlet port and stored in Nalophan sampling bags. Bags of different volumes, i.e., 20 L, 2 L, and 3 L, were filled and used for olfactometric, electronic nose, and GC–MS analyses, respectively. The same flux chamber method was used to perform field trial gas sampling during fertilizer application to open fields. In particular, the chamber was placed onto the soil surface after 5 min. from the fertilizer application, in correspondence to the specific odour emission peak (Misselbrook et al., 1997). All odour measurements were performed once per plot; data reported represent the average of a single measurement replicated twice (two samples per treatment).

Olfactometric analyses were carried out in conformity with the standardized EN method n. 13,725 (CEN, 2003). An Olfaktomat-n 6 olfactometer (PRA-Odournet B.V., Amsterdam, NL), based on the forced choice method, was used as a dilution device. The results of the Dynamic Olfactometry were expressed as odour concentration value OU

($OU_E\ m^{-3}$). The specific odour emission rate SOER ($OU_E\ m^{-2}\ h^{-1}$) was calculated following the equation:

$$SOER = OU_E \times Q/S$$

considering the incoming air rate to the flux chamber (Q ($m^3\ h^{-1}$)) and the surface covered by the chamber (S (m^2), see paragraph 2.2.

Air samples were analysed using a PEN3 electronic nose (Airsense Analytics, Schwerin, Germany) equipped with 10 thermo-regulated (150–500° C) sensors made of metal oxide semiconductors (MOS). Each sensor is sensitive for a group of class compounds (S1: aromatic compounds; S2: nitrogen oxides; S3: ammonia; S4: H_2; S5: alkane and aromatic compounds; S6 and S10: methane compounds; S7 and S9: sulfur compounds; S8: alcohol and similar compounds). The measurement modalities adopted were those reported by Orzi et al. (2010); in brief: (i) 400 s for the clean cycle, (ii) 100 s for the measurement cycle, and (iii) 400 mL min^{-1} as injection flow. Three cycles for each bag were performed. Only the last 20 s of the measurement cycles, when the response of the sensors was stabilized, was used for the creation of the odour fingerprint. The large amounts of data obtained by the EN were analysed by multivariate analysis. In this work, principal component analysis (PCA), in Euclid correlation, was used to compare odour fingerprints. The multivariate analyses were carried out by an ad hoc software (WINMUSTER, Airsense Analytics, Schwerin, Germany).

2.4. Volatile organic compounds characterization by GC–MS

Volatile organic compounds (VOC) from air samples were analysed by SPME/GC–MS as previously reported and tested (Orzi et al., 2010).

A manual SPME device and divinylbenzene (DVB)/Carboxen/polydimethylsiloxane (PDMS) 50–30 lm fiber – Supelco, Bellefonte, PA, USA) was used. The compounds were adsorbed from the air samples by exposing the fiber, preconditioned for 3 h at 250 °C, as suggested by the supplier, in Nalophan bags for 30 min at room temperature. A solution of deuterated p-xylene in methanol was used as internal standard (IS) for quantitative analysis. VOC analysis was performed using an Agilent 5975C Series GC/MSD. Volatiles were separated using a capillary column for VOC (MetaVOC, Teknokroma, Sant Cugat del Vallès, Barcelona, Spain) of 30 m * 250 μm (ID) and a film thickness of 0.25 μm. Carrier gas was helium at a flow rate of 1 mL min^{-1}. VOC were desorbed exposing the fiber in the GC injection port for 3 min at 250 °C. The temperature program was isothermal for 3 min at 35 °C, raised to 200 °C at a rate of 8 °C/min. The transfer line to the mass spectrometer was maintained at 250 °C. The quantitative and qualitative analysis was carried out by integrating the peaks, resulting from the total ion current of each analysate, identified by comparison with NIST library (National Institute of Standards and Technology; USA). A semi-quantitative analysis, for all the identified compounds, was performed by direct comparison with the internal standard.

Results were expressed as mg $m^{-2}\ h^{-1}$, considering the surface area of the chamber and the air flux during the gas sampling.

2.5. Statistical approach

All statistical analyses, if not further specified, were performed with the SPSS statistical software (version 20) (SPSS, Chicago, IL).

Multiple linear regressions of Log UO vs. electronic noise sensors were done using the partial least square method (PLS). The cross-validation leave-one-out approach of un-scaled variables was applied to calculate the goodness of regressions (goodness of fit coefficient-R^2 and goodness of prediction coefficient- Rcv^2, respectively). Taking into consideration all variable values, the PLS regression was calculated and the importance of each independent variable (importance coefficient) defined. Then PLS analysis was repeated removing those variables characterized by less important coefficient (Andries et al., 2011). This procedure was repeated until a final regression model with goodness of regressions coefficient (R^2 and Rcv^2) and the smallest number of variables was achieved. PLS was performed using SCAN software (Minitab Inc., State College, PA).

Principal Component Analysis (PCA) was applied to describe in two dimensions plot experimental GS-MS data. To do so, all data were grouped in chemical classes and successively they were standardized through the application of an autoscaling procedure (mean centering and variance scaling transformation) (Einax et al., 1997).

3. Result and discussion

3.1. Characterization of organic fertilizers matrices

The organic fertilizers' matrices were chemically analysed before their application to the soil (Table 2). Among different parameters reported and characterizing organic fertilizers, two particular parameters can affect odour production during the spreading/injection on soils: ammonia and total solid content.

Total ammonia content (TAN) in separated liquid fractions (as average of data reported in Table 2) was statistically higher (TAN of 2.5 ± 0.6 g kg^{-1} ww) than that reported for digestate (TAN of 1.8 ± 0.8 g kg^{-1} ww) and slurries (TAN of 1.9 ± 1 g kg^{-1} ww), because of both protein degradation during anaerobic digestion and ammonia preferred repartition in the liquid fraction after solid/liquid separation (Tambone et al., 2017). This compound had an olfactory threshold between 0.0266 mg m^{-3} and 39.6 mg m^{-3} (Rice and Netzer, 1982) that can cause nuisance during its spreading. However, the lowest total solid contents for liquid fraction of digestate (average TS content of 6.6 ± 2.4 g kg^{-1} ww, 6.2 ± 1.2 g kg^{-1} ww and 3.8 ± 1.4 g kg^{-1} ww, for slurry, digestate and separated liquid fraction of digestate, respectively) can induce their rapid infiltration into soil pores, limiting odour emissions (Genermont and Cellier, 1997).

3.2. Specific odour emission rate (SOER)

Odour emitted by different matrices used as fertilizers showed a great variability depending on the matrices used (Fig. 1). Cow and pig slurries showed highest odour emissions that were in line with data reported in the literature (Misselbrook et al., 1997). Digestate showed lower odour than corresponding untreated slurries (Fig. 1) because of the anaerobic digestion process which had allowed the degrading of the more readily degradable organic fraction and concentrating the recalcitrant fraction, resulting in a high degree of biological stability (Orzi et al., 2015). Moreover, anaerobic digestion determines a modification of organic volatile compound composition, as previously reported (Orzi et al., 2010).

The liquid fraction of digestates obtained by simple S/L separation showed a tendency to further decrease odour. However, due to the variability of the matrices used, this trend cannot be assumed as general.

Urea, as expected, showed the lowest odour emission. The slow-release formulation of urea used in the fields D and E emitted more odorous molecules, detectable by human nose, than “traditional” urea; this fact was probably correlated with the presence of formaldehyde compounds in slow-release urea (formaldehyde has an odour threshold between 1.47 and 73.5 mg m^{-3}) (Rice and Netzer, 1982).

Odours emitted after fertilizer applications indicated that surface application had a larger impact than the injection system (Table 3), in agreement with the literature (Moseley et al., 1998). In particular, in this study the highest SOER values were obtained for treatments that involved the use of organic fertilizers by surface spreading. Switching from surface to injection methods led to the reduction of odour impact by 50–74% (Table 3). The potential emission abatement through injection is well documented in the literature and it was ascribed to the creation of cavities in the soil that decreased the treated surface (emission surface) (Pahl et al., 2001).

Table 2
Chemical characterization of organic fertilizers matrices.

Field	Fertilizers matrices	Used in treatment	pH	TS (% ww)	VS (% ww)	TKN (g kg^{-1} ww)	TAN (g kg^{-1} ww)	P_2O_5 (g kg^{-1} ww)	K_2O (g kg^{-1} ww)
A	Digestate from pig slurry pre-sowing	T2-T4	7.8ab[c]	8.4g	6.8ef (81)[d]	4.5bc (54)	1.9ab (23)	0.4a (5)	2.6b (31)
	Pig slurry pre-sowing	T5	7.9b	3.2b	2.2b (68)	3.8c (119)	1a (31)	3.5e (109)	5.6de (175)
B	S.l.f[a] of digestate from pig slurry pre-sowing	T2-T4	8.1b	4.4c	2.6bc (59)	3a (68)	2.1b (48)	0.5ab (11)	6.3e (143)
	Pig slurry pre-sowing	T5	8.1b	5.2d	3.7 cd (72)	4.7bc (90)	1.4a (27)	3.2e (61)	4.9c (94)
	S.l.f of digestate from pig slurry topdressing	T2-T4	8.4c	2.2a	1.3a (59)	3.3a (150)	2.2b (100)	0.6ab (27)	7.1ef (323)
	Pig slurry topdressing	T5	7.8ab	4.2c	2.8bc (67)	4.4b (105)	1.3a (31)	3.4e (81)	4.8c (114)
C_1	Digestate from cow slurry pre-sowing[b]	T2-T4	8.1b	7.4f	5.7e (77)	3.4a (46)	2b (27)	1.9d (26)	4.7c (64)
	Digestate from cow slurry topdressing[b]	T2	7.8ab	6.3e	4.7d (75)	4.1b (65)	2.4bc (38)	1.6cd (25)	4.4c (70)
	S.l.f. of digestate from cow slurry topdressing[b]	T4	8b	2.2a	1.6a (73)	2.7a (123)	2.1b (95)	0.5ab (23)	1.8a (82)
	Cow slurry topdressing	T5	8.3	8.6g	7.3f (85)	7.1e (83)	1.7ab (20)	2.1d (24)	5.5d (64)
C_2	S.l.f. of digestate from cow slurry pre-sowing[b]	T2-T4	7.9b	3.5b	2.3b (66)	3a (86)	1.9ab (54)	0.7b (20)	3.5bc (100)
	S.l.f. of digestate from cow slurry topdressing[b]	T2-T4	7.8ab	3.9bc	2.7bc (69)	3a (77)	1.7ab (44)	0.5ab (13)	6.9ef (177)
	Cow slurry topdressing	T5	8.5c	8.3g	6.6ef (79)	6.5d (78)	1.8ab (22)	2.3d (28)	5.4d (65)
D_1	S.l.f. of digestate from pig slurry pre-sowing	T3	7.7ab	4.7cd	3c (64)	3.9ab (83)	2.8c (60)	0.6ab (13)	8.2f (174)
	Pig slurry pre-sowing	T2	7.1a	8fg	5.8e (73)	6d (75)	3.4d (43)	1.2c (15)	6.8ef (85)
	S.l.f of digestate from pig slurry topdressing	T3	7.7ab	6.1e	3.7 cd (61)	3.8ab (62)	2.9c (48)	0.8b (13)	7.9f (130)
D_2	S.l.f of digestate from pig slurry pre-sowing	T3	7.8ab	3.2b	2b (63)	4.1b (128)	3.1cd (97)	0.5ab (16)	2.8b (88)
	Pig slurry pre-sowing	T2	7a	7.9f	6.2ef (78)	5.7 dc (72)	3.7d (47)	0.9b (11)	4.9 cd (62)
E_1	Digestate from cow slurry pre-sowing	T2-T3	7.6ab	5.4d	4.2d (78)	3.2a (59)	1.7ab (31)	0.3a (6)	6.3e (117)
	S.l.f. of digestate from cow slurry topdressing	T3	7.6ab	5.2d	3.3c (63)	3.4a (65)	2.3b (44)	0.3a (6)	5.3d (102)
E_2	Digestate from cow slurry pre-sowing	T2-T3	7.9b	4.6cd	3.3c (72)	3.8ab (83)	2b (43)	0.2a (4)	5.3d (115)
	Digestate from cow slurry topdressing	T3	7.9b	4.4c	2.9c (66)	3.4a (77)	1.5ab (34)	0.2a (5)	5.1d (116)

[a] Separate liquid fraction.
[b] Data previously reported in Riva et al. (2016).
[c] Values followed by the same letter are not statistically different (ANOVA bootstrap and Tukey test, $p < 0.05$).
[d] Data reported on TS basis.

Taking into consideration the kind of organic fertilizers' matrices studied, the odour emission during surface application decreased with digestates use when they were compared to slurries, in agreement with the potential for odour emission measured by the lab approach (Fig. 1) and with previous findings (Moseley et al., 1998; Riva et al., 2016). The spreading of separated liquid fractions of digestate did not always lead to a further reduction of odours when they were compared with unseparated digestate (Table 3).

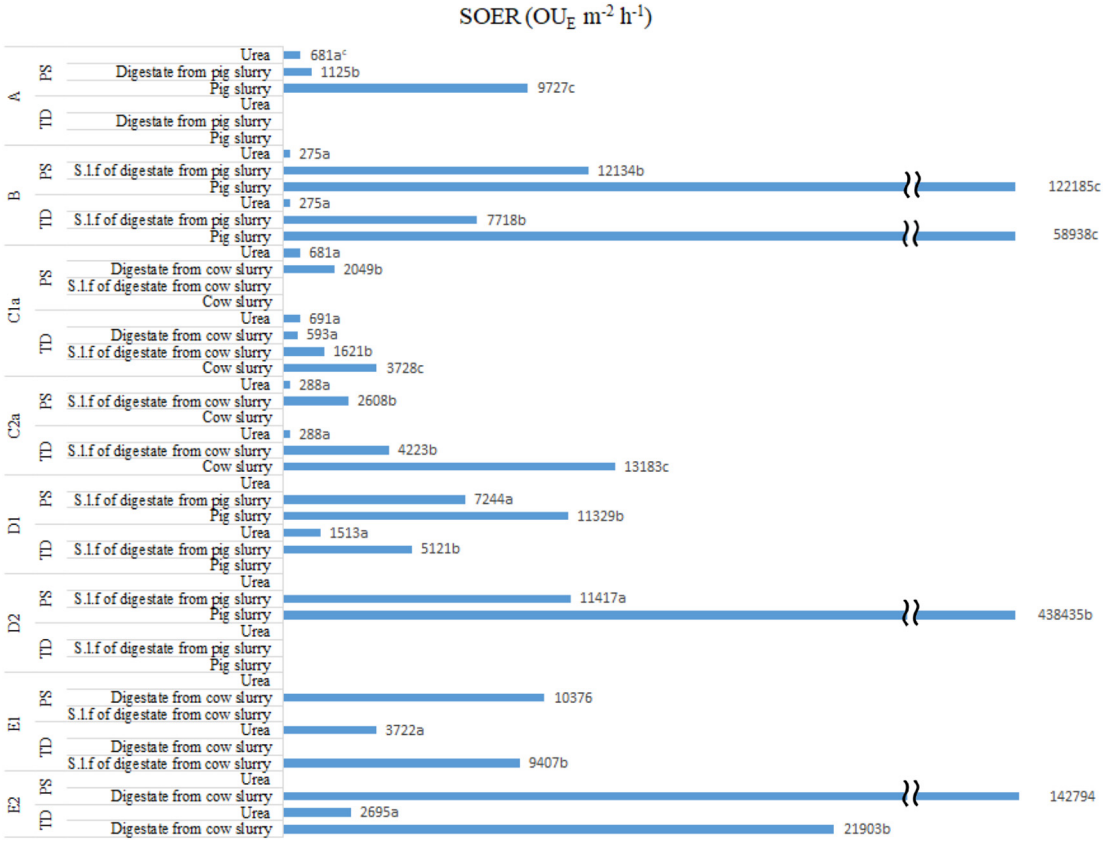

Fig. 1. Odour impact of the fertilizers matrices. [a]Data previously reported in Riva et al. (2016); [b]separate liquid fraction; [c]values followed by the same letter are not statistically different within fertilization made (ANOVA bootstrap and Tukey test, $p < 0.05$).

Table 3
Odour impact of the organic matrices and synthetic fertilizers on soils.

Field	Treatment	Experimental plan design	Pre-sowing (PS)	Experimental plan design	Topdressing (TD)
			SOER ($OU_E\ m^{-2}\ h^{-1}$)		SOER ($OU_E\ m^{-2}\ h^{-1}$)
A	T1	Blank – no fertilization	310a[b]	n.p.[c]	
	T2	Digestate from pig slurry-surface	3318c	n.p.	
	T3	Urea-surface	2893bc	n.p.	
	T4	Digestate from pig slurry- injected	1645b	n.p.	
	T5	Pig slurry-surface	3914c	n.p.	
B	T1	Blank – no fertilization	1452ab	Blank – no fertilization	310a
	T2	S.l.f.[b] of digestate from pig slurry-surface	5221c	S.l.f.[b] of digestate from pig slurry-injected	266a
	T3	Urea-surface	3024b	Urea-surface	262a
	T4	S.l.f.[b] of digestate from pig slurry-injected	840a	S.l.f.[b] of digestate from pig slurry-injected	268a
	T5	Pig slurry-surface	5556c	Pig slurry-surface	636b
C_1[a]	T1	Blank – no fertilization	483a	Blank – no fertilization	560b
	T2	Digestate from cow slurry-surface	2340b	Digestate from cow slurry-injected	279a
	T3	Urea-surface	2458b	Urea-surface	1084c
	T4	Digestate from cow slurry-injected	2030b	S.l.f.[b] of digestate from cow slurry-injected	517b
	T5			Cow slurry-surface	2513d
C_2[a]	T1	Blank –no fertilization	706a	Blank – no fertilization	1202b
	T2	S.l.f.[b] of digestate from cow slurry-surface	1158b	S.l.f.[b] of digestate from cow slurry-injected	1575b
	T3	Urea-surface	1141b	Urea-surface	862a
	T4	S.l.f.[b] of digestate from cow slurry-injected	1102b	S.l.f.[b] of digestate from cow slurry-injected	1563b
	T5			Cow slurry-surface	6474c
D_1	T1	Blank –no fertilization	323a	Blank – no fertilization	612a
	T2	Pig slurry-suface	2724b	Urea-surface	599a
	T3	S.l.f.[b] of digestate from pig slurry-injected	218a	S.l.f.[b] of digestate from pig slurry-injected	704a
D_2	T1	Blank –no fertilization	587a	n.p.	
	T2	Pig slurry-surface	3715c	n.p.	
	T3	S.l.f.[b] of digestate from pig slurry-injected	896b	n.p.	
E_1	T1	Blank –no fertilization	500b	Blank –no fertilization	407a
	T2	Digestate from cow slurry-surface	1185c	Urea-surface	2186b
	T3	Digestate from cow slurry-injected	394a	S.l.f.[b] of digestate from cow slurry-injected	1189b
E_2	T1	Blank –no fertilization	412a	Blank –no fertilization	512a
	T2	Digestate from cow slurry-surface	2848b	Urea-surface	2941c
	T3	Digestate from cow slurry-injected	1846b	Digestate from cow slurry-injected	997b

[a] Data previously reported in Riva et al. (2016).
[b] Values followed by the same letter are not statistically different within fertilization made (ANOVA bootstrap and Tukey test, $p < 0.05$).
[c] Not performed.

Results reported indicated, also, that SOER measured for untreated field plots (Blank) (average SOER of 598 ± 334 $OU_E\ m^{-2}\ h^{-1}$) was lower than those due to digested organic matrices distributed by injection (average SOER of 960 ± 601 $OU_E\ m^{-2}\ h^{-1}$), but was not so far from those figures. The difference was not statistically significant due to the high variability between different fields used and different typology and characteristics of organic fertilizers used (Table 2). Therefore, data reported in Table 3 need to be considered within each single experiment (Table 3).

The urea spreading resulted, on average, in higher odour emissions (SOER of 1745 ± 1064 $OU_E\ m^{-2}\ h^{-1}$) than the blank but was more similar to the value found for digestate used by surface application (SOER of 2423 ± 917 $OU_E\ m^{-2}\ h^{-1}$). Probably ammonia produced by urea hydrolysis was responsible for that as this molecule has a low olfactory threshold (odour threshold between 0.0266 and 39.6 mg m^{-3}) (Rice and Netzer, 1982).

The variability of matrices used and of the locations used for experiments did not allow us to obtain statistically valid differences when the data were considered together. Nevertheless trends were respected when each single experiment and treatment were considered (Table 3), i.e. the use of digestate by injection reduced odour impact in all cases studied.

3.3. Matrices odour fingerprints

Fig. 2 shows the elaboration of the EN response to odour emitted by organic fertilizers matrices under lab conditions represented by a PCA bi-plot graph in which two principal components are reported: PC1 = 73% and PC2 = 23%, in which % represents the total variance explained. In the graph, the high spatial dispersion of the slurry odour fingerprints is visible, particularly those of pig slurries. Pig slurries studied in this work showed, also, the greatest variability of SOER ($OU_E\ m^{-2}\ h^{-1}$) (Fig. 1), indicating that quantitative measurements of odour (SOER) affected, also, the qualitative aspect of them (odour fingerprint) (Fig. 2).

A biological process, i.e. anaerobic digestion, led to the reduction of the qualitative odour variability so that odour fingerprinting become more similar, independently of the organic matrices origin (cow or pig slurry), when digestates were considered (Fig. 2). This result could be due to anaerobic digestion which had resulted in a chemical simplification of the organic matter contained as a consequence of the degradation of the labile fraction and the preservation of more recalcitrant ones (Tambone et al., 2009). Solid/liquid separation does not seem to affect greatly the odour fingerprints in comparison with digestate. Contrarily, the odour fingerprint of urea was even more circumscribed because of its industrial origin and standardized properties. Therefore, the results reported in Fig. 1a suggest that untreated organic matrices possess great variability in terms of odour fingerprints and that anaerobic digestion reduced this variability (Fig. 2), as previously reported, also, for SOER (Fig. 1).

This fact found confirmation in the good correlation found for average sensor response (G/G_0) (qualitative aspect) vs. specific odour emission rate (as Log SOER) (quantitative aspect) ($r = 0.84$; $p < 0.01$; $n = 32$), as also previously suggested by Misselbrook et al. (1997).

Correlations found suggested the possibility to use the EN as a substitute of olfactometry in quantifying odours emitted by fertilizers. To do so, PLS was performed taking into consideration Log SOER and EN-sensor responses (G/G_0). Good regression was found, i.e. $R^2 = 0.73$; $R^2_{cv} = 0.66$; $P < 0.01$, by using sensor S1 (aromatic), S3 (ammonia), S5 (alkane and aromatic compounds) and S9 (sulfur compounds). The sensor importance measured by importance coefficients, i.e. Sensor 1 = 0.314; Sensor 3 = 0.3; Sensor 5 = 0.32; Sensor 9 = 0.643, indicated that sulfur compounds were those more responsible for EN response vs. odour

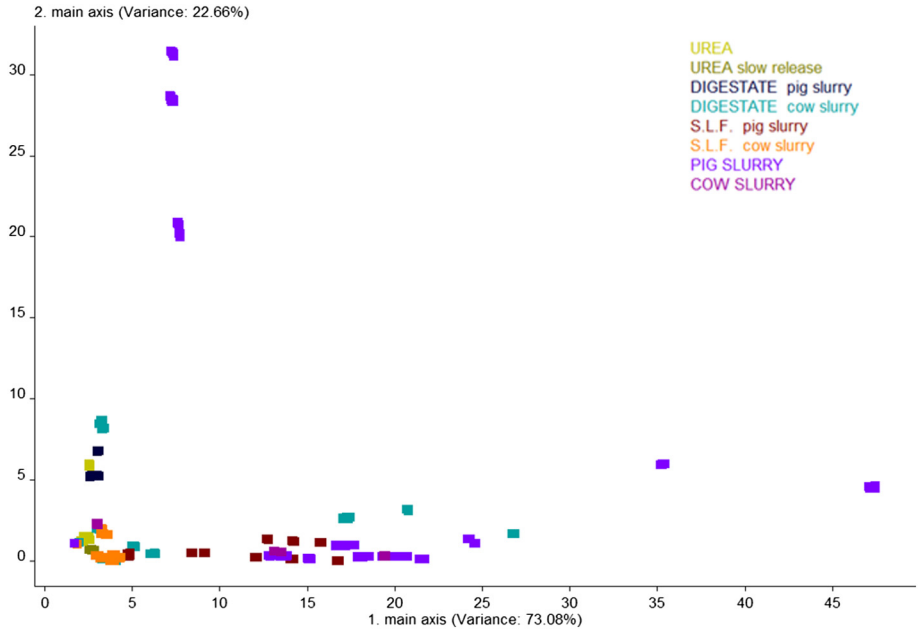

Fig. 2. PCA bi-plot of the odour EN-footprints for fertilizers matrices.

emission. The typical S-compound produced during anaerobic digestion and characterized by a very low odour threshold (0.0007–0.0140 mg m^{-3}) (Rice and Netzer, 1982) is H_2S. Therefore, the ability of EN to detect H_2S (S-compound) can explain its ability to measure odours indirectly (SOER), so that a good regression between these two parameters (Log SOER vs. EN sensors) was achieved.

3.4. Matrices odour fingerprints: Field use

Odour fingerprints obtained by EN were elaborated and results obtained represented by a PCA bi-plot (Fig. 3a and Fig. S1), which represented the 92.73% (51.06% PC1 and 41.67% PC2) of the total variability.

The interpretation of the PCA obtained from the elaboration of EN data of odour emissions derived from soil treatments was very complex. The complexity derived from the fact that in an open field not only the kind of fertilizer matrices used affected the odour fingerprint but, also, the method used to spread the organic matrices played a role (superficial vs. injection). Moreover, environmental boundaries such as soil characteristics, soil moisture, vegetative cover and climatic conditions (in particular temperature) have an impact on odour emission. Nevertheless, in a full scale approach all these parameters cannot be considered and standardized.

To simplify the PCA bi-plot, five matrices clusters were created (Fig. 3a): Blank, Urea, Digestate-superficial (including liquid fraction), Digestate-injected (including liquid fraction), Slurry-superficial (both cow and pig slurries).

Odours' fingerprints for Digestate-superficial (Fig. 3a) and Slurries-superficial showed a great variability, so that it was not possible to discriminate between them, although they were well discriminated from the Urea and Blank. The impossibility to discriminate between slurries and digestate (including liquid fraction) was probably due to their different provenance, which had led to a great variability as suggested, also, by SOER data (Fig. 1). This latter consideration seems to indicate that odours' fingerprints (qualitative aspects of odours) depended on the quantitative data of odours (SOER) (Fig. 3a and Table 3), as supported by the good correlation found for average sensor response (G/G_0) vs. specific odour emission rate (Log SOER) ($r = 0.55$, $p < 0.01$; $n = 54$), confirming previous data reported for organic matrices. The correlation coefficient was lower than those observed for organic matrices because more variability was introduced in determining both qualitative and quantitative aspects of odours by working in open fields. The PLS application for Log SOER vs. G/G0 sensor responses gave a significant regression that, however, showed a low regression coefficient so that it cannot be applied to quantified odour emitted during slurry/digestate spreading ($R^2 = 0.3$; $R^2_{cv} = 0.23$; $P < 0.01$; Sensors: S1 - aromatic compounds, S6–10 - methane, S7–9 - sulfur compounds). Probably, as previously indicated, many variables affected odours emitted from soils so that it was difficult to get a good regression.

Digestate and liquid fractions of digestate, both used by injection, led to the complete discrimination of odour fingerprints by EN (Fig. 3a) from both Slurries-superficial and Digestate-superficial treatment. Moreover, odour fingerprints for this cluster were similar to those of the untreated control (Blank) for all experiments performed, as highlighted directly on the PCA reported in Fig. 3a. Therefore, results obtained indicated that odour emission from soils treated with organic matrices depended partially on the organic matrices themselves (potential odour impact) but also that the injection of digestate (both untreated and liquid fractions) allowed the loss of the matrices' fingerprint, so that odours' characteristics were those of soils. In the Fig. 2b, details for G/G0 sensor responses of EN for Treatments B-PS (Table 1) are reported, for example. Looking at these data it can be seen that effectively G/G0 of Blank (B PS T1) was very similar to that of Digestate injected (B PS T4) but that they were very different for those of Digestate and Slurry superficial (B PS T2 and B PS T5) which were similar to each other. In particular, Fig. 3b indicated that differences were due above all to the Sensor 3 (ammonia); Sensor 6 (methane), Sensor 7 (sulfur compounds) and Sensor 8 (alcohol) that well characterize both slurries and digestate products (Orzi et al., 2010). Therefore, an explanation of the differences observed between the fingerprint of injected and non-injected soils, could be due to the fact that these compounds were trapped in soil (Pahl et al., 2001) and probably subsequently degraded (Fig. 2a). Methane, H_2S and alcohol have been reported to be rapidly adsorbed and/or oxidized in soil. Maximal CH_4 oxidation activity occurred in a zone between 15 and 20 cm below the surface (Scheutz and Kjeldsen, 2005).

This fact can explain, also, differences in SOER observed. Ammonia (S6) and H_2S (S7) that were the major components responsible for odour emission (SOER) because of their low olfactory threshold, after injection were trapped and degraded, reducing the odour impact of injected treatments (Table 3).

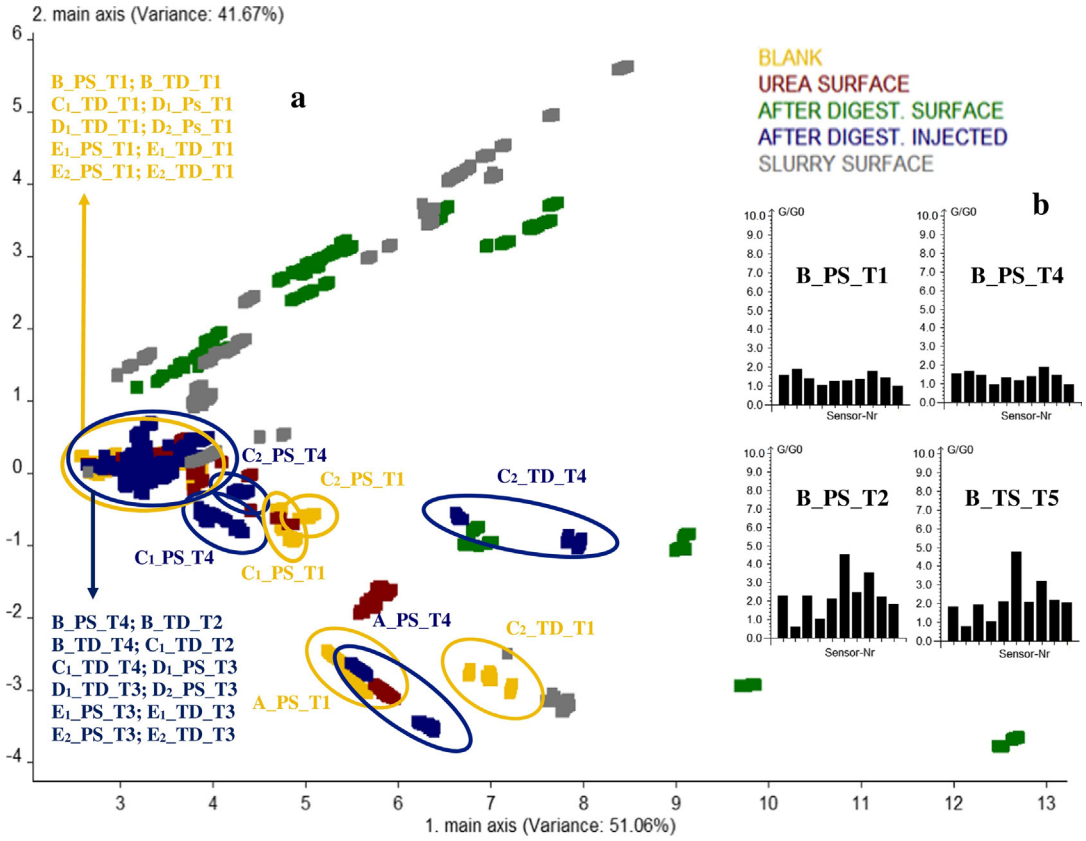

Fig. 3. PCA bi-plot of the odour EN-footprints for soil treated with fertilizers grouped for treatment - Blank vs. Digestate injection for each treatment are highlighted by circles (a), and an example of EN sensors signal patterns (b): Blank (B_PS_T1), Digestate Injected (B_PS_T2), Digestate surface (B_PS_T2) and Pig slurry surface (B_TS_T5).

On the other hand odours emitted (SOER) from injected soil were different from those of the Blank and in many cases they were higher (Table 3), although, on average, differences were not very high and were not statistically significant. Therefore, in order to better detail the molecules emitted from both untreated and treated soil, GC–MS of soil air samples were considered qualitatively. Large numbers of molecules were detected and they were grouped into: alcohol, aldehyde, alkane, alkene, aromatic compound, carboxylic acid, ketone, fatty acid, alogenure, N-, S-compounds and terpene. Successive elaboration of data by multivariate statistical analysis (PCA) allowed us to build a PCA bi-plot (Fig. S2). The first two PCs were able to explain 62.89% of the total variability of the system; the PC1 (which explained 42.6% of total variability) was directly correlated to the aromatic, ketone, S-, N-, and alogenure compounds while the PC2 (which explained 20.29% of total variability) was linked to the fatty acid and carboxylic acids emission. Unfortunately, PCA did not allow any discrimination of samples studies that were randomly distributed. No differences between treated soils (both by surface and injection and with urea) and Blank (control) were evident. This fact seemed to indicate that the use of organic fertilizers did not affect natural "soil odour" (Blank), or at least that the GC–MS carried out was not able to measure differences. These results were different from those obtained by EN, because GC–MS was not able to detect molecules that were important for both odour detection (SOER) and odour fingerprint by EN, i.e. ammonia, H_2S and methane.

Therefore, GC–MS was found to be completely ineffective in detecting the VOCs responsible for the odours emission after the spreading of organic fertilizers. Results obtained indicated that VOCs detected by GC–MS were those typical of soils, as suggested by the absence of differences between Blank (control) and treated soil (Fig. 3) and by the fact that the most abundant molecules detected, i.e. aromatic, alcohol, alkene and alkane, have been reported to be of soil biogenic origin (plant and microorganisms) (Leff and Fierer, 2008; Guenther, 2013).

4. Conclusion

With this work we demonstrated at field scale that anaerobic digestion, by degrading easily degradable organic molecules, reduced the potential odour emission of animal manures. This fact affected, also, the odour emission in the subsequent use of digestate as fertilizers. Digestate injection reduced odour emissions even more, so that differences in comparison with untreated soil were minimal and no differences of odour fingerprint were evident.

An electronic nose was used to detect "odour fingerprints" but also to substitute for olfactometry in odour quantification, with the former being simpler than the latter and directly applicable in open fields. Regressions between Log SOER and EN obtained were optimal for organic and inorganic fertilizers but not for soil treated with the matrices. Therefore, odour measurements in the field need to be performed by the olfactory approach that was found to be a reliable methodology to measure odour in open fields. This approach allowed us to establish that anaerobic digestion together with digestate injection allowed us effectively to nullify odour impact during manure spreading.

Acknowledgement

This project was supported by: "Regione Lombardia DG Agricoltura - Struttura Ricerca, Innovazione tecnologica e Servizi alle imprese: Project N. 1705, 2011: Messa a punto di best practice a ridotta emissione in atmosfera per la gestione e l'utilizzo agronomico di reflui zootecnici – N-Emissione Riduzione Zerø"" and "Ente Regionale per i Servizi all'agricoltura: Supporto tecnico per l'applicazione e il monitoraggio della direttiva nitrati (ARMOSA) + rapporto ambientale per VAS, piano triennale 2014 – 2016. Agreement Collaborazione tecnico-scientifica per azioni finalizzate a valutare la sostenibilità complessiva della gestione".

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.11.249.

References

Andries, J.P.M., Vander Heyden, Y., Buydens, L.M.C., 2011. Improved variable reduction in partial least squares modelling based on predictive-property-ranked variables and adaptation of partial least squares complexity. Anal. Chim. Acta 705, 292–305.

APHA, 1998. Standard Methods for Examination of Water and Wastewater. 20th ed. American Public Health Association, Washington, DC.

CEN, 2003. Air quality — determination of odour concentration by dynamic olfactometry. Standard Method n. 13725. European Committee for Standardization, Brussels, B.

Defoer, N., De Bo, I., Van Langenhove, H., Dewulf, J., Van Elst, T., 2002. Gas chromatography–mass spectrometry as a tool for estimating odour concentrations of biofilter effluents at aerobic composting and rendering plants. J. Chromatogr. 970, 259–273.

Einax, J.W., Zwanziger, H.W., Geiß, S., 1997. Chemometrics in Environmental Analysis. VCH Edition, Weinheim, D.

EPA, 1998. Method 3051: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, Washington, DC.

Feilberg, A., Bildsoe, P., Nyord, T., 2015. Application of PTR-MS for measuring odorant emissions from soil application of manure slurry. Sensors 15, 1148–1167 (Basel, Switzerland).

Genermont, S., Cellier, P.A., 1997. Mechanistic model for estimating ammoniacal volatilization from slurry applied to bare soil. Agric. For. Meteorol. 88, 145–167.

Guenther, A.B., 2013. Biological and chemical diversity of biogenic volatile organic emissions into the atmosphere. ISRN Atmospheric Sciences. 786290.

Leff, J.W., Fierer, N., 2008. Volatile organic compound (VOC) emissions from soil and litter samples. Soil Biol. Biochem. 40 (7), 1629–1636.

Misselbrook, T.M., Hobbs, P.J., Persaud, K.C., 1997. Use of an electronic nose to measure odour concentration following application of cattle slurry to grassland. J. Agric. Eng. Res. 66, 213–220.

Moseley, P.J., Misselbrook, T.H., Pain, B.F., Earl, R., Godwin, R.J., 1998. The effect of injector tine design on odour and ammonia emissions following the injection of bio-solids into arable cropping. J. Agric. Eng. Res. 71, 385–394.

Orzi, V., Cadena, E., D'Imporzano, G., Artola, A., Davoli, E., Crivelli, M., Adani, F., 2010. Potential odour emission measurement in organic fraction of municipal solid waste during anaerobic digestion: relationship with process and biological stability parameters. Bioresour. Technol. 101, 7330–7337.

Orzi, V., Scaglia, B., Lonati, S., Riva, C., Boccasile, G., Alborali, G.L., Adani, F., 2015. The role of biological processes in reducing both odour impact and pathogen content during mesophilic anaerobic digestion. Sci. Total Environ. 526, 116–126.

Pahl, O., Godwin, R.J., Hann, M.J., Waine, T.W., 2001. Cost-effective pollution control by shallow injection of pig slurry into growing crops. J. Agric. Eng. Res. 80, 381–390.

Parker, D.B., Gilley, J.E., Woodbury, B., Kim, K.H., Bartelt-Hunt, S., Li, X., Snow, D., Galvin, G., 2013. Odorous VOC emission following land application of swine manure slurry. Atmos. Environ. 66, 91–100.

Rice, R.G., Netzer, A., 1982. Handbook of Ozone Technology and Application. Vol 1; Ann Arbor Science. Butterworth Publishers, Stoneham, MA.

Riva, C., Orzi, V., Carozzi, M., Acutis, M., Boccasile, G., Lonati, S., Tambone, F., D'Imporzano, G., Adani, F., 2016. Short-term experiments in using digestate products as substitutes for mineral (N) fertilizer: agronomic performance, odours, and ammonia emission impacts. Sci. Total Environ. 547, 206–214.

Scheutz, C., Kjeldsen, P., 2005. Biodegradation of trace gasses in simulated landfill soil cover. J. Air Waste Manage. Assoc. 55, 878–885.

Stuetz, R.M., Fenner, R.A., Engin, G., 1999. Assessment of odours from sewage treatment works by an electronic nose, H_2S analysis and olfactometry. Water Res. 33, 453–461.

Tambone, F., Genevini, P.L., D'Imporzano, G., Adani, F., 2009. Assessing amendment properties of digestate by studying the organic matter composition and the degree of biological stability during the anaerobic digestion of the organic fraction of MSW. Bioresour. Technol. 100, 3140–3142.

Tambone, F., Scaglia, B., D'Imporzano, G., Schievano, A., Orzi, V., Salati, S., Adani, F., 2010. Assessing amendment and fertilizing properties of digestate fromanaerobic digestion through a comparative study with digested sludge and compost. Chemosphere 81, 577–583.

Tambone, F., Orzi, V., D'Imporzano, G., Adani, F., 2017. Solid and liquid fractionation of digestate: mass balance, chemical characterization, and agronomic and environmental value. Bioresour. Technol. https://doi.org/10.1016/j.biortech.2017.07.130.

US Department of Agriculture – US Composting Council, 2002. Test Methods for the Examination of Composting and Compost (TMECC). Edapho International, Houston, TX.