



AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation

This is the author's manuscript Original Citation: Availability: This version is available http://hdl.handle.net/2318/100259 since 2015-09-11T12:46:03Z Published version: DOI:10.1016/j.atmosenv.2007.12.022 Terms of use: Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



UNIVERSITÀ DEGLI STUDI DI TORINO

1 2

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. 3 It is posted here by agreement between Elsevier and the University of Turin. 4 Changes resulting from the publishing process - such as editing, corrections, 5 structural formatting, and other quality control mechanisms - may not be reflected 6 in this version of the text. The definitive version of the text was subsequently 7 published in Atmospheric Environment, Volume 42, Issue 10, March 2008, Pages 8 2448-2459, DOI: 10.1016/j.atmosenv.2007.12.022. 9 10 You may download, copy and otherwise use the AAM for non-commercial purposes 11 provided that your license is limited by the following restrictions: 12 13

(1) You may use this AAM for non-commercial purposes only under the terms ofthe CC-BY-NC-ND license.

(2) The integrity of the work and identification of the author, copyright owner, and
 publisher must be preserved in any copy.

(3) You must attribute this AAM in the following format: Creative Commons BY NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en), doi:
 10.1016/j.atmosenv.2007.12.022

- 21
- 22

Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation

26

27	E. Dinuccio ^{a,} *,	, W. Berg ^b , P. Balsari
----	------------------------------	-------------------------------------

28

^a Department of Agriculture, Forestry, Environmental Engineering and Land Based Economics
 (DEIAFA) Mechanics Section - Turin University via Leonardo da Vinci 44, 10095 Grugliasco (TO)
 Italy.
 ^b Institute of Agricultural Engineering Bornim (ATB), Max-Eyth-Allee 100, D-14469 Potsdam,
 Germany.

³⁴ *Corresponding author. Tel. +39 0116708844; Fax: +39 0116708591; E-mail address:

35 elio.dinuccio@unito.it

36

37

Abstract

A laboratory scale study was set up to investigate the ammonia (NH_3), nitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4) emissions during storage of untreated pig and cattle slurry and the fractions (solid and liquid) obtained by mechanical separation. The solid and liquid fractions were obtained from the same untreated slurry by means of a lab scale mechanical separator.

The manures were stored for a period of 30 days in open vessels (1500 cm³ capacity) in two temperature controlled rooms which were kept at 5 ± 0.5 °C and 25 ± 0.2 °C. Gaseous emissions were determined using a dynamic chamber method and Infrared Photoacoustic Detection (IPD).

Over the storage period, gaseous emissions from pig manures were significantly (P<0.05) higher than those from cattle manures. N₂O fluxes of up to 232 mg m⁻² h⁻¹ were measured but from pig solid fraction only. Between 40.8% (from pig liquid fraction stored at 25 °C) and 3.60% (from untreated cattle slurry stored at 25 °C) of the initial nitrogen content of the manures was lost as

NH₃. Over the 30-days storage period, the predominant emission of carbon was in the CO₂ form. 49 Total C-CH₄ losses expressed as a percent of the carbon initially present in the volatile solids (C-50 VS) ranged from 0.60% to 12.8% for pig manures and from 0.23% to 1.56% for cattle manures. The 51 mechanical separation of cattle slurry increased by up to 30% the emissions of CO₂ equivalents to 52 the atmosphere during the storage of the separated fractions if compared with the slurries. Results 53 indicated that NH₃, N₂O, CO₂ and CH₄ emissions were affected by the interaction between a 54 number of variables, including storage temperature, chemical characteristics and type of manure. 55 Results also indicated that mechanical separation does not reduce emissions but has the potential to 56 increase the emissions of CO₂ equivalents to the atmosphere during the storage of the separated 57 fractions. 58

59

60 Keywords: ammonia, greenhouse gas emissions, manure storage, slurry separation.

- 61
- 62
- 63

1. Introduction

64	Animal excreta can contribute to eutrophication of groundwater and surface waters as a result of
65	nitrogen (N) and phosphorous (P) enrichment (EEA, 2005) and are considered an important source
66	of ammonia (NH ₃), nitrous oxide (N ₂ O), carbon dioxide (CO ₂) and methane (CH ₄) production (Van
67	Der Hoek, 1998; Amon et al., 2001). While N ₂ O, CO ₂ , and CH ₄ are greenhouse gases affecting the
68	global environment and climate change, NH ₃ contributes to eutrophication and acidification of soils
69	and also indirectly contributes to N_2O emissions by increasing the N-cycling in natural ecosystems
70	(Olesen, 2005). Modern intensive animal production methods have increased the volume of manure
71	in the slurry form (Menzi et al., 2002). Several techniques have been developed to manage livestock
72	slurries as cheaply and conveniently as possible and to reduce potential risks of environmental
73	pollution. Among these techniques, solid-liquid separation is a technology that separates slurry into
74	a larger liquid fraction and a minor solid fraction which has a greater concentration of nutrients than

75	the liquid (Kroodsma, 1986; Møller et al., 2000). This could enable more cost-effective transfer of
76	nutrients from areas of high livestock density where they may be in surplus to areas with a lower
77	livestock density. Nevertheless, little data concerning NH ₃ , N ₂ O, CH ₄ and CO ₂ emissions during
78	storage of both liquid and solid fractions are currently available.
79	In consequence a laboratory-scale trial was carried out to better characterize the main parameters
80	affecting NH ₃ and GHG emissions from the storage of untreated liquid manure and both the solid
81	and liquid fractions derived from mechanical separation of slurry. The following aspects have been
82	analyzed:
83	1) the NH_3 , CO_2 , CH_4 and N_2O emissions from the storage of:
84	A. cattle and pig untreated liquid manure
85	B. solid fractions obtained from both untreated liquid manure after solid-liquid
86	separation
87	C. liquid fractions obtained from both untreated liquid manure after solid-liquid
88	separation
89	2) the effects of temperature and chemical characteristics of the three products listed in point 1)
90	on such emissions.
90 91	on such emissions.
	on such emissions. 2. Materials and methods
91	
91 92	2. Materials and methods
91 92 93	2. Materials and methods The trials were carried out at Leibniz-Institute for Agricultural Engineering Potsdam-Bornim
91 92 93 94	2. Materials and methods The trials were carried out at Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB), Germany, in environmentally controlled conditions by means of two climatic rooms.
91 92 93 94 95	 2. Materials and methods The trials were carried out at Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB), Germany, in environmentally controlled conditions by means of two climatic rooms. Fresh slurry was collected from commercial farms. The next day (cattle; pig two days after) it was
91 92 93 94 95 96	2. Materials and methods The trials were carried out at Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB), Germany, in environmentally controlled conditions by means of two climatic rooms. Fresh slurry was collected from commercial farms. The next day (cattle; pig two days after) it was separated and stored in vessels in the emission lab of the institute and measurements began.
91 92 93 94 95 96 97	2. Materials and methods The trials were carried out at Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB), Germany, in environmentally controlled conditions by means of two climatic rooms. Fresh slurry was collected from commercial farms. The next day (cattle; pig two days after) it was separated and stored in vessels in the emission lab of the institute and measurements began. The solid and liquid fractions (B and C) were obtained from the same pig and cattle untreated slurry

A press zone was created fitting the blade to the disc by means of a horizontal bar and a spring. 101 After filling the bowl with the untreated slurry, the blade is manually rotated using the crank and 102 the slurry separated in the press zone. The liquid fraction runs through the disc's holes into the 103 container while the solid fraction remains in the bowl and is collected afterwards. The total input of 104 each untreated slurry (100 kg), as well as the amounts of solid (18.1 kg for cattle and 7.80 kg for 105 pig) and liquid (81.9 kg for cattle and 92.2 kg for pig) recovered, were weighed and recorded. The 106 bulk density of the solid fractions (cattle and pig) was estimated to be 0.40 tm^{-3} . 107 Immediately after mechanical separation, samples of 1000 cm³ of each of the investigated materials 108

were stored for a period of 30 days in open vessels (1500 cm^3 capacity, 0.20 m height, 0.10 m base diameter and 0.095 m top diameter) in two temperature-controlled rooms which were kept at 5±0.5 and 25 ± 0.2 °C. During the test period observations of crust formation and reduction of volume were carried out. Four replicates of each product were tested so that for each type of untreated liquid manure (pig or cattle) a total of 12 vessels were used per climate room.

The samples were analysed for pH, total solids (TS), volatile solids (VS), total Kjeldhal nitrogen (TKN), total ammoniacal nitrogen (TAN), and organic acids at the beginning and at the end of the investigation period. Initial and final slurry analyses are given in Table 1.

117

118 Flux measurements were carried out using infrared photoacoustic detection (IPD) and the dynamic chamber method described by Berg et al. (2006). This method allows the comparison of the effect 119 of different treatments on gaseous emissions during manure storage, under standardized 120 121 experimental conditions. Different conditions, such as volume to surface ratio of the manure stores, in the lab and on farms may yield different gas fluxes. Therefore, this fluxes cannot be used for 122 123 calculating fluxes from on farm storage facilities without further validation. Accordingly, the slurries were stored in open vessels using the dynamic chamber method set up only during 124 measurements. Before starting the measurements each vessel was closed with an air-tight lid 125 provided with two ports for air inlet and outlet (Fig. 2). Air inlet port was connected in an airtight 126

127 way with a flow meter and a compressor. The headspace (chamber) between the slurry surface and

128 the lid was then ventilated with compressed air to create an airflow through the dynamic chamber.

129 The air exchange inside the chambers was adjusted by the flow meters so that the air in the

headspace was always changed once per minute. Measurements were carried out four times a weekaccording to the following scheme:

132 1) lid closure at time t = 0 min;

2) between t=0 and t= 20 min the chamber was only ventilated to achieve steady conditions inside
the chamber;

135 3) t= 20 min beginning of the exhaust air sampling;

136 4) t= 36 min end of the exhaust air sampling and vessel opening.

The gas concentrations in the inlet (atmospheric) and outlet (exhaust) air were analyzed by the 137 INNOVA system 1312 Photoacoustic Multi-gas Monitor and Multipoint Sampler. The system 138 139 provided a real time analysis of 4 gases (NH₃, N₂O, CH₄ and CO₂) plus water vapour. Measured data were related to standard conditions (25 °C and 100 kPa) and stored in a database. Exhaust air 140 leaving each chamber was sampled for 16 min. The instrument needed 2 min to analyze one sample, 141 thus, 8 values were recorded on each measurement occasion. The first 3 values were discarded and 142 the mean of the remaining 5 recorded values was considered representative for the measurement. 143 Gas fluxes F_i in mg m⁻² h⁻¹ were determined according to: 144

145
$$F_j = Q \frac{\left(C_{ex,j} - C_{in,j}\right)}{A} \tag{1}$$

where $C_{in.j}$ is the NH₃, N₂O, CH₄ or CO₂ concentration of air inlet the chamber in mg m⁻³; $C_{ex.j}$ is the NH₃, N₂O, CH₄ or CO₂ concentration of air outlet the chamber in mg m⁻³; Q is the air flow rate through the chamber in m³ h⁻¹; A is the area of emitting surface covered by the chamber in m². Time evolution of the gas fluxes were approximated by spline approximation functions, and by integration of such approximations using adaptive Simpson quadrature formulas (Bronshtein et al., 151 2003) cumulative losses φ_j in mg vessel⁻¹ of each gas over the storage period (30 days) were 152 estimated.

Since measurements were carried out with 1000 cm³ of all substrates respectively, in order to assess
 the effect of mechanical separation on gaseous emissions, cumulative losses were corrected as
 follows:

$$\Phi_i = \varphi_i \ \rho \tag{2}$$

where Φ_j is the corrected cumulative loss of a specified gas in mg vessel⁻¹; ρ is a correction factor that takes into account the mass *Sc* (kg) of separated liquid and solid fractions obtained after separation of the untreated slurry *Mc* (kg), and the amount *Me* (kg) of untreated slurry, liquid and solid fractions used for emission trials:

161
$$\rho = \frac{Sc}{Mc} \frac{1}{Me}$$
(3)

162 The ρ values used are summarized in Table 1.

During storage trials, volume and surface area in contact with the air were the same for all tested 163 materials. Nevertheless, in practical conditions slurries are stored within tanks and solid fraction in 164 heaps on platforms. The slurry NH₃ emitting area is the horizontal cross section of the storage tank, 165 while for solid material it may be considered the surface area of a hypothetical frustum of cone 166 representing the shape of the heap. Considering an angle of repose of $1^{1}/_{2}$: 1 (horizontal : vertical) 167 (CNMP, 2002), the surface/volume ratio for the pig solid fraction was calculated to be 1.83 times as 168 much as pig slurry and 2.44 times as much as cattle untreated slurry for the cattle solid fraction. 169 Thus, to be able to assess the effect of mechanical separation on NH₃ emissions, measured NH₃ 170 emissions from pig solid fraction and cattle solid fraction were therefore multiplied by 1.83 and by 171 2.44 respectively, assuming that the emissions per unit area were homogeneous. The emitting 172 surface area of the liquid fraction was assumed to be that of the untreated slurry. 173

To consider the effect of slurry mechanical separation on GHG emissions as a whole, the lC_jl were converted into CO₂ equivalents by the Global Warming Potential (GWP) of the gases (NH₃: 3.1, N₂O: 310, CH₄: 21) (IPCC, 1997).

177

Significant differences in results and all possible interactions were investigated using the ANOVA procedure. Before analysis some of the parameters were log-transformed in order to fit a normal distribution. For all the statistics, a significant level of P = 0.05 was applied. Assumption of equal variance of different groups was tested using Bartlett's test. All statistical analyses were performed with SPSS 12.0 for Windows.

183

184 **3. Results**

185 3.1 Slurry properties

186 After mechanical separation the liquid fractions produced by mechanical separation showed significant reductions of TS and VS (Table 1). In contrast, the pH, TAN and TKN concentrations of 187 the liquid fractions were very similar to those of the untreated slurries. As expected, the TS and VS 188 content of the solid fractions were significantly greater than those for the untreated slurries. The 189 TKN content of the pig solid fraction was almost double the TKN content of the pig untreated 190 191 slurry, while the TKN content of the cattle solid fraction was approximately 1.4 times lower than the TKN content of the cattle untreated slurry. 192 Analysis of the manures at the end of each experiment are given in Table 2 together with volume 193 194 reductions over the storage period.

195 Water evaporation occurred in all the samples throughout the storage period. As expected,

evaporation was higher from materials stored at 25 °C than 5 °C and was responsible for volume

reductions up to 45% of the stored slurries and of the relative increase of TS and VS amounts.

198 Appreciable volume reduction (30.6%) occurred for cattle solid fraction stored at 25 °C, low

reductions were observed for solid materials stored at 5 °C while no volume reduction occurred for
pig solid fraction stored at 25 °C.

201

202 3.2 Gaseous emissions

 $3.2.1 N_2O$ emissions

Over the storage period (30 days), no N₂O fluxes were measured from any material stored at 5 °C. 204 N₂O emissions from cattle and pig slurries stored at 25 °C occurred on a very few occasions only, 205 e.g. when the crust dried up, but the overall amounts were negligible. Very low concentrations, 206 sometimes slightly above the background concentration of N₂O, were also measured from the cattle 207 solid fraction. Appreciable N₂O fluxes were measured only from the pig solid fraction stored at 208 25 °C (Fig. 3). N₂O emissions started 8 days after the beginning of the storage period and reached a 209 peak of 232 mg m⁻² h⁻¹ at day 21. After that peak, the N₂O flux rapidly decreased to reach values 210 211 close to zero at day 25. The total nitrogen loss via the N₂O pathway accounted for the 4.71% of the initial total Kjeldahl nitrogen (TKN) content of the solid manure (Table 3). 212

213

214 3.2.2 NH₃ emissions

Total losses of NH₃-N, expressed as a percentage of the initial TKN, (Table 3) ranged from 3.60% 215 (from untreated cattle slurry stored at 25 °C) to 40.8% (from pig liquid fraction stored at 25 °C). 216 Under the same storage conditions, there were no significant (P>0.05) differences between NH₃ 217 fluxes from untreated pig slurry and from its liquid fraction (Fig. 4). In contrast, NH₃ fluxes from 218 untreated cattle slurry were significantly less than from its liquid fraction. NH₃ emissions were 219 higher at 25 °C than at 5 °C storage conditions, except when considering the pig solid fraction. 220 From this, significantly (P<0.05) higher NH₃ fluxes at 25 °C than at 5 °C were measured only at the 221 beginning of the storage period, while, after day 8 NH₃ fluxes were significantly lower at 25 °C 222 than at 5 °C storage conditions. 223

$3.2.3 \text{ CO}_2$ and CH_4 emissions

During pig and cattle manure storage, the predominant emission of carbon was as CO_2 (Fig. 5 and Table 3). Total losses of C-CO₂ expressed as a percentage of the carbon initially present in the volatile solids (C-VS) of the manures ranged from 7.76% (from cattle untreated slurry stored at 5 °C) to 33.4% (from pig liquid fraction stored at 25 °C). CO₂ losses were always higher at 25 °C and lower at 5 °C storage conditions.

Under the same storage conditions, CH₄ fluxes from the untreated slurries and from their liquid 231 fractions were not different (P>0.05) (Fig. 6), but total C-CH₄ losses over the storage period, 232 expressed as a fraction of initial C-VS content, were significantly (P<0.05) higher from liquid 233 234 fractions than from untreated slurries (Table 3). Under all storage conditions, total C-CH₄ losses were higher from pig than from cattle slurries. C-CH₄ losses ranged from 0.60% to 12.8% for pig 235 manures and from 0.23% to 2.19% of the initial C-VS content for cattle manures. C-CH₄ losses 236 237 from pig manures were always consistently higher at 25 °C than those at 5 °C. However, the emissions of CH₄ were only observed to be significantly (P<0.05) higher from cattle slurries stored 238 at 25 °C than at 5 °C during the first 3 days of storage. Thereafter, the emissions were lower from 239 cattle slurries stored at 25 °C than at 5 °C. C-CH₄ losses from cattle and pig solid fractions were 240 always significantly lower at 25 °C than at 5 °C storage. 241

242

243 3.2.4 Effect of slurry solid-liquid separation on gaseous emissions

Figure 7 shows the NH₃, CO₂ and CH₄ losses based on the corrected cumulative losses lC_jl and expressed as a percentage of the lC_jl calculated for the untreated slurries (pig and cattle). It can be seen that for pig slurry the combined emissions measured from the storage of the liquid and solid fractions resulted in reduced NH₃ losses compared to the storage of the untreated pig slurry. However for cattle slurry, the combined NH₃ losses measured from the storage of the liquid and solid fractions were 7% and 45% higher than those measured from the untreated cattle slurry stored at 25 C and 5 °C respectively.

The emissions from the storage of the two fractions increased the CO_2 emissions from 8% (when compared to untreated pig slurry stored at 5 °C) to 104% (when compared to untreated cattle slurry stored at 25 °C). During the storage of both liquid and solid fractions, CH₄ losses were 3% higher for pig untreated slurry stored at 25 °C and 4% higher for cattle untreated slurry stored at 5 °C. Instead, solid-liquid separation reduced CH₄ emissions by 8% for pig untreated slurry stored at 5 °C and by 9% for cattle untreated slurry stored at 25 °C. Combining the emissions of CO₂ equivalents from both liquid and solid fractions (Fig. 8), they

resulted in increased greenhouse gases emissions compared to the storage of the untreated slurries, except when considering the pig untreated slurry stored at 5 °C. In this latter case the mechanical separation had no effect in combined emissions of CO_2 equivalents.

261

262 **4. Discussion**

The small N₂O fluxes from cattle and pig slurries storage can be explained by the absence of crust 263 during most of the storage period. N₂O may be emitted during storage of manure either as a by-264 product of incomplete ammonium oxidation or as a by-product of incomplete denitrification 265 (Oenema et al., 2001). The condition in liquid manure is strictly anaerobic, and neither process 266 occurs. In contrast, authors (e.g. Sommer et al., 2000; Berg et al., 2006) found N₂O production from 267 268 stored slurries, but only when a dry crust formed on the surface. These emissions occurred since surface crust may contain a mosaic of anaerobic and aerobic micro-sites which are favourable for 269 N₂O production. Dry conditions, together with air filled porosity, may explain the occurrence of 270 271 N₂O production from pig solid fraction samples. On the other hand, separation of cattle slurry produced a fibrous solid fraction with a compacted structure, this might have created an 272 environment with an oxygen concentration unsuitable for N₂O production. 273 Results confirm a positive relationship between ammonia emission and temperature found by other 274 studies (e.g. Ni, 1999; Dewes, 1996), but not in the case of the pig solid fraction. Total losses from 275

the pig solid fraction were 7.12 and 5.57% of the initial TKN content at 5 and at 25 $^{\circ}$ C storage

277 conditions respectively. This may be explained by ammonium oxidation by nitrifying micro-

organisms with N_2O production. NH_3 emission from manure decreased, therefore, as a greater proportion of the NH_4 -N was oxidized by nitrifying micro-organisms.

CH₄ losses from pig slurries significantly increased with temperature (Table 3). This is confirmed 280 by results of other studies (e.g. Husted, 1994), in which an increase of the CH₄ production with air 281 storage temperature was also found. The lowest CH₄ emissions from cattle slurries stored at 25 °C 282 with respect to those obtained at 5 °C were probably caused by the high water losses from the 283 slurries over time. As a consequence, a relative increase in concentration of constituents, such as 284 NH₃ and organic acids, which could be inhibitory to the methanogens (Kalle and Menon, 1984; 285 Angelidaki et al., 1999), occurred. This was proved by the CH₄ fluxes from both untreated cattle 286 slurry and liquid fraction stored at 25 °C which were observed to be high at the beginning of the 287 storage and to gradually decrease over time (Fig. 6). Additionally, Table 2 shows for cattle slurries 288 289 a relative increase in concentration of organic acids, which can be inhibitory to the methanogens, at the end of the storage compared to the beginning of the storage (Table 1). The combined effect of 290 temperature and slurry concentration had no effect on CH₄ losses from pig slurries, probably due to 291 a more active methanogens population. According to Massé et al. (2003), manure from different 292 animals probably contains different species of anaerobic bacteria, which may be better adapted or 293 294 acclimatized to inhibitive components such as organic acids.

CH₄ emission reductions from the cattle and pig solid fractions stored at 25 °C could also be 295 explained by the high water losses over time. From the beginning of the storage period, when solid 296 fractions started to dry, air entered the pores previously filled with water. The high water losses 297 combined with low volume (1000 cm³) of the samples in storage, resulted in a substantial reduction 298 of the anaerobic zone inside the cattle and pig solid fractions stored at 25 °C. Methanogenesis is 299 inhibited by low moisture content and oxygen availability in the manure. Furthermore, most studies 300 show CH₄ emission reductions due to the methane oxidation during the passage through the porous 301 surface layers of manure heaps (Olesen, 2005). Biological CH₄ oxidation is a process whereby 302

methane is oxidised to carbon dioxide and water by methane oxidizing bacteria (methanotrophs) under aerobic conditions (Cicerone and Oremland, 1988; Kotsyurbenco, 2005). The substantial reduction of the anaerobic zone over time and the biological CH_4 oxidation in the outer layers could be the causes for lower CH_4 emissions from pig and cattle solid fractions stored at 25 °C.

308 5. Conclusion

Results from this study show that emissions of NH₃ and GHGs during the storage of animal 309 manures are influenced by different factors. Since emissions of NO₂, NH₃, CO₂ and CH₄ are 310 affected by microbiological, chemical, and physical processes, complex interactions exist. This 311 312 requires a whole system approach when pollutant abatement technologies have to be adopted. Evidence from the present study suggests that mechanical separation of cattle and pig slurries does 313 not reduce emissions but has the potential to increase the emissions of CO₂ equivalents to the 314 315 atmosphere during the storage of the separated fractions by up to 30% if compared with the untreated slurries. The emission potential of pig slurry was up to 3 times higher than that of cattle 316 slurry. It was determined under the laboratory conditions and assumptions as described. Thus, to 317 confirm these results, experiments should be made under on-farm storage conditions. 318

319

320 Acknowledgements

This study is part of a larger research project "Monitoring of solid-liquid separation technique of pig and cattle liquid slurry" financed in Italy by Piemonte Region which aim is to highlight advantages and disadvantages of solid-liquid separation for slurry management from the operative, agronomic and environmental point of view.

327 **References**

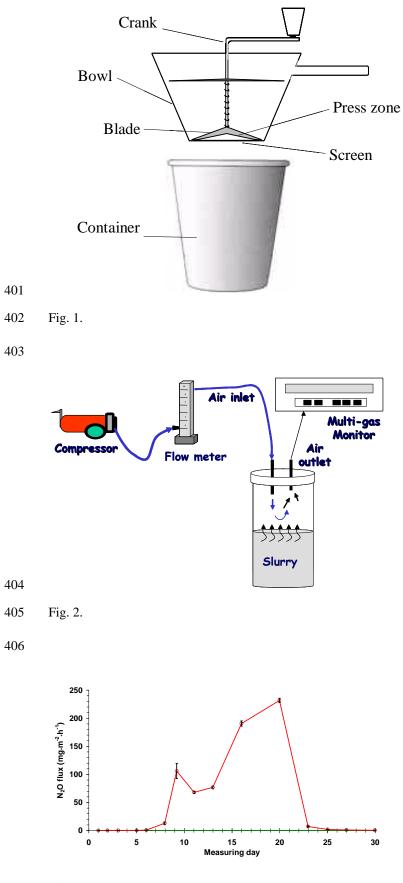
- Angelidaki, I., Ellegaard, L., Ahring B., K., 1999. A Comprehensive Model of Anaerobic
- Bioconversion of Complex Substrates to Biogas. Biotechnology and Bioengineering 63, 363-
- 331 372.
- Amon, B., Amon, T., Boxberger, J., Alt, C., 2001. Emissions of NH₃, N₂O and CH₄ from dairy
- cows housed in a farmyard manure tying stall (housing, manure storage, manure spreading).
- Nutrient Cycling in Agroecosystems 60, 103–113.
- Berg, W., Brunsch, R., Pazsiczki, I., 2006. Greenhouse gas emissions from covered slurry
 compared with uncovered during storage. Agriculture, Ecosystem and Environment 112, 129134.
- Bronshtein, I.N., Semendyayev, K.A., Musiol, G., Muehlig, H., 2003. Handbook of Mathematics
 (4th ed.), Springer, Berlin, pp. 1153.
- Cicerone, R.J., Oremland, R.S., 1988. Biogeochemical aspects of atmospheric methane. Global
 Biogeochem Cycles 2, 299–327.
- 342 CNMP, 2002. COMPREHENSIVE NUTRIENTMANAGEMENT PLAN. Prepared by USDA -
- 343 Natural Resources Conservation Service.
- 344 Dewes, T., 1996. Effect of pH, temperature, amount of litter and storage density on ammonia
- emissions from stable manure. Journal of Agricultural Science, Cambridge 127, 501-509.
- EEA, 2005. Source apportionment of nitrogen and phosphorus inputs into the aquatic environment.
- 347 Technical report N° 7, 49 pp.
- 348 Husted, S., 1994. Seasonal variation in methane emission from stored slurry and solid manures.
- Journal of Environmental Quality 23, 585-592.
- 350 IPCC, 1997. Revised 1996 IPCC guidelines for national green house gas inventories. Vol. 3. UK
- 351 Meteorol. Office, Breaknell.

- Kalle, G. P., Menon, K.K.G., 1984. Inhibition of methanogenesis and its reversal during biogas
 formation from cattle manure. J. Biosci. 6, 315–324.
- Kotsyurbenko, O.R., 2005. Trophic interactions in the methanogenic microbial community of low temperature terrestrial ecosystems. Microbiology Ecology 53, 3-13.
- 356 Kroodsma, W., 1986. Separation and removal of faeces and urine using filter nets under slatted
- floors in piggeries. J. Agric. Eng. Res. 34, 75-84.
- Massé, D.I., Croteau, F., Patni, N.K., Masse, L., 2002. Methane emissions from dairy cow and
 swine manure slurries stored at 10°C and 15°C. Canadian Biosystems Engineering/Le génie des
 biosystèmes au Canada 45, 6.1-6.6.
- Menzi H., Pain B., Sommer, S.G., 2002. Manure management: the European perspective. In:
 Proceedings of the Fourth International Livestock Waste Management Symposium, Penang,
 Malaysia pp. 35–44.
- Møller, H.B., Lund, I., Sommer, S.G., 2000. Solid-liquid separation of livestock slurry: efficiency
 and cost. Bioresource Technology 74, 223-229.
- Ni, J., 1999. Mechanistic models of ammonia release from liquid manure: a review. J. Agric. Eng.
 Res. 72, 1-17.
- Oenema, O., Bannink, A., Sommer S.G., Velthof G.L., 2001. Gaseous nitrogen emissions from
 livestock farming systems. In: Follett R.F. and Hatfield J.L. (Eds), Nitrogen in the Environment:
 Sources, Problems, and Management, Elsevier Science B.V., pp. 255-289.
- 371 Olesen, J.E., 2005. Methane and nitrous oxide emissions from management of livestock manure. In:
- Soliva C.R. et al. (Eds.), 2nd International Conference on Greenhouse Gases and Animal
 Agriculture GGAA, Zürich, Switzerland, pp. 255-263.
- 374 Sommer, S.G., Petersen, S.O., Søgaard, H.T., 2000. Emission of greenhouse gases from stored
- cattle slurry and slurry fermented in a biogas plant. Journal of Environmental Quality 29, 744-
- 376 751.
- 377 SPSS, 2006. SPSS for windows: Advanced statistics, Release 12.0. SPSS, Chicago, IL.

- 378 Van Der Hoek, K. W., 1998. Estimating ammonia emission factors in Europe: summary of the work
- of the UNECE ammonia expert panel. Atmospheric Environment 32, 315–316.

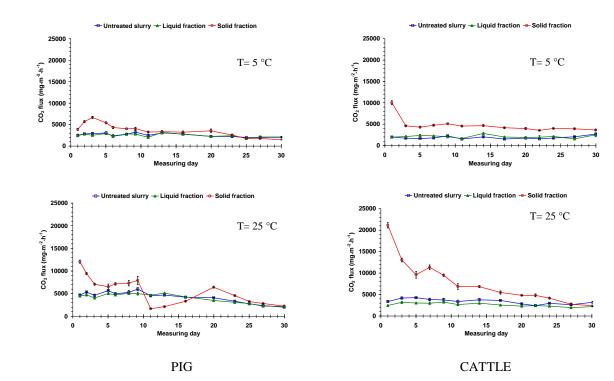
382 Figure legends

- Fig. 1. Main components of the lab-scale mechanical slurry separator.
- Fig. 2. Schematic diagram of the sampling system.
- Fig. 3. Nitrous oxide (N₂O) fluxes from pig solid fraction stored at 25 °C. Error bars indicate standard error (number of
- 386 observations = 4).
- 387 Fig. 4. Emission fluxes of ammonia (NH₃) during storage of the tested materials at 5 °C and 25 °C. Error bars indicate
- 388 standard error (number of observations = 4).
- 389 Fig. 5. Emission fluxes of carbon dioxide (CO₂) during storage of the tested materials at 5 °C and 25 °C. Error bars
- indicate standard error (number of observations = 4).
- Fig. 6. Emission fluxes of methane (CH₄) during storage of the tested materials at 5 °C and 25 °C. Error bars indicate
- 392 standard error (number of observations = 4).
- Fig. 7. Corrected cumulative loss Φ_i of NH₃, CO₂ and CH₄ of the investigated samples in relation to the Φ_i from
- 394 untreated slurries (pig and cattle) samples.
- Fig. 8. Climatic warm potential of untreated slurry (pig and cattle), liquid and solid fractions expressed as CO₂
- 396 equivalents calculated from the cumulated emissions of the single trace gases.
- 397
- 398

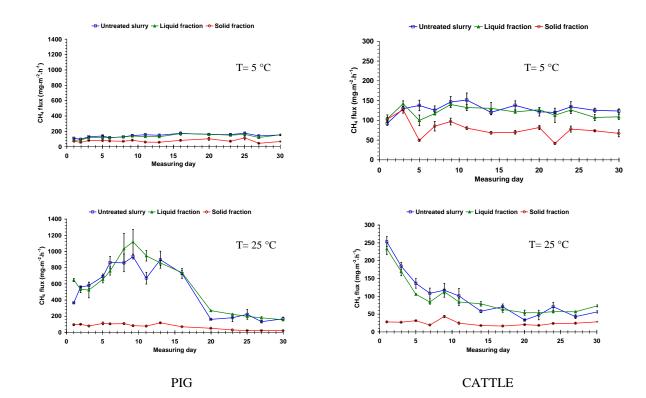


--- Solid fraction Solid fraction Liquid fraction $T=5 \ ^{\circ}C$ $T=5 \ ^{\circ}C$ (,-,4,-2,-un-Bun) xnJ ^EHN 100 50 Measuring day Measuring day . 25 - Untreated slurry - Liquid fraction - Solid fraction - Untreated slurry - Liquid fraction - Solid fraction T= 25 °C T= 25 °C (,,4,²,m-6m) xn1¹,¹HN 200 200 HN³ thx (mg·m⁻²,¹,¹,¹) 100 50 o ‡ ? + ? + ? + + ? 25 30 Measuring day Measuring day n CATTLE PIG

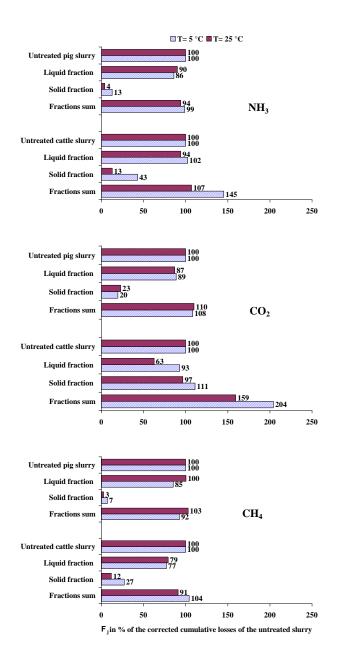








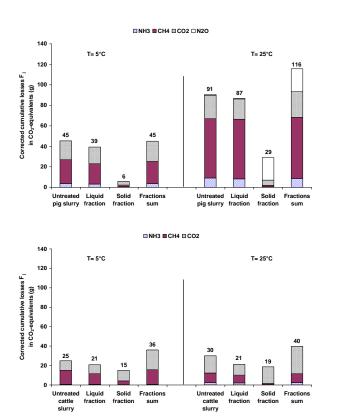
418 Fig. 6.



423 Fig. 7.

-







436 Table legends

- 437 Table 1. Main composition of the manures at the beginning of each experiment
- 438 (n=2) and the correction factors ρ used for Φ_i calculation.
- 439 Table 2. Main composition of the manures at the end of each experiment (n=4) and volume reductions over the storage
- 440 period.
- 441 Table 3. Mean gaseous losses from each of the tested material occurred at the different experimental conditions after 30
- d of storage.
- 443
- 444
- 445
- 446

448 Table 1.

Туре	Product	pН	TS	VS	TAN	TKN	Org.	ρ
of slurry			%	%	g kg ⁻¹	g kg ⁻¹	Acids	
							%	
	Untreated slurry	7.79	5.90	4.21	4.31	6.40	4.78	1.00
Pig	Liquid fraction	7.86	4.65	3.01	4.33	5.90	3.15	0.92
	Solid fraction	8.82	21.1	19.1	4.05	12.2	3.47	0.20
	Untreated slurry	7.11	7.46	6.02	1.47	3.58	4.48	1.00
Cattle	Liquid fraction	7.09	5.12	3.81	1.49	3.59	5.80	0.82
	Solid fraction	8.35	19.2	17.3	1.16	2.65	4.18	0.45

452 Table 2.

Туре	Storage temperature	Product	pН	TS	VS	TAN	N Kjel.	Org. Acids	Volume reduction
of slurry	°C			%	%	g kg ⁻¹	g kg ⁻¹	%	%
	25	Untreated slurry	8.43	8.38	5.31	1.55	4.10	1.46	46.3
	25	Liquid fraction	8.50	6.32	3.39	1.46	3.79	2.23	46.3
Dia	25	Solid fraction	7.25	28.6	25.0	0.28	6.63	1.29	0.00
Pig	5	Untreated slurry	7.92	5.98	4.16	3.65	5.76	3.26	3.72
	5	Liquid fraction	7.95	4.69	2.93	3.70	5.74	4.07	7.48
	5	Solid fraction	8.79	23.9	21.7	2.82	3.13	1.48	7.48
	25	Untreated slurry	6.96	8.63	6.76	1.51	3.22	8.48	38.4
	25	Liquid fraction	7.30	5.74	3.89	1.30	2.90	6.66	34.5
Cattle	25	Solid fraction	8.29	22.1	18.3	0.05	5.87	0.82	30.6
	5	Untreated slurry	6.79	7.67	6.17	1.40	3.32	6.37	3.72
	5	Liquid fraction	6.96	4.99	3.64	1.43	3.23	5.68	7.48
	5	Solid fraction	8.47	18.6	16.3	0.20	3.57	0.80	3.72

462 Table 3.

Type of slurry	Temperature °C	Untreated slurry			Liquid fraction				Solid fraction				
		N-NH ₃	N-N ₂ O	C-CH ₄	C-CO ₂	N-NH ₃	N-N ₂ O	C-CH ₄	C-CO ₂	N-NH ₃	N-N ₂ O	C-CH ₄	C-CO ₂
		(%TKN)	(%TKN)	(%VS)	(%VS)	(%TKN)	(%TKN)	(%VS)	(%VS)	(%TKN)	(%TKN)	(%VS)	(%VS)
	5	15.1 a	ND	3.34 a	20.0 a	15.0 a	ND	4.39 a	27.4 a	7.12 a	ND	0.68 a	11.1 a
Pig		(0.34)		(0.05)	(0.41)	(0.61)		(0.17)	(0.68)	(0.04)		(0.02)	(0.37)
	25	37.8 b	ND	8.53 b	25.6 b	40.8 b	ND	12.8 b	33.4 b	5.57 b	4.71	0.60 b	16.3 b
		(0.57)		(0.43)	(0.64)	(0.22)		(0.47)	(0.35)	(0.11)	(0.12)	(0.02)	(0.26)
	5	3.60 c	ND	1.56 c	7.66 c	4.63 c	ND	2.19 c	13.7 c	5.21 c	ND	0.77 c	16.4 cb
Cattle		(0.09)		(0.05)	(0.19)	(0.14)		(0.10)	(0.42)	(0.10)		(0.01)	(0.36)
	25	16.5 d	ND	1.01 d	13.7 d	18.4 d	ND	1.55 d	16.7 d	6.03 db	ND	0.23 d	25.6 d
		(0.17)		(0.04)	(0.33)	(0.36)		(0.08)	(0.17)	(0.25)		(0.00)	(0.45)
		1				1				1			

463 Error standards are given in parentheses (n=4). Means with unequal letters in each column are significantly different (P<0.05).

464 ND = not detected