Evaluation of ammonia and odours emission from animal slurry and digestate storage in the Po Valley (Italy).

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Abstract

Ammonia and odours emission from one lagoon (Lagoon 1: pig slurry) and three open tanks (Tank 2: cow slurry; Tank 3: digestate from pig slurry and energy crops; Tank 4: digestate from pig and cow slurries plus energy crop) used for slurry storage were seasonally sampled for two years in 2015 – 2017 in four livestock farms that differed for animal breeding (pig or cow) and manure management (anaerobic digestion).

On average, of the two years of observations, the ammonia emission rate (AER) was higher for the Tank 3 (AER of 30.68 ± 28.1 g $N\text{-}NH_3$ m^{-2} d^{-1}) than for Lagoon 1 and Tank 2 and 4, i.e. 9.29 ± 14.89 g$N\text{-}NH_3$ m^{-2} d^{-1}, 9.38 ± 13.75 g $N\text{-}NH_3$ m^{-2} d^{-1}, 15.74 ± 21.91 g $N\text{-}NH_3$ m^{-2} d^{-1}, respectively. PLS regression analysis (R^2 = 0.544; $R^2_{Adj.}$ = 0.484) indicated that temperature was the main predictor of ammonia emitted, followed by the concentration in the slurry of total ammonia and the relative percentage of volatile solids (VS).

On the other hand PLS analysis (R^2 = 0.529, R^2adj. = 0.417) indicated that odour emissions from animal slurry storages depended similarly upon total solids and VS (both referred to fresh weight) slurry contents, TAN/TKN ratio and degrees of biological stability (measured by anaerobic biogas potential – ABP), resulting in the Specific Odours Emission Rates (SOER) of 12,124 ± 7,914 and 35,207 ± 41,706 OUE m^{-2} h^{-1}, 65,430 ± 45,360 and 43,971 ± 53,350 OUE m^{-2} h^{-1}, for Lagoon 1 and Tanks 2, 3 and 4.

Key Word: Ammonia emission; Animal slurries storage; Full scale measurement; Odour emission;

1. Introduction

Livestock production in North America, Europe and Australia is rising because of the increase in demand for livestock commodities (McGilloway, 2005). Intensive farming has been proven to be economically effective but many adverse effects, with particular reference to the handling of livestock wastes, have become evident. In particular, the increase in the quantity of manure produced by the animals has triggered concerns for environmental sustainability in relation to air, surface, ground water and land pollution (Edeogu et al., 2001; McCrory and Hobbs, 2001).

Livestock manure is the most important source of atmospheric NH_3 in Europe. It is estimated that agricultural activities contribute to 80–95% of ammonia emissions across Europe (Hayes et al., 2004). Atmospheric NH_3 readily reacts with atmospheric acids to form ammonium (NH_4^+) which is an important constituent of aerosols causing respiratory diseases and with atmospheric precipitation, acidification and eutrophication of soil and surface waters (Ndegwa et al., 2008). Ammonia is the main precursor for the formation of secondary inorganic particles ($PM_{2.5}$ and PM_{10}) in the atmosphere, which are considered among the most important atmospheric pollutants as regards their potential impact on human health (Carnevale et al., 2010; Erisman and Schaap, 2004).

Environmental regulations are becoming more rigorous concerning ammonia emissions into the atmosphere. In particular, the European Union has recently adopted the new EU directive 2016/2284 concerning the reduction of national emissions of certain atmospheric pollutants, including ammonia, i.e. member states must reduce their annual ammonia emissions progressively from 2020 to 2030.

Italy in particular, should bring its annual ammonia emissions below the permitted threshold of 354.5 $GgNH_3\ y^{-1}$, which is equivalent to a reduction of 10% of the current value (393 $GgNH_3$ for the year 2015). The North of Italy (Po valley) has to make the major effort in ammonia reduction since it contributes greatly to total Italian emissions because this area represents the industrial and agricultural "locomotive" of Italy. In addition the particular geographical conformation of the Po Valley, closed between high mountain ranges on three sides out of four, causes the accumulation of pollutants in the air, especially NO_x, O_3, PM_{10} and $PM_{2.5}$, which in the last decades have always exceeded the limits indicated in the Directive 2008/50/EC.

To counteract this negative phenomenon, the Lombardy Region (North Italy) is implementing a series of measures (DGR 6675/2017; PRIA 2018) aiming for the improvement of the air quality in the area, including ammonia emission reduction in agriculture. National statistics reveal that the agricultural sector in northern Italy contributes to 94% of the total ammonia emitted annually in Italy (year 2017) (ISPRA, 2019). In particular ammonia losses seem to be due, above all, to animal breeding, manure/slurry storage facilities and manure/slurry application to soils (Sommer, 1997). All these are not only responsible for ammonia emissions but they are responsible, also, for annoyance to the inhabitants due to odour production.

Odour is one of the major environmental concerns for the livestock industry. The main sources of odours include building ventilation, manure storage and land spreading. Manure storage represents the major source of complaints and lawsuits. Three major mechanisms control the odour emission from a manure storage facility: i. the chemical-physical characteristics of the state of the manure (e.g. total solid and volatile solids contents, pH, ammonia content, biological stability etc.), ii. the bio-process which the manure has undergone (e.g. aerobic vs. anaerobic digestion) and iii. the state of the air above the manure surface, which controls the process of gases transport (Q. Liu et al., 1995). Often the odours produced are a direct consequence of animal manure decomposed anaerobically to form unstable intermediate by-products, resulting in a complex mixture of over 168 volatile compounds of which 30 are odorous (Hayes et al., 2004). These compounds created from natural biological reactions include organic acids, aldehydes, alcohols, fixed gases, carbonyls, esters, amines, sulphides, mercaptans, aromatics and nitrogen heterocycles (Hayes et al., 2004). Complaints about the nuisance caused by odours from livestock farms have led to the need for alternative manure management and odour control strategies (Edeogu et al., 2001).

Manure/storage ammonia and odour emissions represent an important issue above all in those countries in which storage tank coverage is not obligatory. Unfortunately, there are not many available data with reference to these two types of emissions with particular reference to manure storage. Lab scale data are available but there are very few data from full scale plant studies, although these data are useful to understand the real contribution of manure storage to the total emissions and to propose appropriate counter-measures to reduce emissions.

The goal of this study is to analyse ammonia emissions and odours from uncovered storage tanks/lagoon at full scale to fill in the lack of knowledge, with particular interest to the Po Valley. This work has been financed by the Lombardy Region in search of data to better address practical measures and correct politics for emission reduction.

2. Material and methods

2.1 Experimental design

One lagoon (Lagoon 1) and three open storage tanks (Tank 2, 3 and 4) used for manure storage were seasonally sampled for two years in 2015 – 2017 (Table S1) at four livestock farms located in Lombardy Region (Italy). The farms were chosen for the differences of breeding species (pig or cow) and manure management (untreated manure, anaerobically digested manure post-treated by solid/liquid separation, and anaerobically digested manure post-treated by solid/liquid separation and ammonia stripping) (Table 1).

Table 1. Technical data of farms and storage tanks/lagoon.

FARM	BREEDING CONSISTENCY AND TYPOLOGY	CATTLE FEEDING	MANURE TREATMENT	STORAGE TANK DIMENSION	RETENTION TIME IN STORAGE LAGOON/TANK
1 (Lagoon 1)	700 pigs	Corn mash, bran, soy flour, whey, supplements.	Untreated	Lagoon: Volume: 2400 m^3 Surface 800 m^2	4 months
2 (Tank 2)	350 cows	Soy flour, swiss chard, maize flour, molasses, stable hay, medical hay, ryegrass silage, maize silage, calcium carbonate, magnesium oxide.	Untreated	Tank: Volume: 315 m^3 Surface: 63 m^2	4.5 months
3 (Tank 3)	12,000 pigs	Maize, barley, soybean meal, wheat bran, animal fat, calcium carbonate, monocalcium phosphate, sodium chloride, wheat, sodium bicarbonate.	CSTR mesophilic anaerobic digestors (999 kWe and 42 days HRT) with feed mixture composed by: pig slurry, pollen, corn silage, silage barley, hard wheat flour. Subsequent removal of the solid with helical separator	Tank: Volume: 1980 m^3 Surface: 850 m^2	3 months
4 (Tank 4)	7,400 pigs + 200 cows	Maize, barley, soy, bran, calcium carbonate, monocalcium phosphate, sodium chloride.	Mechanical separation of thick and fine solid fractions. Biological nitrification and denitrification treatment. Anaerobic digestion with biogas recovery.	Tank: Volume: 13750 m^3 Surface: 2750m^2	6 months

2.2 Manure sampling and characterization

During the measurement campaigns of the ammonia and odour emissions from the storage tanks and lagoon, representative samples from each storage tank were taken by using a 500 ml jar with a telescopic bar. At the time of sampling, the air temperature was measured immediately above the surface of the tank or lagoon (about 10 cm above the surface). Samples were chemically characterized and their biological stability was determined. In particular, total solids (TS) and volatile solids (VS) were determined following standard procedures (APHA, 1998). Total N-Kjeldahl (TKN) and total ammonia nitrogen (TAN) were analysed on fresh samples according to the analytical method established for wastewater sludge (APHA, 1998). pHs were determined according to standard procedures (US Department of Agriculture – 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. Biological stability related to long term degradability was performed by measuring the anaerobic biogasification potential test (ABP) according to Orzi et al. (2015) using 0.62 g of dried matter sample, 37.5 ml of inoculum, and 22 ml of deionized water in 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 stored at 37 ± 1 °C for 60 days. The biogas production was determined periodically and expressed as Nl kg TS^{-1}. All analyses were performed in triplicate and data referred to fresh weight (fw) or TS (Orzi et al., 2015).

2.3 Measurement of odour and ammonia emission from manure tanks

From each manure storage facility, the odour and ammonia emissions were collected by positioning over the emitting surface a wind tunnel system (area of 0.1225 m^2). A known neutral air flow (air flow rate of 0.38 $m^3 h^{-1}$) was introduced into the device, simulating the action of wind on the liquid or solid surface (Brattoli et al., 2011). For odour collection and storage, Nalophan bags were connected to the output of the wind tunnel. Air in bags was analysed through dynamic olfactometry within 30 hours of sampling. Inside the wind tunnel, during the fluxing period, ammonia concentration was measured through the exposure of acid coated passive samplers (Tang et al., 2001). All odour measurements and ammonia determinations were performed in triplicate for each storage tank and lagoon.

2.4 Ammonia determination

The exposed filters of acid coated passive samplers were leached with deionized water (3 mL) and then analysed by spectrometric detection (FIAstar 5000 system, FOSS, Denmark) through a gas semi permeable membrane (ISO 11732, 1997), in order to measure the concentration of NH_4-N. The ammonia emission rate (AER) (NH_3 µg m^{2} h^{-1}) was calculated following the equation:

$$AER = NH_3 Q/S$$

Considering the incoming air rate to the air flux (Q) and the surface covered by the wind tunnel (S), see paragraph 2.3.

2.5 Dynamic olfactometry

Olfactometric analyses were carried out in conformity with the standardized EN method n. 13725 (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:

$$SOER = OUQ/S$$

considering the incoming air rate to the air flux (Q) and the surface covered by the wind tunnel (S), see paragraph 2.3. In particular, air velocity was multiplied by the exponent 0.5 for the liquid condition, according to Bliss et al., (1995)(Bliss et al., 1995).

2.6 Statistical analysis

Statistical analyses were conducted using IBM SPSS 25, (IBM Corp. Released 2017. IBM SPSS Statistics for Windows, Version 25.0. Armonk, NY: IBM Corp). To overcome the normality and homogeneity of variance problems the ANOVA analysis and the multiple comparison of means was done with a bootstrap-based procedure (Acutis et al., 2012; Xu et al., 2013). Multiple comparison was done using the Tukey test.

The main predictors of the ammonia emission, of the Lagoon 1 and Tank 2,3, and 4 and the effects corresponding different origin of the slurries contained were determined thanks to partial least square regression (PLS) (Ferreira et al., 2016). PLS is a powerful technique that generalizes and combines features from principal component analysis and multiple regression when the number of predictors is close or bigger than the observations (Abdi, 2003).

3. Results and discussion

3.1 Characterization of the manures

The analytical characterization of the manures (Table 2) was important as these parameters can affect both ammonia and odours emission from tanks/lagoon. On average, the TS was higher for cow manure (Tank 2) (TS of 4.04 ± 2 % fw) because of the presence of straw and residual lignocellulose fractions that were also responsible for the formation of surface crust in the storage tank during the whole period of this study. The TS content was however lower for Tanks (digestates) 3 and 4 (TS of 1.88 ± 0.5 % fw and of 2.55 ± 0.6 % fw, respectively), because of both the biological process degrading TS, and the subsequent solid/liquid separation which digestates underwent as post treatment. Lowest values (TS of 0.99 ± 0.2 % fw) werefound for the pig manure stored in the lagoon (Lagoon 1), in agreement with the literature (Orzi et al., 2018; Sørensen and Amato, 2002).

Table 2. Chemical characterization and biological stability of the manures stored in the tank and lagoon.

Tank/ Lagoon	Sample	pH	TS (% fw)	VS (%)	TKN (g kg^{-1} TS)	TAN (g NH_4^+ kg^{-1} TS)	TAN/TKN (%)	P (g kg^{-1} TS)	K (g kg^{-1} TS)	ABP (Nm^3 mg^{-1} TS)
1	sp I[a]	7.48±0.03c[b]	0.64±0.01b	46.6±0.6b	250±2c	219±1f	88	28.38±1.3d	208±7d	150±7c
1	su I	7.32±0.02b	1.67±0.03e	60.0±0.3e	92.2±2.0a	62.1±1.3a	67	83.4±0.2e	47.2±0.9a	111±1b
1	au I	7.28±0.01b	1.4±0.0d	37.5±1.4a	86.7±0.4a	75.1±1.6b	87	17.33±2.4b	197±2d	21±3a
1	wi I	7.09±0.03a	1.61±0.02e	59.4±1.3e	84.6±6.1a	78.1±3.4b	92	21.65±1.4c	55±0a	230±10e
1	sp II	7.36±0.05bc	0.74±0.02c	52.1±2.7c	214±9.2b	184±5e	86	8.77±2a	193±13d	331±4g
1	su II	7.42±0.01c	0.68±0.02bc	55.7±0.6cd	223±13b	156±5d	70	19.58±2.9bc	132±6b	265±12f
1	au II	7.41±0.04c	0.48±0.03a	48.6±1.1b	260±4c	139±16c	53	20.74±0.6c	166±3c	205±5d
1	wi II	7.05±0.08a	0.68±0.03bc	56.1±0.3d	208±10b	176±17de	85	16.35±0.4b	132±8b	280±3f
1	**Mean**	7.3±0.2	1±0	52±7.6	177±76	136±58	78.5±13.6	27.1±23.4	141±62	199±101
2	sp I	7.03±0.02a	2.75±0.04b	72.1±0.6a	65.9±0.1c	34.2±0.7cd	52	13.3±1c	58.8±1.2d	119±2b
2	su I	7.12±0.02b	3.38±0.08c	80.1±2.1c	75.3±3.1d	35.1±0.1d	47	10±1b	33.3±0.6ab	154±14c
2	au I	7.23±0.01c	3.34±0.02c	74.2±1.6b	61.2±0.4c	32.7±0.4c	53	13.1±1c	55.6±0.9c	105±1a
2	wi I	7.31±0.02d	3.37±0.06c	72.9±2.2ab	66.3±0.4c	32.9±1.0c	50	11.6±1b	63.4±0.6e	108±1a
2	sp II	7.11±0.01b	1.84±0.01a	70.3±1.3a	66.7±0.2c	36.7±1.4d	55	13.5±0.2c	77.3±1.9g	261±3c
2	su II	7.24±0.01c	7.50±0.40e	81.6±1.8c	36.2±1.3a	14.6±1.2a	40	7.9±0.8a	31.5±1.7ab	358±12e
2	au II	7.38±0.02d	3.28±0.08c	70.2±0.9a	72.1±3.2d	26.5±2.7b	37	12.9±1bc	70.5±0.4f	151±10c
2	wi II	7.91±0.02e	6.87±0.11d	82.7±2.0c	42.2±1.4b	35.2±1.3d	83	6.9±0.6a	35.6±0.9b	318±4d
2	**Mean**	7.3±0.3	4±2	75.5±5.1	61±14	30.9±7.3	52±14	11.2±2.6	53.2±16.6	197±101
3	sp I	7.83±0.08c	2.46±0.22d	54.4±1.1bc	123±1a	100±2a	81	18.2±0.7b	149±3a	104±10c
3	su I	7.03±0.02a	1.24±0.04a	47.2±1.3a	253±4e	195±8e	77	22.6±1c	154±4a	45±1.5a
3	au I	7.65±0.03b	1.59±0.06b	46.9±2.5a	184±2c	151±6d	82	20.7±0.6c	176±4a	51±1.3b
3	wi I	7.88±0.02c	2.41±0.03d	56.8±2.2c	168±3b	135±4b	80	13.17±0a	233±6c	97±10c
3	sp II	8.05±0.03d	1.60±0.06b	52.7±0.4b	190±2d	160±1d	84	16.9±0.7b	208±4b	163±12d
3	su II	8.17±0.01e	1.96±0.11c	56.5±1.9c	198±7d	139±6c	70	15.6±0.1b	215±0bc	205±12e
3	**Mean**	7.8±0.4	1.9±0.5	52.4±4.4	186±42	146±31	79±5	17.9±3.4	189±35	111±623
4	wi I	8.82±0.03c	2.05±0.08a	43.1±2.5cd	71.7±4.2c	42.7±3.1cd	60	10.5±0.4c	140±1a	68±7b
4	sp II	8.32±0.01a	2.14±0.02a	44.9±0.5d	80.2±2.8d	37.8±1.2e	92	9.8±0.1bc	181±2b	245±17e
4	su II	8.34±0.03a	2.50±0.08b	42.4±0.3c	67.7±3.4b	49.2±4.3d	73	7.7±0.1a	226±2b	172±16c
4	au II	8.63±0.02b	3.63±0.04c	32.7±1.4a	46.3±1.9a	13.1±1.4a	28	9.7±0.1b	136±1a	43±4a
4	wi II	9.04±0.05d	2.42±0.04b	39.9±0.6b	97±3e	35.2±4.5b	36	10±1c	139±1a	210±5d
4	**Mean**	8.6±0.3	2.5±0.6	40.6±4.8	72.6±18.6	35.6±13.7	57.8±26.3	9.5±1.1	164±39	148±88

[a]wi = winter; sp = spring; su = summer; au = autumn; I = 1st year; II = 2nd year

[b]Values followed by the same letter, in the same tanks, are not statistically different (ANOVA bootstrap and Tukey test, $p<0.05$)

The organic content, expressed as volatile solids (VS) (on average) was high for cow manure (VS of 75.51 ± 5.1 % TS) (Tank 2) because of the presence of straw and carbon residues coming from the polygastric (ruminants) diet. The other tanks/lagoon showed lower VS contents which were similar between them. Tanks 3 and 4 (digestates), indeed, showed reduced volatile solids contents (VS of 52.42 ± 4.4 % TS and of 40.6 ± 4.8 % TS, respectively) because of both the biological process (anaerobic digestion) and the subsequent solid/liquid separation. Finally, Lagoon 1 (pig manure) showed the lowest VS value (52 ± 7.6 % TS) in line with data reported for manure stored in lagoons (Safley and Westerman, 1992).

pH represents an interesting data source as it directly affects ammonia volatilization, with reported high ammonia losses for pHs in the range 7-10 (Ndegwa et al., 2008). pH values (as average) for the four tanks/lagoon studied in this work (Table 3) fell within this range. Above all Tanks (digestates) 3 and 4 showed alkaline pHs, i.e. pH of 7.77±0.4 and 8.63±0.3, respectively.

The concentrations of N (NTK and NH_4-N) contained in the biomasses analysed (average TKN of 177±76 g kg^{-1} TS, 60.7±14 g kg^{-1} TS, 186±42 g kg^{-1} TS and 72.6±18.6 g kg^{-1} TS, for the Lagoon 1, and Tanks 2, 3 and 4, respectively) were always in line with those reported in the past (Akhiar et al., 2017; Orzi et al., 2018; Riva et al., 2016; Tambone et al., 2019) for similar matrices. Looking at the data in detail (Table 2) it will be noted that the NTK and TAN concentrations of each lagoon/tanks showed high variability, with a tendency to their decrease over time because of ammonia volatilization. In addition, measurements made showed that the highest NTK concentrations corresponded to the periods immediately following the addition of new material to the tank/lagoon.

Table 3. Gran mean of emission data and salient values for the ammonia emission (AER) from the manures.

Tank/ Lagoon	AER ($gN\text{-}NH_3\ m^{-2}\ d^{-1}$)	T (°C)	pH	TS (% fw)	VS (%)	TKN ($g\ kg^{-1}$ fw)	TAN ($g\ NH_4^+\ kg^{-1}$ fw)	TAN/TKN (% fw)
1	9.29±14.89a[a]	18±10	7.30±0.15	0.98±0.9	0.52±0.29	91±68	1.13±0.24	78.51±13.61
2	9.38±13.75a	18±10	7.29±0.27	4.04±2.01	3.12±1.77	61±14	1.05±0.22	47.73±6.33
3	30.68±28.1b	20±10	7.97±0.52	2.67±1.81	1.74±1.67	186±43	2.64±0.73	79.14±4.94
4	15.74±21.91a	15±9	8.63±0.81	2.34±0.60	1.04±0.17	73±18	1.00±0.42	57.82±26.25

[a]Values followed by the same letter (AER) are not statistically different (ANOVA bootstrap and Tukey test, $p<0.05$).

3.2 Ammonia emission rate measured from storage tanks

The ammonia emission (AER) was measured once per season over the course of two years (in total 8 measurements per storage lagoon/tank) for all the manure storage facilities monitored (Table 3) (Figure 1). The data obtained (TAN emissions) were in line with those reported in the past (De Bode, 2005; Misselbrook et al., 2016; Sommer, 1997).

Looking at the data in detail (Figure 1) it can be seen that for all tanks and the lagoon monitored, the emission of ammonia (g $N\text{-}NH_3$ m^{-2} d^{-1}) varied with the season, as confirmed by ANOVA analysis (ANOVA bootstrap and Tukey test; $p<0.05$). The season that registered the greatest ammonia emission was the hot season, i.e. summer. Indeed, the PLS regression analysis ($R^2 = 0.544$; $R^2_{Adj.} = 0.484$) applied to the data (Table S2) confirmed that temperature (T) was the main predictor of TAN emitted from tanks (importance of the predictor of 0.45), followed by the TAN concentration in the sample (TAN referred to fw) (importance of predictor of 0.25) and by the percentage of VS in the sample (importance of predictor of 0.12).

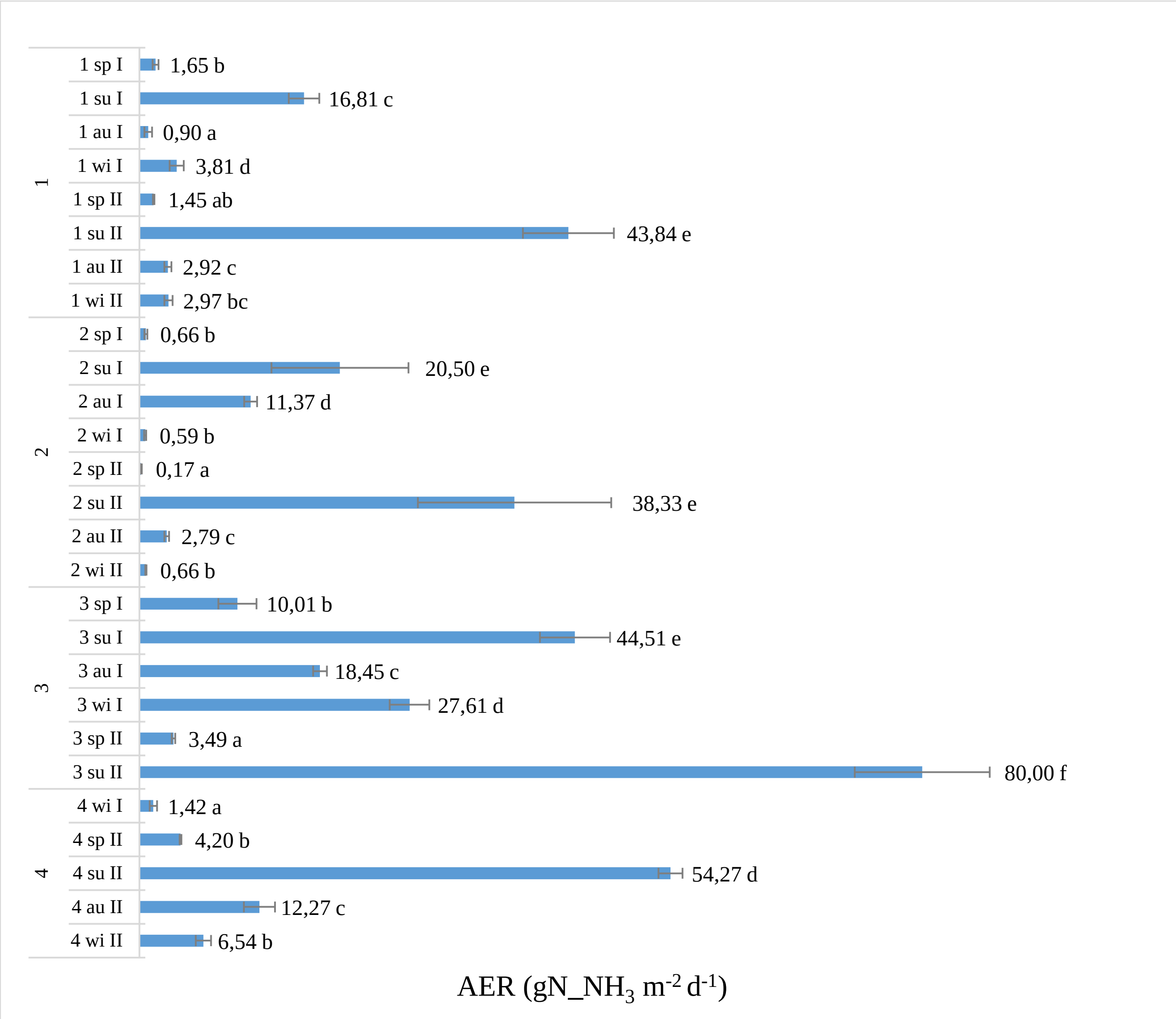

Figure 1. Ammonia Emission Rate (AER) from slurry/digestate storage tanks/lagoon ([a]wi = winter; sp = spring; su = summer; au = autumn; I = 1st year; II = 2nd year). Values followed by the same letter, in the same tanks, are not statistically different (ANOVA bootstrap and Tukey test, $p<0.05$).

The driving force for NH_3 volatilization has been reported to depend upon the difference in the partial pressure of NH_3 between the liquid phase and the atmosphere that depends, mainly, on the NH_4^+ concentration in the slurry, pH and temperature (McCrory and Hobbs, 2001), confirming PLS results (T and TAN). The pH, that is considered of primary importance in determining the quantity of ammonia emitted by a biomass (Webb et al., 2005), was only the fifth predictor, in order of importance (importance of predictor 0.05), affecting TAN emission. This was probably due to the fact that pH remained relatively stable during the year for all tanks (Table 2).

By comparing the TAN emissions during the two years (Grand mean) (Table 3), it can be seen that the Tank 3 emitted a markedly higher amount of NH_3 than the other three storage tanks/lagoon (i.e. AER of 30.68 ± 28.1 g N-NH_3 m^{-2} d^{-1} emitted from Tank 3, to be compared with AER of 15.74 ± 21.91 g N-NH_3 m^{-2} d^{-1}, of 9.38 ± 13.75 g N-NH_3 m^{-2} d^{-1} and of 9.29 ± 14.89 gN-NH_3 m^{-2} d^{-1} emitted from Tank 4 and 2, and Lagoon 1, respectively). The ANOVA analysis (ANOVA bootstrap, $p < 0.05$, Tukey test) confirmed the difference between the amount of ammonia emitted, on average, from the Tank 3 and the other storage facilities, while no significant differences were found between the amounts of ammonia released by the other three tanks/lagoon (Lagoon 1 and, Tanks 2 and 4), despite the different origin of the slurries which they contained.

From Table 3 it can be seen that Tank 3 showed both higher average temperature (20 ± 10 °C) and, NTK and TAN (NTK of 2.64 ± 0.73 g kg^{-1} fw and TAN of 186 ± 43 g kg^{-1} fw, respectively) than those measured for the other three tanks/lagoon, confirming the importance of these parameters in regulating ammonia emissions as indicated, also, by the PLS analysis.

3.3. A tentative in quantifying total ammonia emission from storage tank/lagoon.

Taking into consideration ammonia emitted from storage tanks/lagoon (g N-NH_3 m^{-2} d^{-1}) and total surface area, we calculated the total annual amount of ammonia emitted from the three tanks and lagoon monitored (Table 4). These data represent a rough, but in our opinion useful, estimate of average annual emission. In fact although the data suffer from high standard deviations, these were due to the variability of ammonia emission due to the variability of both atmospheric conditions and slurry composition that occurred during the year, giving approximate but real data.

Results reported in Table 4 reflected specific emissions previously discussed. On the other hand, to rank the contribution of manure/slurry storage to total ammonia emissions, it was interesting to compare these data with those coming from manure/slurry spreading onto the soil, since in this case ammonia emissions are much more studied and well known (Chantigny et al., 2009; Nicholson et al., 2017; Riva et al., 2016). We considered what would be the effect of spreading onto soil of slurries/digestates stored in tanks or in the lagoon studied during the year, assuming the specific ammonia emission rate typical for each slurry (e.g. cow, and pig slurry, and liquid fractions of digestate), as reported in the literature (Table 4).

Table 4. Estimated comparison of ammonia emissions per year in the two different cases hypothesised: slurry/digestate storage Vs. slurry/digestate spreading onto soil (N dosed = 150 – 180 kgN ha^{-1}).

Tank/ Lagoon	**AER ($gN\text{-}NH_3\ m^{-2}\ d^{-1}$)**	**NH_3 emission per year from the tank/lagoon ($tN\text{-}NH_3\ y^{-1}$)**	**NH_3 emission per year in case of manure spreading ($tN\text{-}NH_3\ y^{-1}$)**	**[a]Reference**
1	9.29±14.89a[b]	3.14	2.86	Chantigny *et al.* 2009
2	9.38±13.75a	0.22	0.32	Nicholson *et al.* 2017
3	30.68±28.1b	13.80	9.83	Riva *et al.* 2016
4	15.74±21.91a	21.50	12.94	Riva *et al*. 2016

[a]Literature reference reporting the ammonia emission rate considered to calculate total ammonia emission during manure spreading.

[b]Values followed by the same letter, in the same tanks, are not statistically different (ANOVA bootstrap and Tukey test, $p<0.05$).

Results indicated (Table 4) that there were no differences for the untreated biomasses (not digested) between the ammonia released into the atmosphere during untreated slurries storage and soil spreading, i.e. 3.14 vs 2.86 tN-NH_3 y^{-1} for Lagoon 1 and 0.22 vs 0.32 tN-NH_3 y^{-1} for Tank 2, in agreement with previous Italian data (ISPRA, 2019). On the other hand, anaerobic digestion and the subsequent solid/liquid separation (Tanks 3 and 4) seemed to double the ammonia emissions from tanks compared to those emitted in the case of spreading of digestate in open fields (13.8 vs 9.83 tN-NH_3 y^{-1} for Tank 2 and 21.5 vs 12.94 tN-NH_3 y^{-1} for Tank 3), which makes these biomasses particularly polluting if kept for a long time in uncovered tanks.

3.4 Specific odour emission rates measured from storage tanks

Odours from livestock slurries are due to a complex mixture of volatile compounds arising from anaerobic degradation of plant fibers and protein (McCrory and Hobbs, 2001). Some of these compounds are sulphur compounds, organic acids, phenolic compounds and indoles. Among these, some may even be hazardous to human health, such as (di)hydrogen sulphide (H_2S), which is lethal at high concentrations (Sommer and Feilberg, 2013).

The odorous emissions (SOER) were monitored on a seasonal basis, as well as reported for ammonia sampling, for all four tanks under analysis (Figure 2).

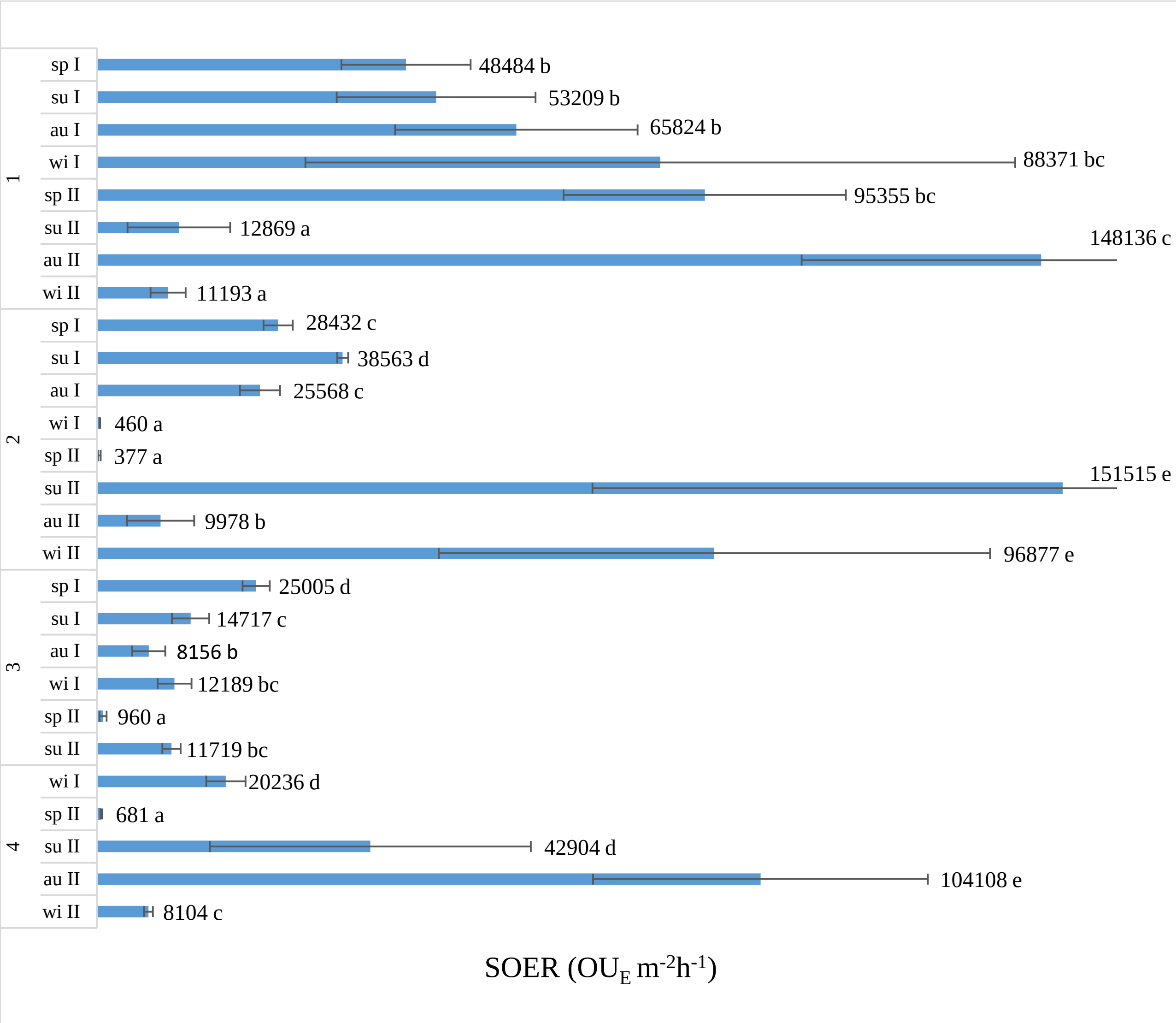

Figure 2. Odour emission (SOER) from slurry/digestate storage tanks/lagoon ([a]wi = winter; sp = spring; su = summer; au = autumn; I = 1st year; II = 2nd year). Values followed by the same letter, in the same tanks, are not statistically different (ANOVA bootstrap and Tukey test, $p<0.05$).

As shown in the graph in Figure 2, the values of odorous emissions were very variable over time and the data showed, as expected, a high standard deviation. This was probably due to the high number of factors that influenced this type of emissions, i.e. environmental factors (temperature and air movements), storage (shape of the tank/lagoon, agitation of the matrix, formation of crusts), treatment (solid/liquid separation, anaerobic digestion) and biomass composition (chemical and biological composition, feeding of the animals) (Edeogu et al., 2001; Hayes et al., 2004; Q. Liu et al., 1995; Sommer and Feilberg, 2013).

The high variability of the levels of odour emissions made it impossible to determine a period of the year during which biomasses are particularly subject to odours emission. However, observing the grand means for each of the storage tanks/lagoon (Table 5), it was possible to note that the Lagoon 1 and Tank 2 showed average odour emissions (SOER of 65,430 ± 45,360 and of 43,971 ± 53,350 OUE m^{-2} h^{-1}, respectively) higher than those measured for Tanks 3 and 4 (SOER of 12,124 ± 7,914 and of 35,207 ± 41,706 OUE m^{-2} h^{-1}, respectively).

Table 5. Gran mean of emission data and salient values for the odour emission (SOER) from the manures.

Tank /Lagoon	SOER (OU_E $m^{-2}h^{-1}$)	TS (% fw[a])	VS (%)	TAN/TKN (% raw)	ABP (Nm^3 mg^{-1} TS)	TAN (gNH_4^+ kg^{-1} fw)	T (°C)	pH	TKN (g kg^{-1} fw)
1	65,430±45,360	0.98±0.9	0.52±0.29	78.51±13.61	199±101	1.13±0.24	18±10	7.30±0.15	91±68
2	43,971±53,350	4.04±2.01	3.12±1.77	47.73±6.33	197±101	1.05±0.22	18±10	7.29±0.27	61±14
3	12,124±7,914	2.67±1.81	1.74±1.67	79.14±4.94	122±74	2.64±0.73	20±10	7.97±0.52	186±43
4	35,207±41,706	2.34±0.61	1.04±0.17	57.82±26.25	148±88	1.00±0.42	15±9	8.63±0.81	73±18

[a]fw = fresh weight

The variables most implicated in determining the levels of odorous emissions from the biomasses were isolated by PLS analysis (R^2 = 0.529, R^2adj. = 0.417) which showed that TS, VS (referred to fresh weight), TAN/TKN and ABP all affected similarly (importance of the predictor in the range 0.18-0.21) (Table S3) the odorous emissions (Table 5). TS and VS affected odour emissions as they represent quantitative data of the total amount of substrate available for microorganisms that degrade organic matter under anaerobic conditions to produce odours (Orzi et al., 2010). The TAN/TKN ratio affected total odour because a high ratio indicates the high presence of N under ammonia forms instead of the organic forms, since ammonia is a gas characterized by a pungent odour that greatly contributes to odours emitted by a matrix (Sommer and Feilberg, 2013). The anaerobic biogasification potential (ABP), contrarily to the TS and VS, represents qualitative data of the organic matter (or VS) contained in a slurry. This variable is a direct measurement of the biological stability of the organic matter and so of its degradability, from which depends the potential of a biomass to produce volatile organic compounds under anaerobic conditions, contributing to biomass odours (Orzi et al., 2010). In particular, the Lagoon 1 and Tank 2 which contained the most odorous matrices (Table 5), showed higher ABP values (ABP of 199 ± 101 and of 197 ± 101 Nm_3 Mg^{-1}TS, respectively) than those reported for tanks 3 and 4 (ABP of 122 ± 74 and of 148 ± 88 Nm_3 Mg^{-1} TS, respectively) that contained digested slurries. This observation agreed with what was previously observed by Orzi and colleagues who identified the ABP index as one of the main indicators of the potential of odours emission from an organic matrix (Orzi et al., 2010). Moreover, these results confirmed the ability of anaerobic digestion to reduce the potential odour emissions of a biomass (Orzi et al., 2015).

TAN, pH and T, similarly, also affected odour emissions (Table 5) although much less than the previous parameters discussed, as, also, indicated by the “importance of the predictor” detected performing PLS, which were much lower than the others (Table 5). These parameters probably affected total odours emission because they directly (TAN referred to the fresh weight) and indirectly (T and pH) influenced the presence of free ammonia.

In any case despite the strong variability of the detected odorous emissions (Figure 2), the intensity of the odours (SOER) was generally very high and in the range of data previously reported for similar organic matrices (Orzi et al., 2018, 2015), underlying the potential impact of these matrices when stored and subsequently used for direct soil applications.

4. Conclusion

In this paper data on ammonia and odours emission have been provided at full scale. Results obtained indicated that the slurry type affects ammonia emission (pig vs. cow slurry) as well as biological/mechanical treatment (anaerobic digestion plus S/L separation vs. untreated slurry). In particular, the liquid fraction of digestate, because of its high ammonia content, showed much higher ammonia emissions that untreated slurries. This fact led, also, to the contribution of storage to ammonia emissions being much higher than those due, potentially, to the subsequent spreading of slurry, suggesting that the covering of tanks/lagoons containing digestate should be a priority in reducing ammonia emissions, as well as digestate injection (Ndegwa et al., 2008; Orzi et al., 2018; Riva et al., 2016; Webb et al., 2005).

On the other hand, digested slurries, because of the biological process to which they have been subjected led to the acquirement of a high degree of biological stability, reducing greatly the odours emitted.

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Notes

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