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Short-term experiments in using digestate products as substitutes for mineral (N) fertilizer: Agronomic performance, odours, and ammonia emission impacts

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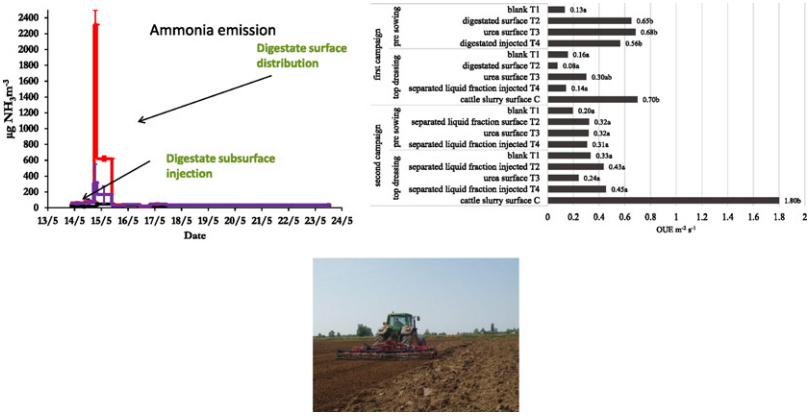
HIGHLIGHTS

- Anaerobic digestion produced useful fertilizers, i.e. the digestate.
- Digestate misuses led to odours and ammonia impacts.
- Pre-sowing and topdressing use of digestate substituted completely N-fertilizers.
- Subsurface injection of digestate reduced greatly odour and NH_3 emissions.
- Digestate use allowed producing maize silage as well as using urea.

GRAPHICAL ABSTRACT



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ABSTRACT

Anaerobic digestion produces a biologically stable and high-value fertilizer product, the digestate, which can be used as an alternative to mineral fertilizers on crops. However, misuse of digestate can lead to annoyance for the public (odours) and to environmental problems such as nitrate leaching and ammonia emissions into the air. Full field experimental data are needed to support the use of digestate in agriculture, promoting its correct management. In this work, short-term experiments were performed to substitute mineral N fertilizers (urea) with digestate and products derived from it to the crop silage maize. Digestate and the liquid fraction of digestate were applied to soil at pre-sowing and as topdressing fertilizers in comparison with urea, both by surface application and subsurface injection during the cropping seasons 2012 and 2013. After each fertilizer application, both odours and ammonia emissions were measured, giving data about digestate and derived products' impacts.
The AD products could substitute for urea without reducing crop yields, apart from the surface application of AD-derived fertilizers. Digestate and derived products, because of high biological stability acquired during the AD, had greatly reduced olfactometry impact, above all when they were injected into soils (82–88% less odours than the untreated biomass, i.e. cattle slurry). Ammonia emission data indicated, as expected, that the correct use of digestate and derived products required their injection into the soil avoiding, ammonia volatilization

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into the air and preserving fertilizer value. Sub-surface injection allowed ammonia emissions to be reduced by 69% and 77% compared with surface application during the 2012 and 2013 campaigns.

1. Introduction

In recent decades, there has been an increasing interest in Europe in the implementation of anaerobic digestion plants in farming contexts because of EU politics and directives leading towards the reduction of greenhouse gases (GHG) and the promotion of renewable energy production (EU, 2008). Anaerobic digestion, can be successfully used to produce renewable energy (biogas) by using both crop energy, and/or animal slurries and organic wastes as biomass feedstocks. In the agricultural context, energy crops represent one of the most important sources for biogas production in Europe (Weiland, 2010). In Germany, for example, more than 50% of total biogas production derives from energy crops, of which corn (*Zea mays* L.) is the most used (Weiland, 2010). This has led to a conflict for soil use, i.e. energy vs. food production (Britz and Delzeit, 2013). Nevertheless, sustainable biogas models are present in the EU. For example, in the Lombardy Region (northern Italy), that accounts for more than 60% of the total existing agricultural Italian biogas plants (400 biogas plants, i.e. ca. 300 MW), biogas feed is composed, on average, of 49% wet weight/wet weight (ww/ww) of animal slurries and by only 32% ww/ww of energy crops (double cropped), the rest of the total being represented by organic bio-products. This is possible because of the presence of intensive animal breeding (about 1.8×10^6 cows, 4.5×10^6 pigs and 36×10^6 poultry are present in the territory) (Adani et al., 2013). All these facts lead to a reduced use of soil for energy crop production, i.e. less than 4% of the total agricultural land of Lombardy (35,000 ha on about 1×10^6 ha of the total agricultural area). Similar figures are reported for the Netherlands, Denmark and Belgium (Flanders), all of which are characterized by intensive livestock activities.

On the other hand, the intensive livestock production systems produce large quantities of slurry and manure that need to be managed because of their impact on soil, water and air. Misuses of slurry are responsible for nitrate leaching into both shallow and deep water and for ammonia emission into the air (Clarisse et al., 2009). The Nitrate Directive (Council Directive, 1991) regulates the use of animal-N slurries (maximum N ha^{-1} allowable), paying particular attention to vulnerable zones to reduce nitrate leaching. Less well known is the problem connected to ammonia in the air. Recent data from the Lombardy Region Environmental Protection Agency (ARPAL, 2015) indicated that about 96% of ammonia polluting the air in Lombardy was from agricultural activity, mainly livestock activities: these data agree with international literature (Clarisse et al., 2009). Ammonia is responsible for water eutrophication, acid deposition, but above all for secondary particulate formation (Renard et al., 2004). The presence of particulates has been recently reported to be a direct cause of lung cancer (Raaschou-Nielsen, 2013). Therefore, although the application of the Nitrate Directive reduces the impact of animal-N on water quality, it does not adequately deal with air pollution because of ammonia emission, which is a new topic that has been little studied. The contribution of ammonia to air particulates becomes important in any area characterized by particular orographic conformation, i.e. in which stagnant weather allows NH_3 concentration to build up (Clarisse et al., 2009), and with high agricultural activities (livestock), such as the Po Valley. These factors lead to a high concentration of ammonia in the air (Clarisse et al., 2009), producing secondary particulate matter (particularly those of the <2.5 μm) (Renard et al., 2004) that worsen the already serious situation for regional air quality which is due to traffic, high population density and industrial activities (ARPAL, 2015).

Anaerobic digestion transforms the ingestate (e.g. animal slurries) into the digestate, a biologically stable and partially sanitized product (Tambone et al., 2010; Möller and Müller, 2012; Orzi et al., 2015), characterized, also, by the presence of nutrients in available form (N) (Tambone et al., 2010). Organic-N contained in the ingestates, in particular, is transformed during the AD process into a mineral form, i.e. ammonia, suggesting the potential use of digestate as fertilizer in substitution for mineral fertilizers (N) (Alburquerque et al., 2012a,b; Walsh et al., 2012), with both economic and environmental benefits. The Nitrate Directive limits the use of digestate as fertilizer because digestate is considered to be in the category of slurries, and so it is considered to need to undergo the same N-application restriction. This fact appears anachronistic, since anaerobic digestion increases the efficiency of N (Sorensen and Moller, 2009) so that digestate can be used to replace mineral N fertilizers (Alburquerque et al., 2012a,b). If N recovery from digestate can promote nutrient recycling and circular economy, in line with more recent EU indications (EU, 2014), the Nitrate Directive becomes an obstacle to that. Current opinion is that the Nitrate Directive needs to be reviewed, both because it is dated (1991), and because AD is nowadays amply diffused in the EU, representing a good chance to recover nutrients producing renewable energy and reducing the GHG which is due to production of synthetic fertilizers.

Animal residues treatment needs, also, reducing pathogen content of the digestate because pathogens could constitute a problem for health of people exposed to them causing a risk for the dissemination of diseases (Sahlström et al., 2008). In this way a recent work performed by Orzi et al. (2015) on full-scale plants indicated that mesophilic AD processes were able reducing pathogen and/or indicator of pathogen so that digestate resulted much better than animal slurries from a sanitation point of view.

To make a convincing argument, research needs to produce experimental data (Möller and Müller, 2012) to support digestate use as fertilizers, and to promote digestate management methods which will minimize the impact derived from its usage.

The purpose of this study was to provide information about the use of the digestate and/or the liquid fraction of digestate coming from a farm AD plant using a mix of cattle slurries and energy crops, as a substitute for mineral fertilizers (N-fertilizers) in a short-term full field experiment. Digestate and the liquid fraction of digestate were used in this experiment in which we compared different methods of application management, to find out which would promote reduced odours and ammonia emissions. To assess yields, urea was also included, and to assess odours, cattle slurry was also included as a treatment.

2. Methods

2.1. Characterization of the anaerobic digestion plant

The Anaerobic digestion (AD) plant operates at farm level in an agro-industrial context in the Brescia Province (Northern Italy). The feeding mixture consists of cattle slurry (15,440 Mg y^{-1}) mixed with energy crops (maize silage, triticale silage) (15,150 Mg y^{-1}) (Table S1). Energy crops were cultivated on 200 ha, of which 70% were monoculture corn and 30% double crops: triticale plus corn.

The plant operated by continuously-stirred-tank-reactors (CSTR) under "wet" conditions at 40 °C with an HRT of 80 days. The digestate coming from the AD process was treated with solid–liquid separation (screw separator and centrifuge) and the liquid fraction was stored in covered ponds.

Table 1
Experimental plan design.

First campaign (2012)				
Treatment	Pre-sowing (130 kg N ha^{-1})	Application modality	Topdressing (200 kg N ha^{-1})	Application modality
T1a–T1b	Blank — no fertilization	n.a.[a]	Blank — no fertilization	n.a.
T2a–T2b	Digestate	Surface	Digestate	Injected
T3a–T3b	Urea	Surface	Urea: application	Surface
T4a–T4b	Digestate	Injected	Separate liquid fraction of digestate	Injected
Second campaign (2013)				
Treatment	Pre-sowing (180 kg N ha^{-1})		Topdressing (160 kg N ha^{-1})	
T1a–T1b	Blank — no fertilization	n.a.	Blank	n.a.
T2a–T2b	Separate liquid fraction of digestate	Surface	Separate liquid fraction of digestate	Injected
T3a–T3b	Urea	Surface	Urea	Surface
T4a–T4b	Separate liquid fraction of digestate	Injected	Separate liquid fraction of digestate	Injected

[a] No application.

The biogas plant was monitored for a period of five months before field trials started. Representative samples of both ingestate and digested and derived products (separate liquid fraction and separate solid fraction) were collected, by using a 500 ml jar with a telescopic bar. In particular, samplings were performed after that digestate or liquid fraction of digestate were accurately mixed, taking then five different samples that were mixed together getting a final representative sample. Samples were then stored in a 500 ml bottle without headspace for chemical characterization and biological characterization. In total five (one per month) samples were taken during the preliminary observation period.

2.2. Experimental field plan

A field study was conducted in the years 2012–2013 on an experimental field of 5.5 ha (Fig. S1) located near the AD plant. 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. Experimental design aimed at studying the efficiency of digestate and liquid fraction of digestate, depending by theirs availability in the farm, to substitute for mineral-N fertilizers by adopting different digestate management methods: surface and subsurface injection application and pre-sowing and topdressing applications. One treatment adopted normal fertilization i.e. the treatment was fertilized with mineral NPK, using urea, superphosphate and potassium chloride (T3), for comparison with the treatments fertilized with digestate and the liquid fraction of digestate (T2 and T4) and control (no fertilizer was applied, i.e. T1). The total amounts of digestate and liquid fraction of digestate were those allowing us to apply the same amount of N as on the plots dosed with mineral fertilization (urea) (T3) (Table S2). Digestate and derived products were spread superficially (T2) and by subsurface injection (T2 and T4). Superficial distribution could not always be provided for T2 due to technical problems. The complete scheme of management of applications of digestate and derived products is reported in Table 1.

During the first year (2012), a crop of silage corn (DKC-6903, FAO 700, Monsanto Italy) was sown on May 15–2012 following a winter wheat crop, adopting a plant density of 8 plants m^{-2}. In the second year DKC-5401 corn hybrid (FAO class 300/400, Monsanto Italy) was sown on April 27–2013, with a plant density of 9.5 plants m^{-2}. Crop management followed the standard agronomic practices used in the area (soil preparation, crop cycles, fertilization and phytosanitary treatments, etc.) and was identical for all treatments, except for the fertilization methods used.

Crops were harvested on August 23–2012 and on August 22–2013. Harvesting was carried out by using a cutter blower. All plants in each plot were weighed together to give the total production figure. Representative samples were then taken from each plot in order to assess the total solids (TS) content. Representative soil samples (six samples/parcel of about 1 kg were mixed getting one representative sample of 1 kg to be delivered to the lab) were taken before sowing, after presowing fertilization, after topdressing fertilization (maize plant with 4–6 leaves) and after harvesting in both 2012 and 2013. Soil analyses were performed by following a standardized method (MIPAF, 2000).

2.3. Digestate and derived products sampling and characterization

During full field trials, representative samples (see Section 2.1) of the substances used to fertilize the plots (digestate, separate liquid fraction of digestate,) were sampled by using a 500 ml jar with a telescopic bar. Samples were then stored in a 5 liter PTFE bottle without headspace for chemical characterization and/or odour determination. Samples were brought to the laboratory and worked on within 2 h.

Table 2
Chemical characterization of the input and output biomasses from the anaerobic digestion plant.

	pH	TS (% ww)	VS (% TS)	TKN (g N kg^{-1} ww)	TAN (g $NH4^+$ kg^{-1} ww)	VFA (mg l^{-1} acetic acid)	ALK (mg l^{-1} $CaCO_2$)	OD_{20} (mg O_2 g^{-1} TS)	ABP (Nl kg^{-1} TS)
Ingestate	5.14 ± 0.93a[a]	18.1 ± 6.4b	91.8 ± 2.3b	3.75 ± 0.80a (20.7)[b]	1.14 ± 0.11a (6.29)[a]	7909 ± 3336a	9023 ± 1010a	147 ± 27c	554 ± 131b
Digestate	8.10 ± 0.14b	5.66 ± 0.24a	75.9 ± 2.4a	3.56 ± 0.39a (62.9)[a]	1.80 ± 0.39ab (31.8)[a]	401 ± 97a	10,483 ± 3678a	27.8 ± 5.4b	224 ± 137°
Separated liquid fraction of digestate	8.38 ± 0.16b	4.36 ± 0.17a	71.8 ± 4.7a	3.44 ± 0.22a (78.8)[a]	2.08 ± 0.13b (47.7)[a]	1068 ± 781a	11,521 ± 5172a	33.2 ± 3.8b	251 ± 103a
Separated solid fraction of digestate	9.73 ± 0.31c	25.6 ± 2.7c	93.3 ± 2.9b	5.54 ± 0.43b (21.6)[a]	1.59 ± 0.68a (6.1)[a]	215 ± 155a	5010 ± 986a	14.3 ± 2.7a	179 ± 87a

[a] Values of the same column followed by the same letter are not statistically different (ANOVA bootstrap and Tukey test, $p < 0.05$).
[b] Data reported as g N kg^{-1} TS.

Table 3
Chemical characterization of digestate and liquid fraction of digestate used in field trials.

			TS (% ww)	VS (% ww)	pH	TKN (g N kg^{-1} ww)	TAN (g NH4^{+} kg^{-1} ww)	TAN/TKN (%)	P_2O_5 (g kg^{-1} ww)	K_2O (g kg^{-1} ww)	OD20 (mg O_2 g^{-1} TS)
First campaign	Pre-sowing	Digestate	7.4 ± 0.1e[a]	5.7 ± 0.1e(76.8)[b]	8.1 ± 0.4a	3.4 ± 0.1c (45.9)[a]	2 ± 0b (27)[a]	59	1.88 ± 0.02d (25.46)[a]	4.66 ± 0.04c (62.93)[a]	24.7 ± 4.4a
	Topdressing	Digestate	6.3 ± 0.1d	4.7 ± 0.1d (76.2)[a]	7.8 ± 0.1a	4.1 ± 0.1d (65.1)[a]	2.4 ± 0.1c (38.1)[a]	59	1.58 ± 0.02c (25.45)[a]	4.36 ± 0.02c (70.42)[a]	25.7 ± 0.7a
		Separated liquid fraction of digestate	2.2 ± 0.1a	1.6 ± 0.1a (72.4)[a]	8.0 ± 0.2a	2.7 ± 0.1a (122.7)[a]	2.1 ± 0.1b (95.4)[a]	78	0.54 ± 0.02a (24.72)[a]	1.84 ± 0.04a (83.56)[a]	64.1 ± 7.3c
Second campaign	Pre-sowing	Separated liquid fraction of digestate	3.5 ± 0.1b	2.3 ± 0.1b (71.0)	7.9 ± 0.3a	3 ± 0b (85.7)[a]	1.9 ± 0.1a (54.8)[a]	63 (51)[c]	0.72 ± 0.02b (22.64)	3.51 ± 0.08b (109.58)	37.2 ± 3.7b
	Topdressing	Separated liquid fraction of digestate	3.9 ± 0.1c	2.7 ± 0.1c (69.9)[a]	7.8 ± 0.2a	3 ± 0b (76.9)[a]	1.7 ± 0.1a (17.9)[a]	59 (50)[c]	0.54 ± 0.01a (14.1)[a]	6.86 ± 0.07d (176)[a]	26.5 ± 3.3a

[a] Values of the same column followed by the same letter are not statistically different (ANOVA bootstrap and Tukey test, $p < 0.05$).
[b] Data reported on TS basis.
[c] TAN/TKN (%) of digestate from which liquid fraction was derived.

2.4. Chemical characterization of the digestate and derived products

Total solids (TS) and volatile solids (VS) were determined following standard procedures (APHA, 1992). Ammonia (TAN) and total N-Kjeldahl (TKN) were analysed on fresh samples according to the analytical method established for wastewater sludge (IRSA CNR, 1994). Volatile fatty acids (VFA), alkalinity (ALK) and pH were 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 biomass samples. All analyses were performed in triplicate.

2.5. Biological stability measurement

Medium-term degradability was performed by measuring the potential biogas production (ABP) according to Orzi et al. (2015), i.e. 0.62 g of dried matter sample, 37.5 ml of inoculum, and 22 ml of deionized water were put into 100-ml serum bottles. A control blank was prepared with 60 ml of inoculum. Inoculum was incubated at 37 ± 1 °C for 15 days before being used in ABP assays. The bottles were incubated at 37 ± 1 °C for 60 days. The biogas production was determined periodically and expressed as Nl kg TS^{-1}.

Short-term biological stability was detected by measuring the oxygen demand to degrade readily degradable organic matter (Adani et al., 2003). To do so, 0.2–1 g of wet matter sample was placed in a flask with 500 ml of deionized water, 12 ml of phosphate buffer solution (KH_2PO_4, $Na_2HPO_4 \cdot 7H_2O$), and 5 ml of nutritive solution ($CaCl_2$, $FeCl_3$, and $MgSO_4$) prepared according to the standard BOD test procedures (Orzi et al., 2010). The oxygen uptake potential is the result of the oxygen demand accrued in a 20-h test (OD20, mg O_2 g TS^{-1}).

2.6. Potential specific odour emissions rate and field specific odour emission rate measured for treatments

Potential odour emissions of the substances used in the field trials were measured on gas collected from 5 l samples by following the method previously described (Orzi et al., 2015). In brief, the test substance (i.e. urea, digestate, separate liquid fraction and cattle slurry, this latter added as example of untreated biomass) was put in a tray container and covered with a Plexiglas rectangular chamber (38.8 × 50.5 × 40 cm) having a surface area of 0.196 m^2. The flux chamber was then continuously flushed for 10 min with air (airflow rate of 0.35 m^3 h^{-1}) (APAT, 2003; Orzi et al., 2010), i.e. 0.097 l s^{-1}. Output gas from the chamber was then taken from the outlet port and stored in Nalophan sampling bags (Orzi et al., 2010, 2015). Sampling bags containing gas sampled were analysed for odours by Dynamic Olfactometry (CEN, 2003) within 24 h from sampling. Analyses were performed in triplicate.

The same flux chamber method, as described above, was used to perform field trial gas sampling, during fertilizer application. In particular, the chamber was placed on the soil surface after five minutes from the fertilizer application and in correspondence with the specific odour emission peak (Misselbrook et al., 1997). All odour measurements were performed once per plot; data reported represent the average of single measurement replicated twice (two plots per treatment).

Dynamic Olfactometric analyses were carried out in conformity with the standardized EN method n. 13725 (CEN, 2003). An Olfaktomat-N 6 (six stations) 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 m^{-3}). The specific odour emission rate SOER (OU_E m^{-2} s^{-1})

Table 4
Potential odour emission of the fertilizers matrices.

	First campaign		Second campaign	
	Pre-sowing	Topdressing	Pre-sowing	Topdressing
	$OU_E\ m^{-2}\ s^{-1}$ ($OU_E\ m^{-2}\ s^{-1}$ kg N)			
Urea	0.19 ± 0.01[a][b] (0.08 ± 0.01A)	0.19 ± 0.01[c]a (0.08 ± 0.01A)	0.08 ± 0.01a (0.03 ± 0.01A)	0.08 ± 0.01[c]a (0.03 ± 0.01A)
Cattle slurry	–	1.04 ± 0.04c (52.1 ± 1.9D)	–	3.66 ± 0.13c (171 ± 6C)
Digestate	0.57 ± 0.02b (33.5 ± 0.9B)	0.17 ± 0.01a (8.04 ± 0.2B)	–	–
Separated liquid fraction	–	0.45 ± 0.02b (33.4 ± 1.2C)	0.72 ± 0.02b (48.3 ± 1.6B)	1.17 ± 0.04b (78.2 ± 2.6B)

[a] Urea used was different for first (large grain) and second (small grain) campaign.
[b] Values of the same column followed by the same letter are not statistically different: small letter for data referred to $OU_E\ m^{-2}\ s^{-1}$ $OU_E\ m^{-2}\ s^{-1}$ kg N (ANOVA bootstrap and Tukey test, $p < 0.05$).
[c] Data reported was that determined previously.

was calculated by using the following equation:

$$SOER = 1000 \times (CQ/S)$$

in which C is the specific odour concentration ($SOU_E\ m^{-3}$), Q is the incoming air rate to the flux chamber (0.097 l s^{-1}), and S the surface covered by the chamber (0.196 m^2).

Because experimental design did not consider thesis fertilized with untreated slurry, and in order to magnify the effect of AD on odours reduction due to high biological stability acquired by digestate or its liquid fraction, cattle slurry applications on soil surface was considered and included in odours sampling plan, during top dressing fertilization. Cattle slurry application was performed on a cultivated parcel having the same area of the other parcels and that was closed to the area interested to the experimentation.

2.7. Ammonia emission

Ammonia emissions were quantified by using concentration-based dispersion modelling (Flesch et al., 1995; Loubet et al., 2001). This method relates downwind NH_3 concentration measurements with atmospheric turbulence measurements and the area of the source (Flesch et al., 2004). Air NH_3 concentration was measured through the exposure of acid coated passive samplers (Tang et al., 2001) placed in the geometrical centre of each experimental plot at the height of 50 cm both from the soil surface, during the pre-sowing period, and from the crop canopy during the topdressing fertilization. Background NH_3 levels were assessed 1.8 km away from the field and from any potential NH_3 source. Samplers were exposed in three replicates and replaced every 6 or 12 h in function of the proximity of the spreading time. In order to measure the parameters of atmospheric turbulence, a three-dimensional sonic anemometer (USA-1, METEK GmbH, Elmshorn, Germany) was placed at 1.5 m height in the centre of a 2.5 ha field next to the experimental plots. Emissions from each plot were estimated by means of the backward Lagrangian stochastic dispersion model WindTrax 2.0 (Thunder Beach Scientific, Halifax, Canada), detailed in Carozzi et al., 2013.

3. Results and discussion

3.1. Anaerobic digestion plant: performance

Anaerobic digestion led to the extensive degradation of the OM, as indicated by the strong reduction of the relative VS content (Table 2), and by the acquirement of strong biological stability, as suggested by the marked reduction of the OD_{20} and ABP parameters, that measured the substrate degradability in short and medium term periods (Orzi et al., 2015).

Protein degradation under anaerobic condition determined the increase of ammonia content in the digestate with respect to the ingestate (Tambone et al., 2010). Ammonia content was responsible for both alkalinity and pH increase in the digestate. Volatile fatty acid contents strongly decreased during the AD process as the consequence of the methanogenic activities that consumed VFA, producing CH_4. In the digestate, VFAs content was low and far from a concentration reported to inhibit the AD process. The AD process was able to degrade extensively the organic matter contained in the ingestate, producing biologically stable products containing high value nutrients in forms available for plants (N) (Tambone et al., 2010).

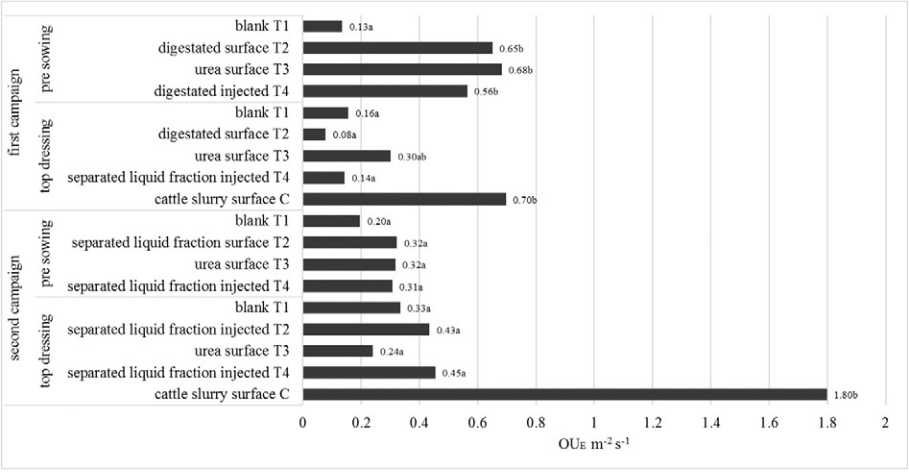

Fig. 1. Odour emission from soils after fertilization (values followed by the same letter are not statistically different within fertilization made (ANOVA bootstrap and Tukey test, $p < 0.05$).

Table 5
Odour reduction during slurry/digestate application as consequence of different management.

Treatment compared	Odours variation	References
Pig slurry injected vs. pig slurry superficial	−38%	Lau et al. (2003)
Digestate from pig slurry vs. pig slurry	−17%	Hansen et al. (2003)
Digestate liquid fraction from pig slurry vs. digestate from pig slurry	−40%	Hansen et al. (2003)
Digestate superficial Vs. slurry superficial	−75%	Nicolas et al. (2013)
Digestate superficial from pig slurry vs. pig slurry superficial	−70/80%	Pain et al. (1990)
Digestate injected (cattle manure + energy crops) vs. digestate superficial (cattle manure + energy crops)	−13.4%	This work (Fig. 2)
Liquid fraction of digestate superficial (cattle manure + energy crops) vs. cattle slurries superficial	−88%	This work (Fig. 2)
Liquid fraction of digestate injected (cattle manure + energy crops) vs. Liquid fraction of digestate superficial (cattle manure + energy crops)	+4%	This work (Fig. 2)
Liquid fraction of digestate injected (cattle manure + energy crops) vs. cattle slurries superficial	−82%	This work (Fig. 2)

3.2. Digestate and liquid fraction of digestate

Chemical characteristics of digestate and liquid fractions of digestate used in this experiment are shown in Table 3. Chemical characteristics of the digestate and liquid fraction were different from the average chemical composition calculated on the basis of the preliminary 5-months digestate and derived products sampling programme. Getting constant digestate composition at a full-scale plant is very difficult because of feedstock changes, digestate recycling to control the process, digestate dilution by rain and S/L performances that can be different during the year, affecting the final liquid fraction composition. Taking into consideration the 5-months average data reported for digestate (Table 2) and those from actual digestates used in field trials (Table 3), it can be seen that the first was less concentrated (see TS contents) than the second samples were. On the other hand, TKN content was quite similar, although digestate used in field trials contained more ammonia. The liquid fractions of digestate used during the first campaign differed a lot from those coming from 5-months average AD plant data for TS content (Tables 2 and 3), but less for NTK and TAN contents (Tables 2 and 3). The liquid fraction used in the second campaign did not differ a lot from the 5-months average data, apart from the slightly lower TS content (Tables 2 and 3).

The samples of substances used in field experiments differed not only for average composition, but they also differed from each other for TS, TKN and TAN contents, and TAN/TKN ratio (Table 3); P_2O_5 and K_2O contents were almost constant among digestates. However the S/L separation affected nutrient contents as it diluted the P_2O_5 contents (Table 3). If on the one hand chemical variability was a negative factor, as similar fertilizers could not be used during the whole experiment, on the other hand, the use of actual digestate-derived fertilizers having different compositions gave a more general significance to the experiment in terms of the overall ability of digestate and related liquid substrate to substitute for mineral fertilizers. In fact TS, NTK and ammonia contents largely varied through the sample fertilizer products used, i.e. they ranged from 2.2 to 7.4 g kg^{-1} ww, from 2.7 to 4.1 g kg^{-1} ww, and from 58 to 78% of TKN, for TS, NTK, and ammonia, respectively.

3.3. Specific odour emission during digestate and derived product application

Potential specific odour emissions from sample substances used as fertilizers, i.e. digestate, liquid fractions of digestates and urea are reported in Table 4. Cattle slurries, used in the mix with energy crops in the AD, was also considered as untreated biomass to be compared during the two campaigns with the biologically AD treated samples used to fertilize crops. Results obtained indicated that untreated biomass (cattle slurry) exhibited very high potential odours when compared with the treated (digested) biomasses. These results were expected as anaerobic digestion determined the strong reduction of the potential odours because of the OM degradation and the acquirement of high biological stability of digestate and derived products, as their low OD20, i.e. oxygen uptake to degrade readily degradable organic matter, values confirmed (Table 3), in agreement with recent literature on the subject (Orzi et al., 2015).

The liquid fraction presented higher potential specific odour emissions rate compared with the unseparated digestate. This was probably due to the high ammonia content of these fractions (Table 3), although there was not a clear relationship of odours from the ammonia content in the separate liquid fractions. Urea, as expected, showed very low potential odours.

Specific odour emissions during full field application of fertilizer samples were very interesting and reflected the data of potential specific odour emissions (Fig. 1). The application of digestate and liquid fraction of digestate did not show substantial differences in specific odour emissions when applied superficially or injected. These results can be ascribed to the low potential odours of digestate (Table 4). This was confirmed by the fact that urea application gave similar results (Fig. 1) and that when cattle slurry was applied to soil, odours emitted were much higher than those coming from digestate, liquid fraction of digestate and urea application, according to the potential odour data (please compare Fig. 1 with Table 4). All these data indicate that the AD resulted in the production of digestate and derived products with

Table 6
NH_3 emission after fertilizers spreading and emission factors (EF) expressed as the ratio between the N–NH_3 emitted and the TAN applied.

			kg N ha^{-1}	NH_3 losses EF (% TAN)	Std[a]
First campaign	Pre-sowing (130 kg N ha^{-1})	T2 Digested surface	23.3b[b]	30.4	3.3
		T3 Urea surface	17.8ab	13.7	7.7
		T4 Digested injected	7.1a	9.3	5.3
	Topdressing (200 kg N ha^{-1})	T2 Digested injected	2.5a	1.6	0.30
		T3 Urea surface	2.5a	1.3	0.18
		T4 Separate liquid fraction injected	6.9b	4.5	0.46
Second campaign	Pre-sowing (180 kg N ha^{-1})	T2 Separate liquid fraction surface	52.6b	46.3	7.4
		T3 Urea surface	17.6a	9.7	1.6
		T4 Separate liquid fraction injected	12.0a	10.6	0.6
	Topdressing (160 kg N ha^{-1})	T2 Separate liquid fraction injected	16.9 a	14.7	9.75
		T3 Urea surface	13.7 a	6.8	1.8
		T4 Separate liquid fraction injected	13.2 a	8.5	0.2

[a] The standard deviation (Std) is calculated between the EF of the same treatment.
[b] Values of the same column followed by the same letter are not statistically different within each fertilization (ANOVA bootstrap and Tukey test, $p < 0.05$).

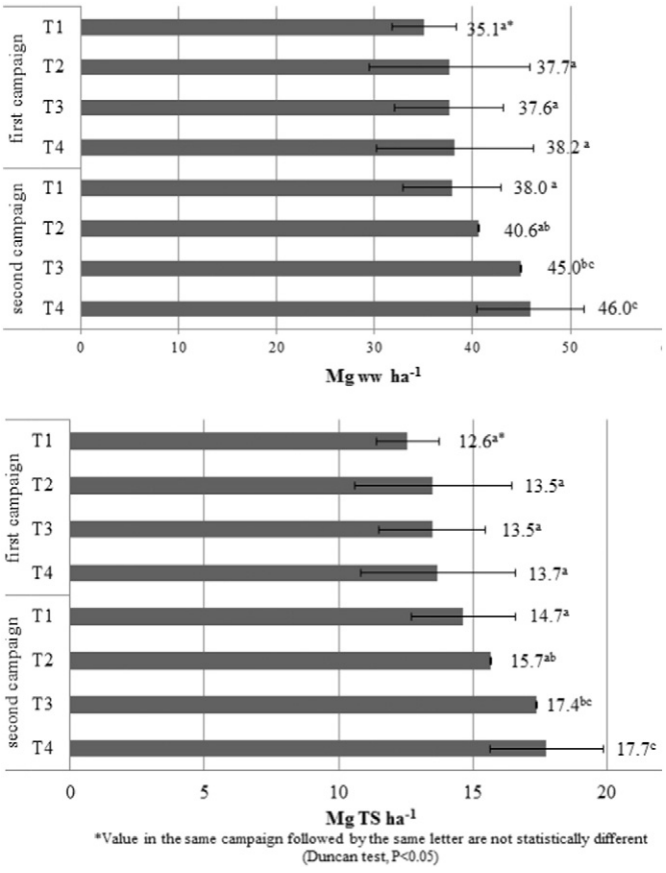

Fig. 2. Maize silage production of for each treatment studied (wet weight: top; dry weight: bottom).

low odour potential so that no differences occurred when they were applied at the surface or by injection.

Few international works have been published on specific odour emissions during digestate applications. The available literature agreed that AD reduced odour emissions during manure and slurries application (Hansen et al., 2003; Holm-Nielsen et al., 2009). Nicolas et al. (2013) in particular, reported that after 30 h from the digestate application odours disappeared completely, while odours coming from slurry applications continued for over 60 h; moreover digested produced much lower odours than raw slurry. In Table 5, data of this work are compared to literature data. It was interesting to observe that odour reductions can be obtained by: i. slurry/digested injection, ii. anaerobic digestion of slurries and, iii. S/L separation of digestate. We concluded that anaerobic digestion coupled with the use of the liquid fraction of digestate (this work), allowed the highest odour reduction, i.e. 82–88% with respect to the untreated samples (cattle slurries) (Table 5).

3.4. Ammonia emissions during digestate and derived product application

Ammonia emissions measured for both 2012 and 2013 campaigns are detailed in Table 6. Data indicated, as expected, that the biomass application (surface or injected) greatly affected ammonia emission.

In general, higher ammonia emission rates were obtained when digestate was applied at the surface (T2 trials during pre-sowing period) with respect to both urea application and digestate injection (Table 6). Compared to surface spreading, the injection of the digestate or of the derived liquid fractions greatly reduced NH_3 emissions, by 69% and 77% for 2012 and 2013, respectively. Other authors working with undigested slurry (Erisman et al., 2008a, 2008b; Carozzi et al., 2013) reported similar figures. Surface digestate and derived products application, led to serious TAN losses, i.e. EF of 38 ± 11% TAN (Table 6), that were much higher than those calculated from Table 6 for both digestate (EF of 5.4 ± 5.4% TAN; n = 2) and liquid fraction of digestate (EF of 9.75 ± 4.2% TAN; n = 4). Ammonia losses (as EF) from injected digestate and derived product, as average (EF of 9.52 ± 3.6%; n = 5), were similar to those calculated for urea application (average N losses of 7.8 ± 5.2% TAN; n = 4), which is the common fertilization practice used. Digestate and derived products composition did not seem to influence ammonia emission, although it was not possible to compare directly different biomasses, as they were applied at different periods of the experiment (Table 1).

Not many data are reported in the literature about ammonia emissions when using digestate in comparison with untreated animal slurry. Recent literature reported average ammonia emissions of 43.6% TAN (Smith et al., 2007) after slurry surface spreading in small plots in the absence of crops: this is in line with data obtained in this work using digestate. In this type of study, data can vary a lot: Huijsmans et al.

Table 7
Soil characteristics measured before sowing (BS), after sowing (AS), after topdressing fertilization (AC) and after corn harvest (AH) for the different Theses studied and for the years 2012 and 2013.

Treatment	Silt-2012 (%)	Silt-2013 (%)	Clay-2012 (%)	Clay-2013 (%)	Sand-2012 (%)	Sand-2013 (%)	CEC-2012 $cmol^{(+)}\ kg^{-1}$ TS	CEC-2013 $cmol^{(+)}\ kg^{-1}$ TS	pH-2012 $-Log\ [H^+]$	pH-2013 $-Log\ [H^+]$
T 1	23.3 ± 7.6a[a]A[b]	24.4 ± 7.2aA	9.5 ± 0.1bA	5.9 ± 0.9aA	67.2 ± 7.7a	69.6 ± 6.3a	12.4 ± 0.9aA	15.5 ± 0.7bA	6.8 ± 0.2aA	7.4 ± 0.3bA
T 2	27.0 ± 3.7aA	28.2 ± 5.2aA	11.7 ± 1.1bA	6.5 ± 1.7aA	61.4 ± 4.8a	65.3 ± 6.8a	13.2 ± 0.5aA	16.1 ± 1.7bA	6.8 ± 0.6aA	7.0 ± 0aA
T 3	25.7 ± 8.8aA	30.4 ± 1.6aA	11.5 ± 0.6bA	6.9 ± 0.3aA	62.9 ± 8.2a	62.7 ± 1.9a	13.5 ± 0.5aA	15.7 ± 2.4bA	6.8 ± 0.3aA	7.3 ± 1.1bA
T 4	27.2 ± 5.4aA	28.3 ± 1.7aA	11.3 ± 2.2bA	5.8 ± 1.2aA	61.5 ± 7.5a	65.8 ± 2.9a	12.4 ± 1.1aA	15.0 ± 2.0bA	7 ± 0aA	6.9 ± 0bA

	TKN-BS-2013	TKN-AS-2012	TKN-AC-2012	TKN-AH-2012 (mg kg^{-1} TS)	TKN-BS-2013	TKN-AS-2013	TKN-AC-2013	TKN-AH-2013
T 1	1.14 ± 0.09abA	1.33 ± 0.22bA	1.32 ± 0bA	1.18 ± 0.01abA	1.22 ± 0.06abA	1.18 ± 0.14abA	0.93 ± 0.19aB	0.99 ± 0.22aA
T 2	1.17 ± 0.20abA	1.27 ± 0.28bA	1.24 ± 0.22bA	1.24 ± 0.12bA	1.11 ± 0.02abA	1.19 ± 0.12abA	0.85 ± 0.04aAB	1.06 ± 0.2abA
T 3	1.23 ± 0.18cA	1.22 ± 0.13cA	1.21 ± 0.13cA	1.16 ± 0.10bcA	1.14 ± 0.09bcA	1.25 ± 0.14cA	0.77 ± 0.13aA	0.95 ± 0.08abA
T 4	1.2 ± 0.1aA	1.21 ± 0.02aA	1.32 ± 0.18bA	1.29 ± 0.02bA	1.17 ± 0.01aA	1.23 ± 0.05aA	1.10 ± 0.24aB	1.18 ± 0.21aB

	TOC-BS-2012	TOC-AH-2012	TOC-BS-2013	TOC-AH-2013 (mg kg^{-1} TS)	P[c]-BS-2012	P-AH-2012	P-BS-2013	P-AH-2013
T 1	11.6 ± 0.3aA	11.4 ± 0.5aA	11.3 ± 0.2aB	10.7 ± 1.8aA	41.8 ± 8.1aA	41.1 ± 10.3aA	75.6 ± 17.1cB	59.0 ± 13bB
T 2	10.6 ± 1.2aA	11.6 ± 0.8aA	9.8 ± 2.3aAB	10.3 ± 1.8aA	28 ± 16.9aA	30.5 ± 15.1aA	46.9 ± 29.1bA	41.2 ± 21.7abAB
T 3	11.8 ± 1.1bA	11.1 ± 0.8bA	7.4 ± 2.9aA	9.7 ± 2.2abA	33.7 ± 21.7aA	26.9 ± 17.4aA	43.0 ± 18.0bA	37.9 ± 17.4abA
T 4	11.1 ± 0.6bA	11.6 ± 0.5bA	9.4 ± 1.1aAB	11.9 ± 0.9bB	32.2 ± 15.3aA	25 ± 14aA	46.3 ± 26.1bA	48.2 ± 6.1bAB

[a] Values of the same line followed by the same small letter are not statistically different (ANOVA bootstrap and Tukey test, $p < 0.05$).
[b] Values of the same column followed by the same capital letter are not statistically different (ANOVA bootstrap and Tukey test, $p < 0.05$).
[c] P = available P.

(2003) for example reported that EF ranged from 33.9 to 100% TAN when slurries were superficially applied.

Soil incorporation of slurries strongly reduced ammonia emissions, so that emissions of 2% TAN (Huijsmans et al., 2003) and 17% TAN (Hansen et al., 2003) have been proposed. These data are in the range of those obtained in this work adopting similar application procedures, i.e. EF of 9.52 ± 3.6% (n = 5).

3.5. Agronomic performance of digestate and derived products

Agronomic performances for trials performed by using digestate and liquid fraction of digestate in substitution for urea are shown in Fig. 2. During the first year, non-statistical differences were found between treatments studied, although higher yields were registered for treatments fertilized with digestate and derived products (T2–T4) in comparison with the blank (T1). Unfortunately, problems which occurred during the full-scale trial, i.e. non-uniform irrigation, meant that there were high standard deviations in yield data; moreover, it is well known that unfertilized crops can yield as well as fertilized crops during the first year of experimentation because of residual soil fertility.

The second experimental year gave results that were more interesting: treatments T3 and T4, i.e. soil fertilized with urea (T3) and with the separated liquid fractions of digestate by injection in both pre-sowing and topdressing (T4), gave the highest yields. These crop yields were statistically different from the blank (+18.3% and +18% for T3 and, +21% and 20.4% for T4, on ww and TS basis). The method used to apply the liquid fraction of digestate affected corn yield, i.e. Thesis T4 statistically differed from Thesis T2 (+13.3 and +12.7% on ww and TS basis, respectively) (Fig. 2), this latter characterized by pre-sowing fertilization performed by surface application which allowed ammonia losses by volatilization. This treatment, in fact, was characterized by the highest ammonia losses registered during the two-year experiment, i.e. 52 kg ha^{-1} (Table 6), that was, taking into consideration total ammonia applied, i.e. 340 kg N ha^{-1}, about 15% of total N dosed. Literature data reported lower fertilizer N-values of digestate in comparison with N-fertilizers (calcium ammonia nitrate) for ryegrass because of ammonia volatilization (Quakernack et al., 2012). Again, De Boer (2008) reported that, apparently, digestate N-value was equal to slurry N-value when digestate was not incorporated in soil because of ammonia volatilization from digestate. On the other hand, Möller and Müller (2012) reviewing literature, reported that N uptake from digestate exceeded N uptake from undigested slurry by about 10% to 28%, when it was incorporated in the soil.

Results obtained indicate that the use of digestate and/or the liquid fraction of digestate would allow the replacing of the use of urea, while getting similar or higher crop production (not statistically significant), in agreement with previous works that attested the comparability of digestate to mineral fertilizers (N) (Alburquerque et al., 2012a,b; Walsh et al., 2012).

Soil characteristics did not seem to be affected by fertilizer management (Table 7). Although some statistical differences were found between parameters studied, they were probably due to the variability in soil analysis because of both soil sampling and soil analyses. In particular, if no differences were evident for CEC and pH, the NTK content showed an increase during 2012 after soil fertilization. Nevertheless, as this trend occurred also for the control and as it was not detected during 2013 it was probably a random variation. More interesting was the fact that NTK contents in 2013 were in general higher than those for 2012 (as average the increment was of 8–12%), particularly for the control, although there was not any statistical significance. Moreover, the fact that control, although it did not receive any fertilization, contained the same amount of NTK as the fertilized treatments, suggests that differences found were due to normal variability in soil sampling and analyses, rather than to the fertilization applied. TOC content as well as other parameters did not vary a lot, although at the end of 2013, it was, in general, less than that measured for 2012. Again, variation was small and did not assume any statistical relevance apart from some sporadic cases, e.g. T3 and T4, TOC-BS-2013, for which there was no explanation.

In general, soil characteristics were not affected by the use of digestate and derived products, at least for the short period considered.

4. Conclusion

This work aimed to test the use of digestate and derived products from an AD plant in substitution for N-chemical fertilizers to produce maize silage during crop years 2012 and 2013. Results obtained indicated that sub-surface injection of digestate and derived products at pre-sowing and topdressing, gave crop yields similar to those obtainable by the use of urea. Subsurface injection allowed, also, the reduction of ammonia emissions to levels that were similar to those obtained by using urea. Again, the efficient use of these products, in combination with the high biological stability of digestate through the anaerobic process, allowed the impact of odours to be strongly reduced.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.12.156.

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