Measuring ammonia and odours emissions during full field digestate use in agriculture.

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Abstract

The use of digestate in agriculture represents an opportunity for reducing the use of synthetic fertilizers while promoting nutrient and organic matter recycling, i.e. contributing to a circular economy. However, some environmental impacts could result from digestate use, with particular reference to N emissions, which can contribute to particulate matter formation in the atmosphere. So, correct digestate spreading methods need to be tested to reduce ammonia emission and, possibly, also to avoid annoyance to the inhabitants. In this work a digestate from organic wastes was used as a fertilizer by its injection at 15 cm, in comparison with a synthetic one (urea) for three consecutive years in open fields, measuring ammonia and odours emission. On average, the ammonia emission from digestate was of 25.6 ± 9.4 kg N Ha^{-1} (11.6% ± 4 of Total Ammonia Nitrogen - TAN - dosed), while urea emitted 24.8 ± 8.3 kg N Ha^{-1} (13.4% ± 4.5 of TAN dosed). The injected digestate also

emitted less odour than urea (601 ± 531 and 1,767 ± 2,221 OU m^{-2} h^{-1}, respectively), being ammonia coming from urea hydrolysis responsible for odour productions.

The different N fertilizers did not lead to differences in crop yields, i.e. 18.5 ± 2.9 Mg grain Ha^{-1} and 17.4 ± 1.2 Mg grain Ha^{-1} for digestate and urea respectively.

Keywords: Ammonia emissions; Anaerobic digestion; Digestate fertilization; Odour emissions; Open field measurements; Organic wastes.

1. Introduction

Climate change is pushing the world into shifting production processes towards more sustainable models, lowering environmental impacts and reducing greenhouse gas emissions (European Commission, 2019; Frantzeskaki et al., 2019). One of the main challenges is how to manage the transition towards circular economy models based on the recovery of wastes, that become raw material for the subsequent production cycle (Lüdeke-Freund et al., 2019; Pieroni et al., 2019).

Nutrient recovery from organic wastes represents an interesting circular economy model able to upgrade waste into fertilizers to be used in substitution for synthetic ones (Toop et al., 2017). Indeed, N and P dispersion in the environment causes many problems and these two elements have been reported to be over "planetary boundaries" (Rockström et al., 2009; Steffen et al., 2015). Moreover, fertilizer production requires large amounts of energy consumption or the exploitation of non-renewable mineral deposits that strongly impact on environmental and climate change (Springmann et al., 2018).

However, untreated organic wastes do not represent acceptable fertilizers (Westerman and Bicudo, 2005). Technology/biotechnology is needed to transform them into useful products (Sigurnjak et al., 2019). In the last decades, anaerobic digestion has been proposed as a valid biotechnology for producing bioenergy but, also, to produce bio fertilizers, i.e. the digestate, to be used in agriculture as a substitute for synthetic fertilizers (Riva et al., 2016; Tambone et al., 2019; Verdi et al., 2019).

Furthermore, the possibility of using digestate in agriculture has raised many doubts regarding its possible environmental impacts. The high amounts of nitrogen in the mineral form (ammonia-N), which is useful for plant nutrition, can cause environmental problems due to both nitrates (NO_3^-) leaching and N emission to the atmosphere (N_2O and NH_3) (Cameron et al., 2013; Delgado, 2002). Although problems connected with nitrate leaching have received much attention in the past (Padilla et al., 2018), less is known regarding N emissions.

The anthropogenic emission of ammonia causes a series of impacts on both climate, ecosystems and health. In fact, once in the upper atmosphere, ammonia combines with other molecules generating a wide range of nitrogen compounds which fall to the soil causing acidification and eutrophication of ecosystems (Clark and Tilman, 2008; Hautier et al., 2014). Furthermore, ammonia in the atmosphere contributes to the formation of secondary particulate matters (Erisman and Schaap, 2004) influencing the planet climate because they act as condenser nuclei for atmospheric water forming clouds (Bianchi et al., 2016). In addition particulate matters affect human health causing acute or chronic respiratory diseases (Comunian et al., 2020; Fennelly, 2020; Losacco and Perillo, 2018; Setti et al., 2020). In previous work (Riva et al., 2016) it was reported for the Lombardy Region (North Italy) that about 96% of ammonia polluting the air was due to agricultural activity (livestock), with these data being confirmed by the international literature (Clarisse et al., 2009).

In recent decades, many studies have tried to clarify the ammonia emissions from both mineral and animal fertilizers (Sommer and Hutchings, 2001; Sommer and Olesen, 2000), but not many data are available for digestate. Getting real data is sometimes very difficult because working at full field scale is costly and complicated. Therefore, the data proposed have often been obtained at lab or pilot scale (Finzi et al., 2019) and so, rather distant from the reality. In addition, studying only at lab scale makes it impossible to test innovative technologies such as digestate injection into the soil, coupled with precision farming, to reduce ammonia emissions (Morken and Sakshaug, 1998; Nicholson et al., 2018).

Ammonia has been reported having a very low odour threshold causing inhabitants annoyance during fertilization. Therefore, reducing ammonia emission means, also, reducing odour emission. In addition, organic fertilizers contain organic matter that can produce many volatile organic odorous molecules as the result of microbial bioprocess such as fermentation and anaerobic respiration (Orzi et al., 2015). Thus, spreading organic fertilizers such as digestate in the field introduces another problem in addition to ammonia emission, i.e. odour impact, which is interesting to study.

In previous work it was reported that anaerobic digestion, because it degrades the easily degradable organic matter, strongly reduced the potential odour emission but, because it mineralize organic-N to ammonia, odours potentially can increase if ammonia emission are not controlled (Orzi et al., 2015). The digestate injection into the soil has been reported reducing odour emission at values even below that measured for mineral fertilizers spreaded onto the surface, such as urea (Orzi et al., 2018), taking into consideration that odours from urea is the result of ammonia coming from its hydrolysis.

Digestate is incresingly indicated as a useful N-fertilzers able to replace mineral fertilizers (e.g. urea) for crop production (Riva et al., 2016). Therefore its use should be promoted, but taking into account correct and safe management.

The objective of this study was to provide data on ammonia and odour emissions resulting from the use of digestate from organic wastes (mainly sewage sludge) in the open field in a full-scale production context, by adopting a low emission strategy, i.e. digestate injection, to reduce both ammonia and odour emissions.

The study was performed by comparing digestate with conventional N-fertilization (urea) and discussing the results obtained with the literature data. The experiments were repeated for three consecutive years (2018, 2019 and 2020). They were carried out on a maize crop located in the Po valley (northern Italy), one of the most intensely cultivated areas in Europe, and consequently with serious problems about ammonia in the atmosphere (ISPRA, 2019).

2. Material and Methods

2.1 Spreading and experimental setup

All the experiments were carried out to compare emissions and agronomic performance of two different fertilizers (slurry-like digestate and solid granular urea, plus an unfertilized control) dosed following standard agricultural procedure used in the Po Valley. The experimental fields were located in the Po valley, northern Italy, and the experiments were carried out on a maize field, with experimental plots in triplicate and using a randomized scheme.

Digestate was spread by injection in soil at a depth of 15 cm by using a tank car joined to a rigid multi-anchor-subsoiler coupled with a Retrofit Variable-Rate Control (VRT control). Digestate was dosed in order to satisfied N maize requirements, adopting an N efficiency of 0.5, such as suggested by the Regional Plan for Water Protection from Nitrate from Agriculture (Regione Lombardia, 2020). Doing so efficient N dosed for digestate was equal to that coming from urea (Table 1). Urea was spread as the solid form on the soil surface following a routine procedure typical of Po Valley. Fertilization date, fertilizers used and doses applied, and spreading methodology are reported in Table 1.

The ammonia and odours measurements took place at pre-sowing fertilization in three consecutive years, 2018-2019-2020, adopting the same agronomic and emission measurement technique, and fertilizer doses.

2.2 Fertilizer sampling and analysis

The digestates used in this work were sampled immediately before they were injected in the field. The analyses took place in the hours immediately following.

The main characteristics of the digestate used in this work are shown in Table 2. Digestate pH was determined in aqueous solution using a 1:2.5 sample/water ratio. Total solids (TS) and total organic carbon (TOC) determinations were carried out following standard procedures of the American Public Health Association (APHA, 1992). Total nitrogen (TKN) and ammonia nitrogen (TAN) were determined according to the analytical method for wastewater sludges (IRSA CNR, 1994). Total P content was assessed by inductively coupled plasma mass spectrometry (Varian, Fort. Collins, USA), preceded by acid digestion (EPA, 1998) of the samples. All the analyses were carried out in triplicate.

2.3 Soil sampling and analysis

The soils studied in this work were sampled just before the spreading by taking three random samples (made by 3 sub-samples)/plot of soil (20 cm); this procedure was repeated each year and no statistical differences occurred. Samples were air dried, sieved to 2 mm and then ground to 0.5 mm. The main characteristics of soils are reported in Table S1. Soil pH was determined in aqueous solution using a 1:2.5 sample/water ratio (McLean, 1982), and texture by the pipette method (Gee and Bauder, 1986). Cation Exchange Capacity (CEC) was determined by saturating the samples with $BaCl_2$ (Rhoades, 1982). Total organic carbon (TOC) was determined using the Walkley and Black method (Olsen et al., 1982), total nitrogen by the Kjeldahl method (Faithfull, 2002). All the analyses were carried out in triplicate.

2.4 Ammonia emission measurement

For all the experiments, the ammonia emitted from the experimental plots was measured in the hours following the pre-sowing injection/spreading (Figure 1). All the digestate injections took place at the same hour (h. 11:00), and the first sampling was always carried out 10 hours later (21:00).

The experiments were repeated for three consecutive years on the same experimental plots, which main soil chemical characteristics are reported in Table S1. In particular, the soil used showed a neutral pH (7 ± 0.4), it was rich in silt (44% ± 2.1) and it was relatively poor in clay (10% ± 0.5). The amounts of ammonia nitrogen dosed at pre-sowing were kept almost unchanged for all the three years tested, i.e. 200 - 229 and 185 kg N Ha^{-1} for digestate and urea, respectively (Table 1).

The concentration of NH_3 was monitored by the exposure of ALPHA passive samplers (Riva et al., 2016; Tang et al., 2001). For each plot, the ALPHA samplers were exhibited in sets of three. To obtain background environmental concentration values, an additional sampling point was placed at a distance of about 1,000 meters away from the fertilized fields and other possible point sources of NH_3.

Each sampler located in the plot was replaced a minimum of twice a day near sunrise and sunset, to be able to monitor the variation of atmospheric turbulence which has a direct effect on the dispersion of pollutants. During the application day and the following day, the substitution was done when the vehicles entered the field, for fertilization and for incorporation. The study of atmospheric turbulence was carried out by using an ultrasonic anemometer (10 Hz) positioned in the plots near to the samplers.

By processing the NH_3 concentration information, an analysis of the dispersion of NH_3 in the atmosphere was performed through the application of the dispersion model (WindTrax, Tunderbeach Scientific, CA). The obtained dispersion coefficient (*D*; s m^{-1}) was used to determine the flow (*S*; ng NH^3 m^{-2} s^{-1}) emitted from the fertilized surface, on the basis of the concentrations measured in each plot (*C*; µg m^{-3}) and environmental (C_{bgd}; µg m^{-3}), according to the following equation:

$$S = \left(C - C_{bgd}\right) \times D^{-1}$$

The ammonia emission factor (EF%) was obtained from the ratio between the released N-NH_3 (kg ha^{-1}) and the calculated amount of ammonia nitrogen (N-NH_4; kg ha^{-1}) spread onto the soil with fertilizations.

2.5 Potential odour emission and field odour emission measurement

Potential odour emissions were measured on gas samples collected in the laboratory following the protocol reported by Riva and colleagues (Riva et al., 2016). The sampling was carried out by spreading the sample homogeneously on a surface that was then covered with a steel chamber having a sampling area of 0.127 m^2. A continuous flow of air was continuously flushed inside the chamber for 5 minutes (rate 0.38 m^3 h^{-1}). Output gas from the chamber was collected in Nalophan sampling bags, which were then analysed through dynamic olfactometry (CEN, 2003) within 24 hours from sampling. Analyses were performed in three replicates.

The same method was used for full field sampling. The chamber was placed above the newly fertilized soil, taking care to eliminate any air leaks from the edges. All measurements were made once per plot.

The results of the Dynamic Olfactometry were expressed as odour concentration value (OU m^{-3}). The specific odour emission rate SOER (OUE m^{-2} h^{-1}) was calculated by using the following equation:

$$SOER = 1000 \times (C \times Q/S)$$

in which C is the odour concentration (OU m^{-3}), Q is the incoming air rate to the flux chamber (0.38 m^3 h^{-1}) and S the surface covered by the chamber (0.127 m^2).

2.6 Maize yield quantification and N content in grain

The annual yields for each of the experimental plots were assessed by manual harvesting of the grain. The data obtained from each plot were then aggregated in order to obtain a value (in Mg Ha^{-1}) for each treatment, i.e. digestate, urea and control.

The quantification of the N content in the harvested maize grain was performed through combustion method (Dumas method) (Saint-Denis and Goupy, 2004). Before analysis, the grain samples (20 g of dry matter) were prepared by grounding them using a ball mill. N was detected by using an elemental analyser (Rapid max N exceed model, Elementar, Lomazzo, Italy). Each analysis was performed in triplicate.

2.7 Statistical analysis

The statistical analyses were carried out using IBM SPSS® 23 software. Unless otherwise specified, the significance limit value p was set at 0.05 for all the analyses carried out. The plots were obtained through the use of Microsoft EXCEL 2016.

3. Results and discussion

3.1 Maize yield

At the end of each of the crop seasons, the grain yield from soils fertilized with digestate and urea was evaluated (Table 3). In agreement with data from previous work (Riva et al., 2016; Verdi et al., 2019; Walsh et al., 2012), the production, as a three-year average, for the plots fertilized with digestate (18.1 ± 2.9 Mg Ha^{-1}) was very similar to that obtained from the plots fertilized with urea (17.4 ± 1.2 Mg Ha^{-1}) (one-way ANOVA analysis, p = 0.72, *n* = 3). Low standard deviation indicated that the yields were very similar throughout the three years. The use of digestate determined, as an average value over the three years, an N content in the grain of 12 ± 0.9 gN kg^{-1} DM, higher than that of the control (9.26 ± 0.6 gN kg^{-1} DM) and treatment with urea (11.3 ± 0.7 gN kg^{-1} DM) (one-way ANOVA, n = 6, $p<0.01$, Tukey post-test).

3.2 Ammonia emission

The ammonia emission measurements were done using passive ALPHA samplers and processing the data with dispersion models (see Section 2.4). This approach has advantages and disadvantages: passive samplers fully exposed to the atmosphere do not allow maintaining controlled micro-environmental conditions, unlike other methods such as wind tunnels (Misselbrook et al., 2005). Therefore measurement made at different time can be affected by environmental parameters, introducing variability. On the other hand, passive ALPHA sampler, taking into consideration the environmental conditions occurred during the measurements, allows realistic measurements of emission that occurred at that particular time and condition (Misselbrook et al., 2005).

~~A comparison between techniques is not the aim of this work, however the technique used was chosen well knowing its limits and strengths.~~

The fluxes of NH_3 released from the soil after spreading (years 2018, 2019 and 2020) are shown in Figure 1. Observing each of the three graphs alone (Figure 1), it can be clearly seen that there is a strong overlap between the emission curves of NH_3 from soils fertilized with digestate (solid lines) and urea (dashed lines). In each of the three years, the soils fertilized with urea and digestate were therefore found to have emitted similar amounts of ammonia over time, thus responding in a similar way to the main environmental factors that may have influenced this process (Bouwmeester et al., 1985; Cameron et al., 2013; Sommer and Hutchings, 2001). Among these factors, the most important in this specific case were the climatic conditions in the days preceding and following the spreading (Tables S2 and S3), given that the chemical characteristics of the soil remained unchanged. However, it was not possible to obtain a coherent model that correlated emission flows with climatic conditions by using multivariate statistical analysis (Partial Least Squares Analysis, PLS) (Table S4), probably due to the high variability of data acquired between years and complexity of the factors involved in the open field.

Comparing instead the emission flows year by year (2018, 2019 and 2020), they appeared very variable (Figure 1). In fact, the graphic corresponding to the experiment of 2018 showed a strong emission peak between the 10^{th} and 20^{th} hour after fertilization, corresponding to the night, followed by a higher modest peak close to the 50^{th} hour after spreading, corresponding instead to the morning hours. The ammonia losses at the end of the experiment were of 32.2 kg N Ha^{-1} and 25 kg N Ha^{-1} for digestate and urea, respectively, corresponding to a loss of 14.9% and 13.5% of the TAN dosed, and were very similar between digestate and urea (Table 3). The graph reporting data on 2019 showed a completely different pattern: in this case, in fact, in the first 20 hours after fertilization, the emission flows appeared very low, then increased starting from the 20^{th} h after fertilization with urea and later for fertilization with digestate. Emission peaks were reached after 45 hours, at 6:00 in the morning. A second peak of similar intensity was then recorded at the 70^{th} h after the spreading, again at 6:00

in the morning. In this case, the loss of ammonia was 26.9 kg N Ha^{-1} and 33 kg N Ha^{-1} for digestate and urea (12% and 17.8% loss of TAN dosed), respectively (Table 3). 2019 was the year in which urea lost more ammonia (%TAN) than in other years of experimentation. This was probably due to climatic conditions; in fact, the soil received several showers of rain in the days before the spreading (Table S3) and the low temperatures combined with the high atmospheric humidity probably contributed to maintaining high soil moisture (Table S2). It is well known that these conditions tend to increase the loss of ammonia from urea, especially if dosed on the surface, because of moisture enhanced urea hydrolysis (Cameron et al., 2013).

Finally, for the year 2020 high emission levels were already observed during the first measurement, i.e. 10 hours after fertilization, reaching a peak at the 25^{th} h, at noon. After this single peak, the ammonia emission was reduced to very modest values and was close to zero for the rest of the experiment.

At the end of the experiment, the total ammonia emitted was of 15.6 kg N Ha^{-1} and of 16.4 kg N Ha^{-1} for digestate and urea respectively, corresponding to a loss of 7.8% and 8.9% of the TAN dosed. These were the lowest values measured over the three years of experiments, for both digestate and urea. Such low emissions were probably caused by the particularly dry environmental conditions, especially in the days before and immediately following the spreading (Table S2). On the third day after spreading, rains were recorded (2.6 mm) (Table S3) which, however, were not enough to have a significant effect on ammonia emission.

Ultimately, observing all the data from the three years together it was not possible to identify a similar pattern for ammonia emissions, since they showed such a strong variability between the three years due probably to environmental condition. In particular, from the above discussion and taking into consideration environmental parameters reported in Table S2 and S3, both highest solar radiation and wind speed for the year 2020 led to dry condition (lowest air moisture) reducing ammonia emission, according, also, to what reported in the literature (Cameron et. al, 2013).

Therefore, data collected on 2018, 2019 and 2020 (Table S2) in this work, represented real emissions occurred under those particular environmental conditions. However, considering that three measurements were made in three different years characterized by diverse conditions, the average emission values obtained can be assumed as a good approximation of real ammonia emission occurred during fertilizers injection/spreading.

At the end of the trials, the average ammonia losses were similar and not statistically different (One-way ANOVA p = 0.92, n = 6), i.e. 11.6 ± 4 % TAN and 13.4 ± 4.5% TAN, respectively for digestate and urea (mean of the years 2018, 2019 and 2020) (Figure 2). Furthermore, according to Sommer and Olesen (2000), on average, about 48% of the total ammonia emitted during such experiments was likely to be emitted in the first 24 hours after fertilization. For all the three years, the ammonia emissions recorded were stable and close to zero after 80 h from the spreading (Figure 2).

To include the data reported in this work in a broader context, a comparative study was carried out with data from the literature, deriving from similar studies carried out using digestate (Table 4) both injected and spread on the surface, and urea (Table S5) distributed onto the surface. Unfortunately, not many data were reported from digestate used on maize so that the comparisons made include other crops. In addition, the use of different methods to measure ammonia emission make this comparison more difficult and this must be taken into consideration discussing the result afterwards.

The loss of ammonia (% TAN dosed) reported in this work for digestate (11.6% ± 4 on average, Table 3) was very similar to the data reported by Riva and colleagues (10.8%, Table 4) (Riva et al., 2016), which were carried out in the same climatic zone (Lombardy, Italy), with the same distribution technique (injection at 15 cm) and crop (maize) and adopting the same measurement method, i.e. passive sampler. However, it is interesting to note that Riva et al. (2016) dosed an amount of ammonia N (65.7 kg N Ha^{-1}) equal to about one third to the amount used in this work (200 - 229 kg N Ha^{-1}), from which it seems that the amount of N dosed was probably less relevant than other variables (i.e. climate and spreading techniques) in determining ammonia loss.

Comparison made with other literature data (Table 4) was more difficult because all data were obtained using a different methodology, i.e. wind tunnel. Anyway, by using digestate distributed by injection on grass (Nicholson et al., 2018) and on rygrass (Rubæek et al., 1996) emission measured were not so far from those measured in this work, i.e. N loss of 22.5± 9.1% TAN and N loss of 14.6 ± 4.7% TAN (average data), respectively. These values were lower than N loss obtained by distributing the digestate on the surface, which was, as average, of 38.9 ± 12% TAN (Chantigny et al., 2004; Rubæek et al., 1996). These data underlined the importance to inject digestate reducing N emission.

Ammonia emission due to urea use in this work have been compared with data in the literature (Table S5) that, like the spreading modality used in this work, all considered surface spreading. In our work the ammonia loss (% TAN dosed) registered was of 13.4 ± 4.5% TAN and so lower than the average calculated from the literature, i.e. 24.8% ± 16.6 (n = 17). However, since different methods have been used, the comparison made is only indicative. However, reports revealed a very wide range of data, from 10% TAN to 66% TAN (Black et al., 1987; Cai et al., 2002; Ellington, 1986; Fan et al., 2005; Musa, 1968; Rojas et al., 2012) (Table S5).

These differences may be due to multiple factors related to both climatic conditions and soil characteristics (Harrison and Webb, 2001). Unfortunately, from such a heterogeneous group of studies, it was not possible to reconstruct a complete picture. However, as regards the data reported in this work, it is possible to hypothesize that the low percentage of ammonia lost by urea, compared to the average of the other works (Table S5), may be attributable to the low rainfall at our site during the period of the observations (Table S2 and Table S3), since moisture is one of the main drivers for ammonia emission from urea (Cameron et al., 2013).

Taking into consideration results obtained and the literature data, some suggestions can be given to reduce the ammonia emission using N fertilizers. First of all, spreading or distributing fertilizers onto the surface causes large ammonia emission so that it becomes essential to inject liquid fertilizers (i.e. digestate) and bury solid fertilizers (i.e. urea) (Sommer and Hutchings, 2001), above all in presence of humid soil. Humidity has been reported playing an important role in ammonia emission from urea because it promotes its hydrolysis releasing ammonium (Cameron et al., 2013). On the other hand, abundant rainfall or irrigation immediately after spreading have the effect to reduce ammonia emission for both urea and digestate, thanks to water that drains the dissolved ammonium in deep soil removing it from the soil-atmosphere interface (Sanz-Cobena et al., 2011).

Contrary to what one might think the amount of nitrogen dosed does not seem to have an impact on the percentage of ammonia lost.

3.3 Odour emission

The odour emission measurements reported in this work were carried out in both lab scale (potential odour emission) and open field. Measuring potential odour (lab scale) is very useful because it allows to measure the odour emitted by different fertilizers and so their potentiality in emitting odours when then they are used in full field. In addition, this measurement allows measuring odours from fertilizers excluding all environmental variables that in the open field can heavily influence the result (Orzi et al., 2018; Riva et al., 2016). The successive comparison between potential odour emission (lab scale measurement) and odour emitted in the open field for the same fertilizer, allows estimating the impact of environmental variables on the values measured in open field, including soil injection and soil incorporation (Orzi et al., 2018).

However, odors emission detections suffer for high variability that is an intrinsic characteristic of these measurements (Hudson et al., 2007), making it difficult to carry out statistically robust comparisons. The variability is due to both the large number of factors affecting odour emission, especially from biomass (Zilio et al., 2020), and technical difficulties in performing measurements (Hudson et al., 2007). In addition, the dynamic olfactometry method, despite it being the reference method for this type of measurement, suffers from low reproducibility of data due to human error (Van Harreveld et al., 1999; Hove et al., 2017). Keeping in mind these limitations, data obtained in this work are below discussed.

Digestate used in this work showed a potential odour emission measured at lab scale of 3,740 ± 846 OU m^{-2} h^{-1} (Figure 3) in line with data reported, on average, for agricultural digestate ($OU_{dig.}$ = 4,454 ± 5,217 OU m^{-2} h^{-1}; n = 25) (Orzi et al., 2015; Orzi et al., 2018).

Literature reported that anaerobic digestion, because it degrades the easily degradable organic matter and concentrates the more recalcitrant compounds (Orzi et al., 2015; Orzi *et al.*, 2018; Zilio *et al.*, 2020) reduces potential odour production (Orzi et al., 2015). Therefore, it was interesting, for the purposes of the discussion, to compare the odour emission values from the same substrates before and after anaerobic digestion. Unfortunately, in this work it was not possible to test feed sewage sludge, because it was represented by a mix of different substrates (more than 60) that varied during the year. However, the liquid digestate used, because it was stocked in a 50,000 m^3 tank before agricultural use, allowed taking representative samples to be measured.

Therefore, data obtained for the digestate used in this work were compared with those coming from previous studies for both digestates and non-digested material (Orzi et al., 2018, 2015). From Figure 3 the digestate for this work showed a lower potential odour emission than those reported for pig and cow digestates (7,460 ± 4,080 and 6,598 ± 7,166 OU m^{-2} h^{-1} respectively), although the high standard deviation did not allow statistical differences to be established. On the other hand, observing the potential odour emission from the same undigested biomasses, very high values were registered for pig slurry (128.123 ± 179.426 OU m^{-2} h^{-1}), unlike cow slurry that showed a potential odour emission (8.456 ± 6.686 OU m^{-2} h^{-1}) not so far from that of cow digestate. The difference between pig and cow slurry can be ascribed to the fact that the second one was made by lignocellulosic residual material partially anaerobically digested (by a polygastric mammal), which underlined the importance, in addition to anaerobic digestion, of the organic substrate's origin (Scaglia et al., 2018). In this way, because sewage sludge represents a partially digested organic material coming from a wastewater treatment plant, low potential odour emission can be ascribed to both the material origin and to the subsequent anaerobic digestion. This fact was confirmed by biological stability degree of digestate measured by both aerobic (OD_{20}) and anaerobic (BMP) tests (Scaglia et al., 2018), i.e. OD_{20} of 22.7

± 6.1 mg O_2 g^{-1} dw and BMP of 57 ± 23 L_{biogas} kg^{-1} dw that were in line (OD_{20}) or lower (BMP) than those measured for two green composts, i.e. 15.06 ± 0.3 mg O_2 g^{-1} dw and 10.3 ± 1.1 mg O_2 g^{-1} dw, and 144 ± 3.8 L_{biogas} kg^{-1} dw and 201 ± 20 L_{biogas} kg^{-1} dw, respectively (Scaglia et al., 2018).

The urea, as expected, showed the lowest potential odour emission value, i.e. 150 ± 106 OU m^{-2} h^{-1}, not so far with previous data 454 ± 215 OU m^{-2} h^{-1} (Orzi et al., 2018).

In open field experiments (2018, 2019 and 2020) odour emissions from the experimental plots were measured each year immediately after fertilization (Table 3). The results showed that, considering the three years average, the odour emitted by the plots fertilized with digestate was very low, i.e. 601 ± 531 OU m^{-2} h^{-1}, and similar to that emitted by non-fertilized plots (633 ± 494 OU m^{-2} h^{-1}). The plots fertilized with urea, on the other hand, showed a higher average odour emission (1,767 ± 2,221 OU m^{-2} h^{-1}) than the digestate-fertilized plots, but were not statistically different, probably due to the high variability that is typical of odour measurements.

Therefore, odour emission measured for digestate studied in this work in the open field was much lower than the potential odour measured at lab scale (Figure 3). This difference was most likely due to the injection of digestate into the soil which was able to reduce the odour emission, as previously described (Orzi et al., 2018; Riva et al., 2016). On the other hand, urea odour emission measured in the full field, was, as an average of the three years tested, of 1,767 ± 2,221 OU m^{-2} h^{-1} much higher than the potential measured i.e. 150 ± 106 OU m^{-2} h^{-1}. Probably in this case soil and air moisture, promoting a fast urea hydrolysis, stimulated ammonia emission. As known, ammonia has a low olfactory threshold (odour threshold between 0.0266 and 39.6 mg m^{-3}) (Rice and Netzer, 1982), thus its rapid release may have produced an increase in odour emission.

Observing the data reported in Figure 4, the digestate used in this work by injection showed odour emission that was not so different from data reported for injected pig and cow digestates, measured previously adopting the same methodologies (Orzi et al., 2018), i.e. 900 ± 584 OU m^{-2} h^{-1} and 1347 ± 749 OU m^{-2} h^{-1}, respectively). These data confirmed the validity of the injection method to limit odour emission, confirmed by the comparison of data for injected pig digestate with spread pig digestate, i.e. 900 ± 584 OU m^{-2} h^{-1} vs 4,280 ± 1,346 OU m^{-2} h^{-1}, respectively (Orzi et al., 2016). On the other hand, no substantial differences can be observed between injected cow digestate and surface spread cow digestate, i.e. 1,347 ± 749 OU m^{-2} h^{-1} vs 1,883 ± 847 OU m^{-2} h^{-1}, respectively (Orzi et al., 2018), indicating that the most important factors involved in odour reduction during agronomic use of digestate are the spreading technique (injection vs. surface spread), the treatment (digestate vs. non-digestate) and the biomass origin.

4. Conclusions

This work showed that the use of digestate from sewage sludge as a fertilizer in agriculture can replace urea without increasing ammonia emission. The injection of digestate into the soil has been confirmed as a good technique for reducing ammonia emission, allowing it to reach levels comparable to those typical of surface fertilization with urea. Ammonia emission can be further reduced by improving the injection system: preliminary data indicated that the use of a flexible anchor reduced emissions with respect to the use of rigid ones.

Concerning the emission of odour, it has been observed that digestate from sewage sludge emits less odour than digestates from livestock manure, and if injected into the soil its emission was reduced to a level that was no longer distinguishable from that of non-fertilized soil.

The digestate dosed allowed producing maize at the same rate as the urea confirmed the good fertilizing properties of both dressings.

In conclusion, anaerobic digestion plus liquid digestate injection were confirmed as good practice to provide a suitable fertilizer, replacing the synthetic fertilizer in an environmentally sustainable way, i.e. with low ammonia and odours emissions.

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Notes

The authors declare no competing financial interest

Author Contributions

FA: designed the project, elaborated and interpreted the data and wrote the paper

MZ: collected, elaborated and interpreted the data and wrote the paper

AG and GG: managed the experimental field and the agronomic operations

AP and BR: collected the data

EM and OS: Scientific contribution and manuscript correction.

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Table 1. Main information regarding fertilization plan adopted: fertilization date, fertilizers used, and dose applied.

Campaign	Plots	Date	Fertilization	Fertilizer	Ntot applied (kg N Ha^{-1})	Efficient N applied[a] (kg N Ha^{-1})	Total NH_4^+ applied (kg N Ha^{-1})	Type of spreading
2018	Digestate	23/04/2018	Pre-sowing	Digestate	370	185	229	Injection 15 cm
		22/06/2018	Top-dressing	Ammonia sulphate	100	100	100	Fertigation
	Urea	23/04/2018	Pre-sowing	Urea	185	185	185[b]	Spread in surface
		22/06/2018	Top-dressing	Ammonia sulphate	100	100	100	Fertigation
2019	Digestate	16/04/2019	Pre-sowing	Digestate	370	185	229	Injection 15 cm
		1/08/2019	Top-dressing	Ammonia sulphate	100	100	100	Fertigation
	Urea	16/04/2019	Pre-sowing	Urea	185	185	185 [b]	Spread in surface
		1/08/2019	Top-dressing	Ammonia sulphate	100	100	100	Fertigation
2020	Digestate	28/05/2020	Pre-sowing	Digestate	370	185	200	Injection 15 cm
		31/07/2020	Top-dressing	Ammonia sulphate	90	90	90	Fertigation
	Urea	28/05/2020	Pre-sowing	Urea	185	185	185 [b]	Spread in surface
		31/07/2020	Top-dressing	Ammonia sulphate	90	90	90	Fertigation

[a]Data calculated taking into consideration N efficiency for digestate of 0.5 and for urea of 1, according to Regional Plan for Water Protection from Nitrate from Agriculture (Regione Lombardia, 2020).

[b]Ureic ammonia considered as 100% ammonia.

Table 2. Main characteristics of the digestates used in this work (mean ± SD, n=3).

Parameter	Unit	2018	2019	2020
pH	pH unit	8.6 ± 0.3	8.4 ± 0.3	8.5 ± 0.4
Total solids (TS)	%	10.3 ± 0.48	10.5 ± 0.5	10.5 ± 0.2
Total Organic Carbon (TOC)	% dw[a]	29.2 ± 4.13	31.2 ± 4.2	30.9 ±0.2
Total Nitrogen (TKN)	% dw	7.7 ± 0.3	7.5 ± 0.5	7.3 ± 0.8
N-NH_4 (TAN)	% dw	4.6 ± 0.4	4.5 ± 0.3	3.9 ± 0.1
TAN/TKN	%	60	60	53

[a]dw = dry weight

Table 3. Ammonia emissions, maize productions yield and N content in grain for the three years of experiments. Ammonia and odour emission are reported as mean ± SD (*n*=3). Yield are reported as dry grain yield produced per hectare (mean ± SD; *n*=3). N content in grain are reported as grams of N per kilograms of dry grain material (mean

Campaign	Fertilizer	Total cumulated ammonia emission (kg N Ha^{-1})	Loss of NH_3 (%Ntot)	Loss of NH_3 (%TAN)	Odour emission (OU m^{-2} h^{-1})	Grain yield DM (Mg Ha^{-1})	N content in grain (gN kg^{-1})
2018	Unfertilized	Undetectable[a]	-	-	277 ± 7a	6.5 ± 0.8a	9.08 ± 0.2a
	Digestate	34.2	9.25	14.9	262 ± 52a	16.8 ± 1.4b	11.4 ± 0.8b
	Urea	25	13.5	13.5	259 ± 31a	17.4 ± 2.1b	11.3 ± 0.5b
2019	Unfertilized	Undetectable	-	-	367 ± 22a	11.6 ± 1.2a	9.12 ± 0.3a
	Digestate	26.9	7.44	12	444 ± 122a	16.1 ± 1.4b	12.8 ± 0.2c
	Urea	33	17.8	17.8	404 ± 54a	16.2 ± 1.6b	11.3 ± 0.9b
2020	Unfertilized	Undetectable	-	-	1,257 ± 311a	13.3 ± 1.8a	9.56 ± 1a
	Digestate	15.6	4.33	7.8	1,097 ± 730a	21.4 ± 3.1c	11.7 ± 0.7b
	Urea	16.4	8.85	8.9	4,638 ± 1,097b	18.6 ± 2.1b	11.4 ± 0.9b
Mean	Unfertilized	Undetectable	-	-	633 ± 494a	10.4 ± 3.5a	9.26 ± 0.6a
	Digestate	25.6 ± 9.4a[b]	7.01 ± 2.5a	11.6 ± 4a	601 ± 531a	18.1 ± 2.9b	12 ± 0.9c
	Urea	24.8 ± 8.3a	13.4 ± 4.5b	13.4 ± 4.5a	1,767 ± 2,221a	17.4 ± 1.2b	11.3 ± 0.7b

[a]ammonia emission in unfertilized plots did not differ from background.

[b]Letters are referred to One-way ANOVA analysis carried out comparing for each year the odour emitted from the three treatments (Tukey post-test, $p < 0.01$; *n* = 3).

Table 4. Ammonia emission measured in this work in comparison with literature data reporting experiment performed at full field.

Digestate origin	**Spreading technique**	**Crop**	**Season**	**Ntot dosed (kg N Ha^{-1})**	**NH_4^+ dosed (kg N Ha^{-1})**	**NH_3 cumulated emission (kg N Ha^{-1})**	**Loss of NH_3 (%Ntot)***	**Loss of NH_3 (%TAN)[a]**	**Measurement method**	**Reference**
Sewage sludge	Injection 15 cm	Maize	Spring	370	229	34.2	9.24	14.9	ALPHA passive samplers	This work
		Maize	Spring	370	229	26.9	7.27	11.7		This work
		Maize	Spring	370	200	15.6	4.22	7.82		This work
Cattle slurry + energy crops	Injection 15 cm	Maize	Spring	130	65.7	7.1	5.46	10.8	ALPHA passive samplers	(Riva et al., 2016)
Food waste	Injection 10 cm	Grass	Spring	142	100	17	12	17	Wind tunnels	(Nicholson et al., 2018)
		Grass	Spring	106	75.3	17	16	22.6		(Nicholson et al., 2018)
		Grass	Autumn	117	79.6	12	10.3	15.1		(Nicholson et al., 2018)
		Grass	Autumn	151	122	43	28.5	35.2		(Nicholson et al., 2018)
Cattle + pig slurry	Injection 5 cm	Ryegrass	Spring	86	67	12	14	17.9	Wind tunnels	(Rubæek et al., 1996)
		Ryegrass	Spring	106	80	9	8.49	11.3		(Rubæek et al., 1996)
Pig slurry	Surface spreading	Timothy	Spring	700	485	200	28.6	41.2	Wind tunnels	(Chantigny et al., 2004)
Liquid Pig slurry		Timothy	Spring	140	-	17.7	12.6	-		(Chantigny et al., 2007)
Cattle + pig slurry		Ryegrass	Spring	110	70	35	31.8	50		(Rubæek et al., 1996)
		Ryegrass	Spring	106	78	20	18.9	25.6		(Rubæek et al., 1996)

Caption Figures

Figure 1. Ammonia emissions (kg N Ha^{-1} h^{-1}, *n* = 3) measured in the hours following injection/spreading of fertilizers on maize crop in the years 2018, 2019 and 2020. X axis on the top of the figure shows the time after fertilization (hours), while X-axis on the bottom of the figure shows the daytime. Error bars show the SD.

Figure 2. Cumulated ammonia loss (% TAN) in the hours following the spreading. The data reported refer to the average of the three years of experimentation on maize fields (2018, 2019 and 2020).

Figure 3. Potential odour emissions measured in laboratory for the digestate used in this work in comparison with other organic matrices (data from Orzi *et al.*, 2015, 2018) (mean ± SD).

Figure 4. Odour emissions measured in full field for different fertilizers (data from Orzi *et al.*, 2018) compared with those measured for digestate and urea used in this work (mean ± SD).

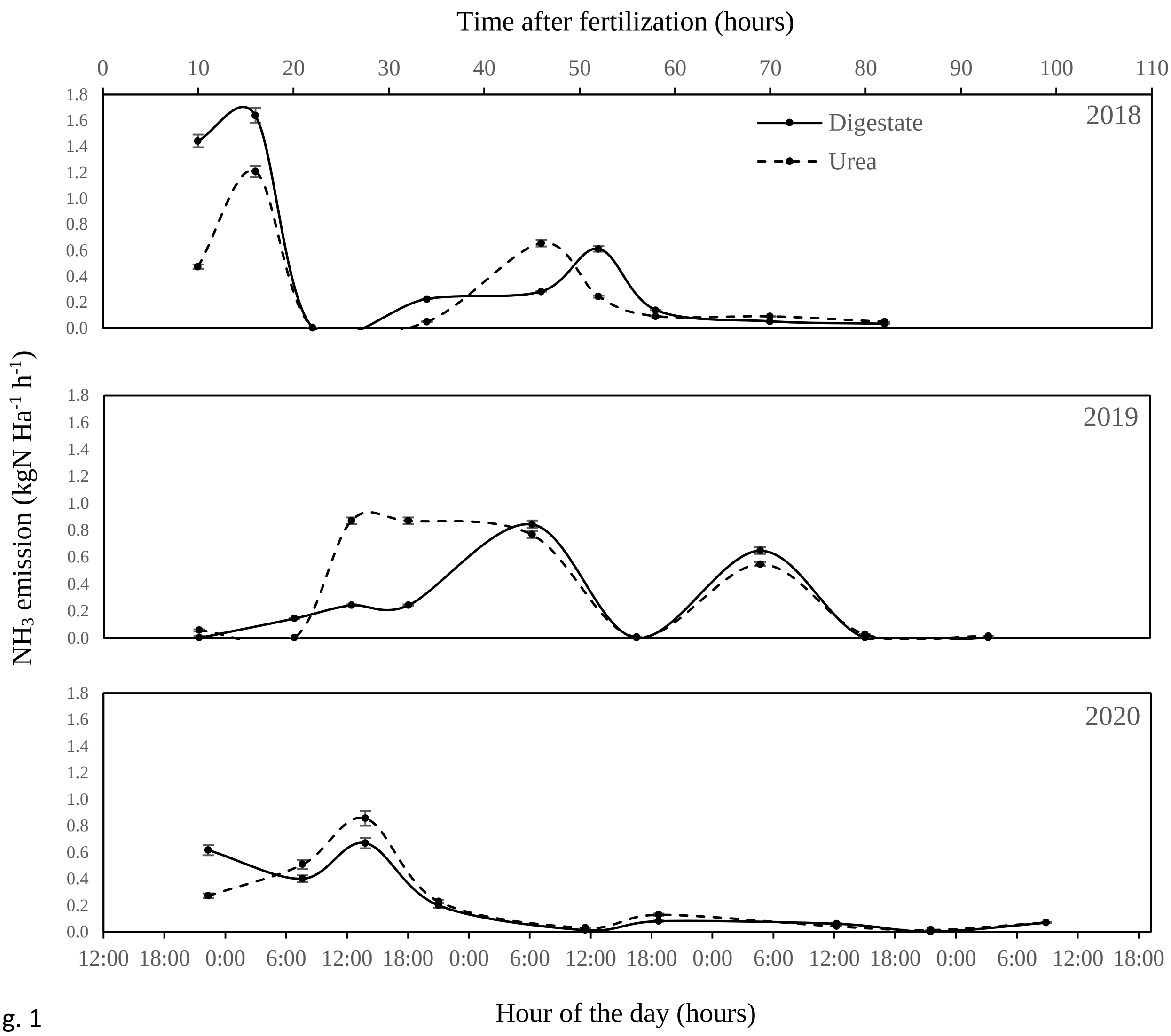
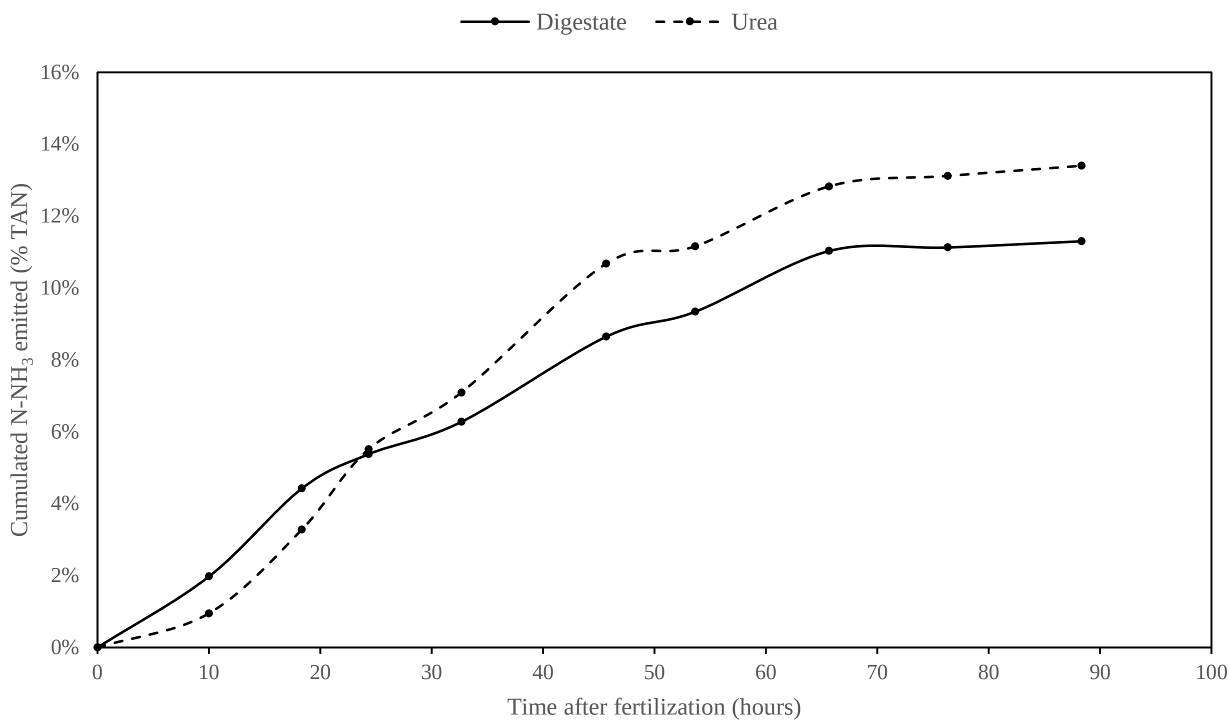

Time after fertilization (hours)
0
10
20
30
40
50
60
70
80
90
100
110
Digestate
Urea
2018
2019
2020
NH3 emission (kgN Ha-1 h-1)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
12:00 18:00 0:00 6:00 12:00 18:00 0:00 6:00 12:00 18:00 0:00 6:00 12:00 18:00 0:00 6:00 12:00 18:00
Hour of the day (hours)

Fig. 1


Digestate
Urea
16%
14%
12%
10%
8%
6%
4%
2%
0%
Cumulated N-NH3 emitted (% TAN)
0
10
20
30
40
50
60
70
80
90
100
Time after fertilization (hours)

693

694 Fig. 2

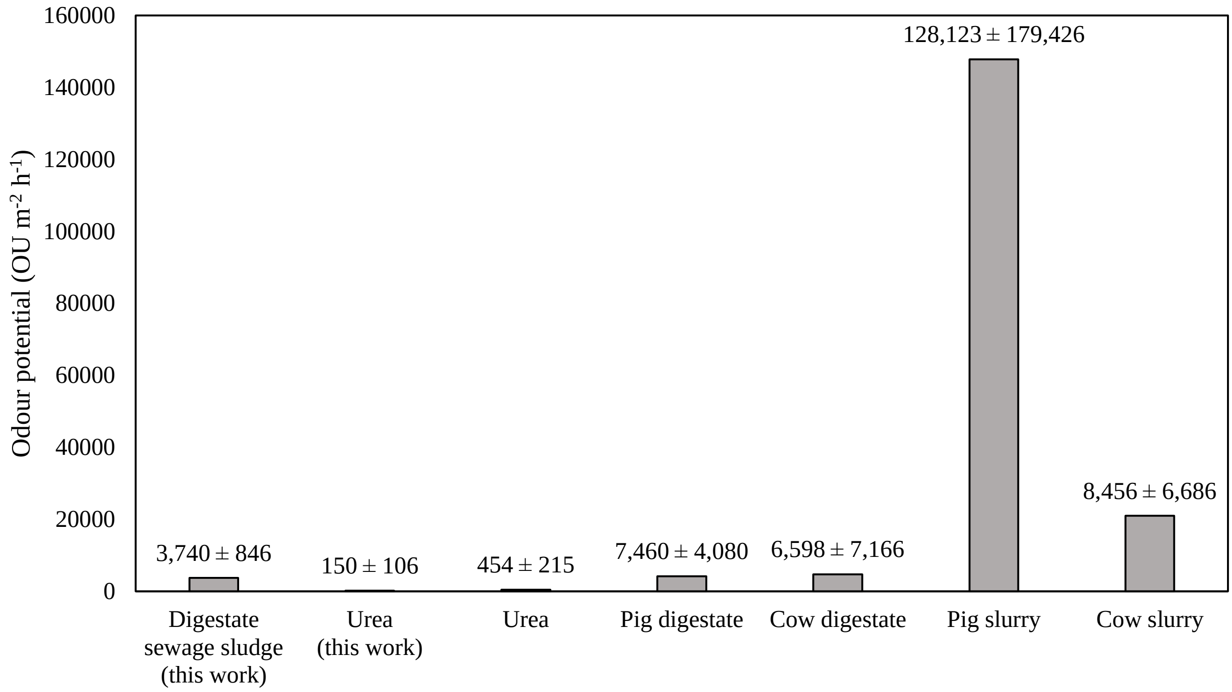
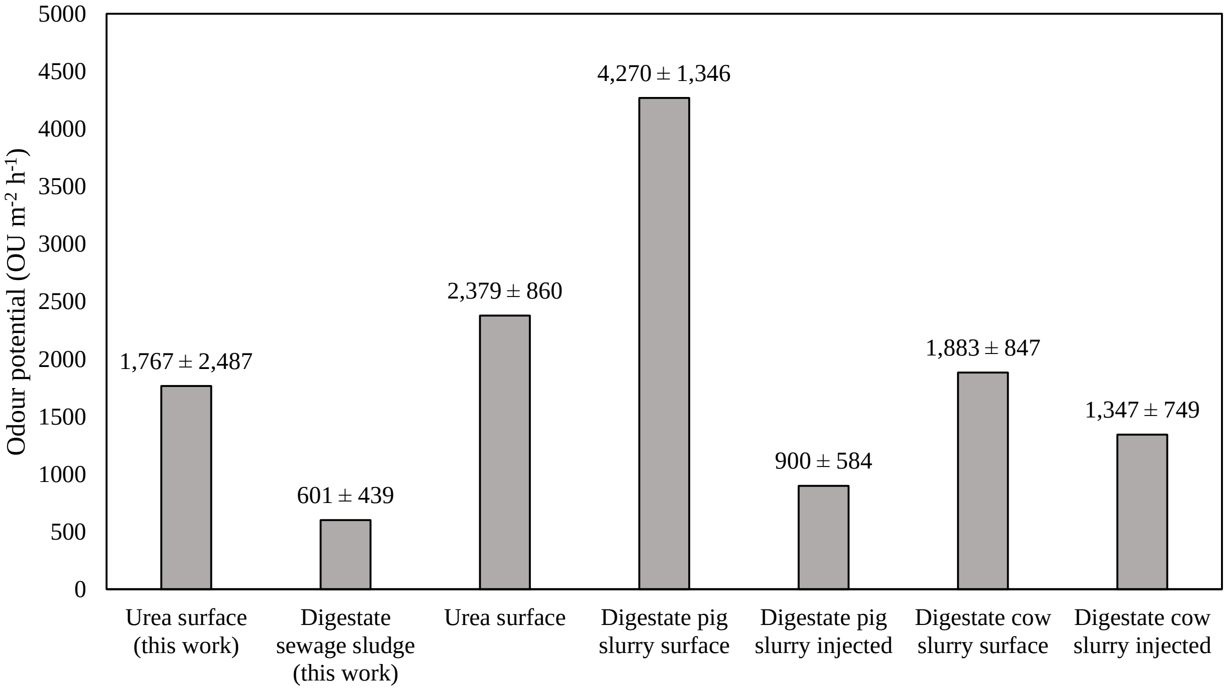

160000
140000
120000
100000
80000
60000
40000
20000
0
Odour potential (OU m-2 h-1)
3,740 ± 846
150 ± 106
454 ± 215
7,460 ± 4,080
6,598 ± 7,166
128,123 ± 179,426
8,456 ± 6,686
Digestate sewage sludge (this work)
Urea (this work)
Urea
Pig digestate
Cow digestate
Pig slurry
Cow slurry

Fig. 3



698

699 Fig 4.

700