

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

3 This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier.
4 It is posted here by agreement between Elsevier and the University of Turin.
5 Changes resulting from the publishing process - such as editing, corrections,
6 structural formatting, and other quality control mechanisms - may not be reflected
7 in this version of the text. The definitive version of the text was subsequently
8 published in Atmospheric Environment, Volume 42, Issue 10, March 2008, Pages
9 2448–2459, DOI: 10.1016/j.atmosenv.2007.12.022.

10

11 You may download, copy and otherwise use the AAM for non-commercial purposes
12 provided that your license is limited by the following restrictions:

13

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

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

18 (3) You must attribute this AAM in the following format: Creative Commons BY-
19 NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), doi:
20 10.1016/j.atmosenv.2007.12.022

21

22

23

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

26

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

28

29 ^a Department of Agriculture, Forestry, Environmental Engineering and Land Based Economics
30 (DEIAFA) Mechanics Section - Turin University via Leonardo da Vinci 44, 10095 Grugliasco (TO)
31 Italy.

32 ^b Institute of Agricultural Engineering Bornim (ATB), Max-Eyth-Allee 100, D-14469 Potsdam,
33 Germany.

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

35 elio.dinuccio@unito.it

36

37

Abstract

38 A laboratory scale study was set up to investigate the ammonia (NH₃), nitrous oxide (N₂O), carbon
39 dioxide (CO₂) and methane (CH₄) emissions during storage of untreated pig and cattle slurry and
40 the fractions (solid and liquid) obtained by mechanical separation. The solid and liquid fractions
41 were obtained from the same untreated slurry by means of a lab scale mechanical separator.

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

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

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

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 (NH₃), nitrous oxide (N₂O), carbon dioxide (CO₂) and methane (CH₄) production (Van
67 Der Hoek, 1998; Amon et al., 2001). While N₂O, CO₂, and CH₄ are greenhouse gases affecting the
68 global environment and climate change, NH₃ contributes to eutrophication and acidification of soils
69 and also indirectly contributes to N₂O 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 NH₃, N₂O, CH₄ and CO₂ 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 NH₃ 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 NH₃, CO₂, CH₄ and N₂O 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.

91

92 **2. Materials and methods**

93 The trials were carried out at Leibniz-Institute for Agricultural Engineering Potsdam-Bornim
94 (ATB), Germany, in environmentally controlled conditions by means of two climatic rooms.

95 Fresh slurry was collected from commercial farms. The next day (cattle; pig two days after) it was
96 separated and stored in vessels in the emission lab of the institute and measurements began.

97 The solid and liquid fractions (B and C) were obtained from the same pig and cattle untreated slurry
98 (A) by means of a laboratory-scale mechanical separator. This latter was made up of (Fig. 1): a

99 1500 cm³ bowl with handle; a stainless steel disc (screen) with circular holes 2.3 mm in diameter; a
100 stainless steel blade integral with a crank; a container collecting the liquid fraction.

101 A press zone was created fitting the blade to the disc by means of a horizontal bar and a spring.
102 After filling the bowl with the untreated slurry, the blade is manually rotated using the crank and
103 the slurry separated in the press zone. The liquid fraction runs through the disc's holes into the
104 container while the solid fraction remains in the bowl and is collected afterwards. The total input of
105 each untreated slurry (100 kg), as well as the amounts of solid (18.1 kg for cattle and 7.80 kg for
106 pig) and liquid (81.9 kg for cattle and 92.2 kg for pig) recovered, were weighed and recorded. The
107 bulk density of the solid fractions (cattle and pig) was estimated to be 0.40 t m^{-3} .
108 Immediately after mechanical separation, samples of 1000 cm^3 of each of the investigated materials
109 were stored for a period of 30 days in open vessels (1500 cm^3 capacity, 0.20 m height, 0.10 m base
110 diameter and 0.095 m top diameter) in two temperature-controlled rooms which were kept at 5 ± 0.5
111 and $25 \pm 0.2 \text{ }^\circ\text{C}$. During the test period observations of crust formation and reduction of volume were
112 carried out. Four replicates of each product were tested so that for each type of untreated liquid
113 manure (pig or cattle) a total of 12 vessels were used per climate room.
114 The samples were analysed for pH, total solids (TS), volatile solids (VS), total Kjeldhal nitrogen
115 (TKN), total ammoniacal nitrogen (TAN), and organic acids at the beginning and at the end of the
116 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
119 chamber method described by Berg et al. (2006). This method allows the comparison of the effect
120 of different treatments on gaseous emissions during manure storage, under standardized
121 experimental conditions. Different conditions, such as volume to surface ratio of the manure stores,
122 in the lab and on farms may yield different gas fluxes. Therefore, this fluxes cannot be used for
123 calculating fluxes from on farm storage facilities without further validation. Accordingly, the
124 slurries were stored in open vessels using the dynamic chamber method set up only during
125 measurements. Before starting the measurements each vessel was closed with an air-tight lid
126 provided with two ports for air inlet and outlet (Fig. 2). Air inlet port was connected in an airtight

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

- 132 1) lid closure at time $t = 0$ min;
- 133 2) between $t=0$ and $t= 20$ min the chamber was only ventilated to achieve steady conditions inside
134 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.

137 The gas concentrations in the inlet (atmospheric) and outlet (exhaust) air were analyzed by the
138 INNOVA system 1312 Photoacoustic Multi-gas Monitor and Multipoint Sampler. The system
139 provided a real time analysis of 4 gases (NH_3 , N_2O , CH_4 and CO_2) plus water vapour. Measured
140 data were related to standard conditions (25°C and 100 kPa) and stored in a database. Exhaust air
141 leaving each chamber was sampled for 16 min. The instrument needed 2 min to analyze one sample,
142 thus, 8 values were recorded on each measurement occasion. The first 3 values were discarded and
143 the mean of the remaining 5 recorded values was considered representative for the measurement.

144 Gas fluxes F_j in $\text{mg m}^{-2} \text{h}^{-1}$ were determined according to:

$$145 \quad F_j = Q \frac{(C_{ex.j} - C_{in.j})}{A} \quad (1)$$

146 where $C_{in.j}$ is the NH_3 , N_2O , CH_4 or CO_2 concentration of air inlet the chamber in mg m^{-3} ; $C_{ex.j}$ is
147 the NH_3 , N_2O , CH_4 or CO_2 concentration of air outlet the chamber in mg m^{-3} ; Q is the air flow rate
148 through the chamber in $\text{m}^3 \text{h}^{-1}$; A is the area of emitting surface covered by the chamber in m^2 .

149 Time evolution of the gas fluxes were approximated by spline approximation functions, and by
150 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.

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

$$156 \quad \Phi_j = \varphi_j \cdot \rho \quad (2)$$

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

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

162 The ρ values used are summarized in Table 1.

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

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

177
178 Significant differences in results and all possible interactions were investigated using the ANOVA
179 procedure. Before analysis some of the parameters were log-transformed in order to fit a normal
180 distribution. For all the statistics, a significant level of P = 0.05 was applied. Assumption of equal
181 variance of different groups was tested using Bartlett's test. All statistical analyses were performed
182 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
187 significant reductions of TS and VS (Table 1). In contrast, the pH, TAN and TKN concentrations of
188 the liquid fractions were very similar to those of the untreated slurries. As expected, the TS and VS
189 content of the solid fractions were significantly greater than those for the untreated slurries. The
190 TKN content of the pig solid fraction was almost double the TKN content of the pig untreated
191 slurry, while the TKN content of the cattle solid fraction was approximately 1.4 times lower than
192 the TKN content of the cattle untreated slurry.

193 Analysis of the manures at the end of each experiment are given in Table 2 together with volume
194 reductions over the storage period.

195 Water evaporation occurred in all the samples throughout the storage period. As expected,
196 evaporation was higher from materials stored at 25 °C than 5 °C and was responsible for volume
197 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

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

201

202 3.2 Gaseous emissions

203 3.2.1 N₂O emissions

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

213

214 3.2.2 NH₃ emissions

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

224

225 3.2.3 CO₂ and CH₄ emissions

226 During pig and cattle manure storage, the predominant emission of carbon was as CO₂ (Fig. 5 and
227 Table 3). Total losses of C-CO₂ expressed as a percentage of the carbon initially present in the
228 volatile solids (C-VS) of the manures ranged from 7.76% (from cattle untreated slurry stored at
229 5 °C) to 33.4% (from pig liquid fraction stored at 25 °C). CO₂ losses were always higher at 25 °C
230 and lower at 5 °C storage conditions.

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

242

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

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

251 The emissions from the storage of the two fractions increased the CO₂ emissions from 8% (when
252 compared to untreated pig slurry stored at 5 °C) to 104% (when compared to untreated cattle slurry
253 stored at 25 °C). During the storage of both liquid and solid fractions, CH₄ losses were 3% higher
254 for pig untreated slurry stored at 25 °C and 4% higher for cattle untreated slurry stored at 5 °C.
255 Instead, solid-liquid separation reduced CH₄ emissions by 8% for pig untreated slurry stored at 5 °C
256 and by 9% for cattle untreated slurry stored at 25 °C.
257 Combining the emissions of CO₂ equivalents from both liquid and solid fractions (Fig. 8), they
258 resulted in increased greenhouse gases emissions compared to the storage of the untreated slurries,
259 except when considering the pig untreated slurry stored at 5 °C. In this latter case the mechanical
260 separation had no effect in combined emissions of CO₂ equivalents.

261

262 **4. Discussion**

263 The small N₂O fluxes from cattle and pig slurries storage can be explained by the absence of crust
264 during most of the storage period. N₂O may be emitted during storage of manure either as a by-
265 product of incomplete ammonium oxidation or as a by-product of incomplete denitrification
266 (Oenema et al., 2001). The condition in liquid manure is strictly anaerobic, and neither process
267 occurs. In contrast, authors (e.g. Sommer et al., 2000; Berg et al., 2006) found N₂O production from
268 stored slurries, but only when a dry crust formed on the surface. These emissions occurred since
269 surface crust may contain a mosaic of anaerobic and aerobic micro-sites which are favourable for
270 N₂O production. Dry conditions, together with air filled porosity, may explain the occurrence of
271 N₂O production from pig solid fraction samples. On the other hand, separation of cattle slurry
272 produced a fibrous solid fraction with a compacted structure, this might have created an
273 environment with an oxygen concentration unsuitable for N₂O production.
274 Results confirm a positive relationship between ammonia emission and temperature found by other
275 studies (e.g. Ni, 1999; Dewes, 1996), but not in the case of the pig solid fraction. Total losses from
276 the pig solid fraction were 7.12 and 5.57% of the initial TKN content at 5 and at 25 °C storage

277 conditions respectively. This may be explained by ammonium oxidation by nitrifying micro-
278 organisms with N₂O production. NH₃ emission from manure decreased, therefore, as a greater
279 proportion of the NH₄-N was oxidized by nitrifying micro-organisms.

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

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

303 methane is oxidised to carbon dioxide and water by methane oxidizing bacteria (methanotrophs)
304 under aerobic conditions (Cicerone and Oremland, 1988; Kotsyurbenco, 2005). The substantial
305 reduction of the anaerobic zone over time and the biological CH₄ oxidation in the outer layers could
306 be the causes for lower CH₄ emissions from pig and cattle solid fractions stored at 25 °C.

307

308 **5. Conclusion**

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

319

320 **Acknowledgements**

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

325

326

327 **References**

328

329 Angelidaki, I., Ellegaard, L., Ahring B., K., 1999. A Comprehensive Model of Anaerobic
330 Bioconversion of Complex Substrates to Biogas. *Biotechnology and Bioengineering* 63, 363-
331 372.

332 Amon, B., Amon, T., Boxberger, J., Alt, C., 2001. Emissions of NH₃, N₂O and CH₄ from dairy
333 cows housed in a farmyard manure tying stall (housing, manure storage, manure spreading).
334 *Nutrient Cycling in Agroecosystems* 60, 103–113.

335 Berg, W., Brunsch, R., Pazsiczki, I., 2006. Greenhouse gas emissions from covered slurry
336 compared with uncovered during storage. *Agriculture, Ecosystem and Environment* 112, 129-
337 134.

338 Bronshtein, I.N., Semendyayev, K.A., Musiol, G., Muehlig, H., 2003. *Handbook of Mathematics*
339 (4th ed.), Springer, Berlin, pp. 1153.

340 Cicerone, R.J., Oremland, R.S., 1988. Biogeochemical aspects of atmospheric methane. *Global*
341 *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
345 emissions from stable manure. *Journal of Agricultural Science, Cambridge* 127, 501-509.

346 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.
349 *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*.

352 Kalle, G. P., Menon, K.K.G., 1984. Inhibition of methanogenesis and its reversal during biogas
353 formation from cattle manure. *J. Biosci.* 6, 315–324.

354 Kotsyurbenko, O.R., 2005. Trophic interactions in the methanogenic microbial community of low-
355 temperature terrestrial ecosystems. *Microbiology Ecology* 53, 3-13.

356 Kroodsma, W., 1986. Separation and removal of faeces and urine using filter nets under slatted
357 floors in piggeries. *J. Agric. Eng. Res.* 34, 75-84.

358 Massé, D.I., Croteau, F., Patni, N.K., Masse, L., 2002. Methane emissions from dairy cow and
359 swine manure slurries stored at 10°C and 15°C. *Canadian Biosystems Engineering/Le génie des*
360 *biosystèmes au Canada* 45, 6.1-6.6.

361 Menzi H., Pain B., Sommer, S.G., 2002. Manure management: the European perspective. In:
362 *Proceedings of the Fourth International Livestock Waste Management Symposium, Penang,*
363 *Malaysia* pp. 35–44.

364 Møller, H.B., Lund, I., Sommer, S.G., 2000. Solid-liquid separation of livestock slurry: efficiency
365 and cost. *Bioresource Technology* 74, 223-229.

366 Ni, J., 1999. Mechanistic models of ammonia release from liquid manure: a review. *J. Agric. Eng.*
367 *Res.* 72, 1-17.

368 Oenema, O., Bannink, A., Sommer S.G., Velthof G.L., 2001. Gaseous nitrogen emissions from
369 livestock farming systems. In: Follett R.F. and Hatfield J.L. (Eds), *Nitrogen in the Environment:*
370 *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:
372 Soliva C.R. et al. (Eds.), *2nd International Conference on Greenhouse Gases and Animal*
373 *Agriculture GGAA, Zürich, Switzerland*, pp. 255-263.

374 Sommer, S.G., Petersen, S.O., Søggaard, H.T., 2000. Emission of greenhouse gases from stored
375 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
379 of the UNECE ammonia expert panel. *Atmospheric Environment* 32, 315–316.

380

381

382 **Figure legends**

383 Fig. 1. Main components of the lab-scale mechanical slurry separator.

384 Fig. 2. Schematic diagram of the sampling system.

385 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
390 indicate standard error (number of observations = 4).

391 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).

393 Fig. 7. Corrected cumulative loss Φ_j of NH₃, CO₂ and CH₄ of the investigated samples in relation to the Φ_j from
394 untreated slurries (pig and cattle) samples.

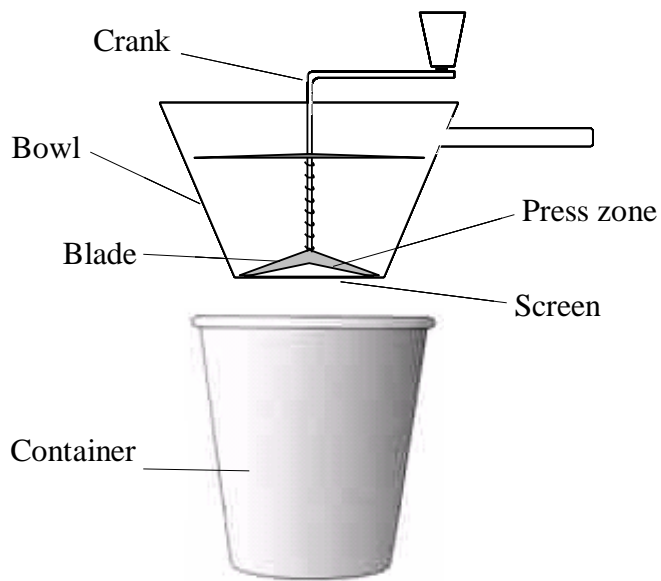
395 Fig. 8. Climatic warm potential of untreated slurry (pig and cattle), liquid and solid fractions expressed as CO₂
396 equivalents calculated from the cumulated emissions of the single trace gases.

397

398

399

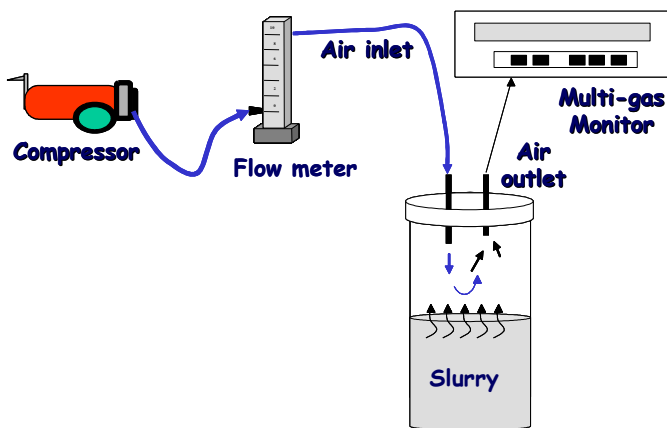
400



401

402 Fig. 1.

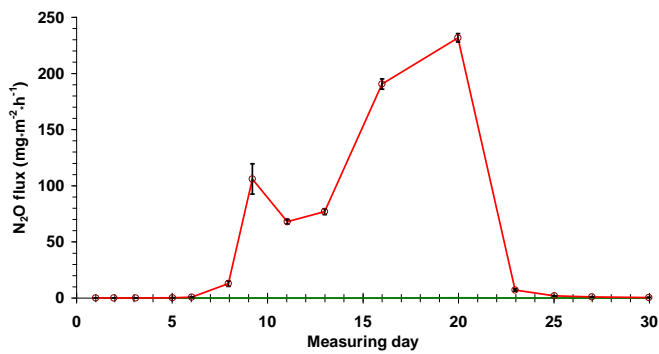
403



404

405 Fig. 2.

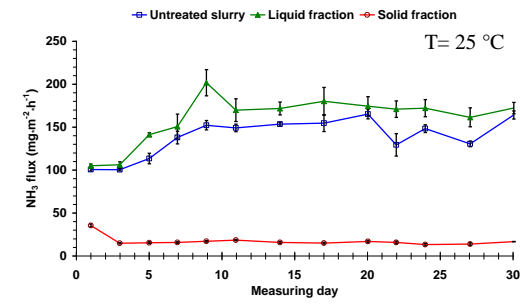
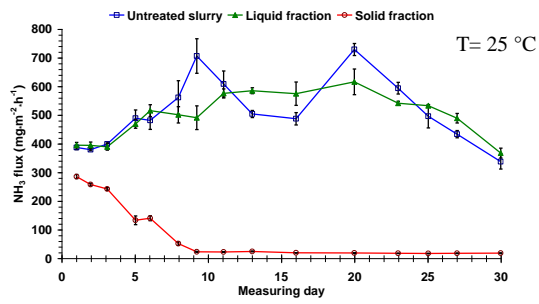
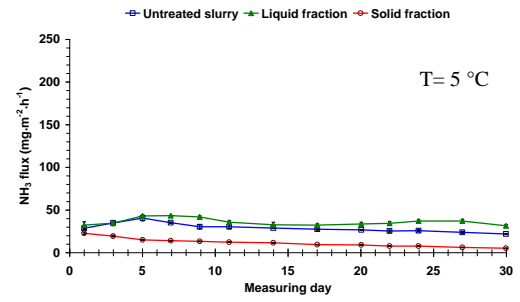
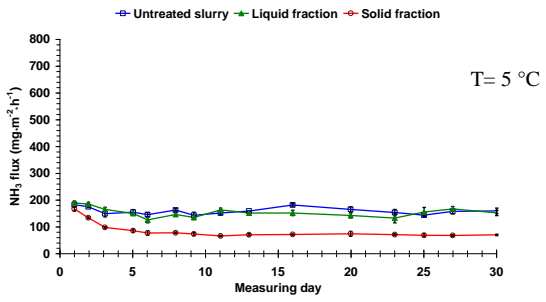
406



407 Fig. 3.

408

409



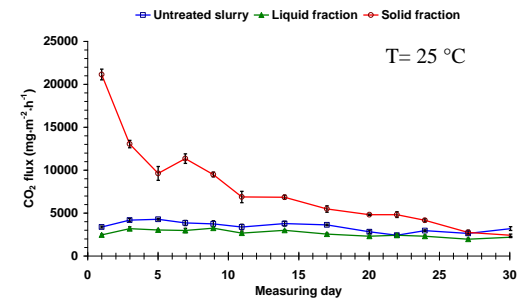
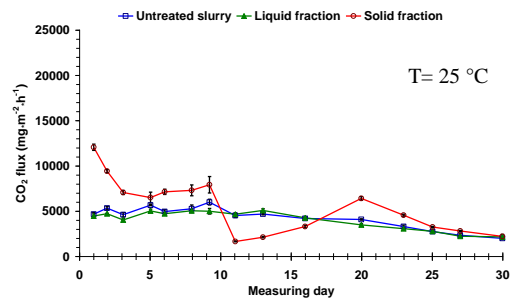
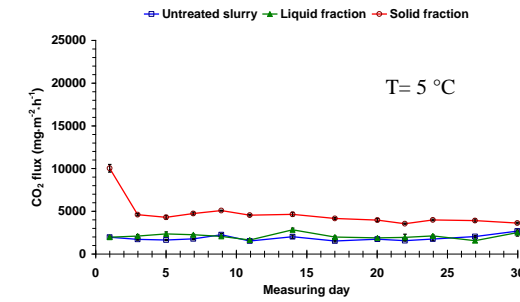
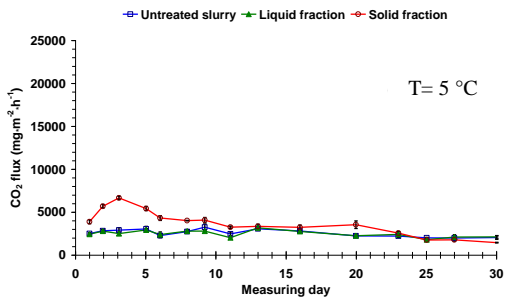
PIG

CATTLE

410 Fig. 4.

411

412

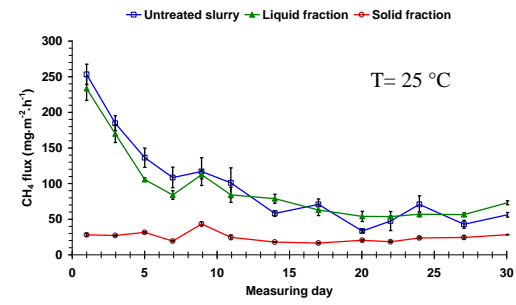
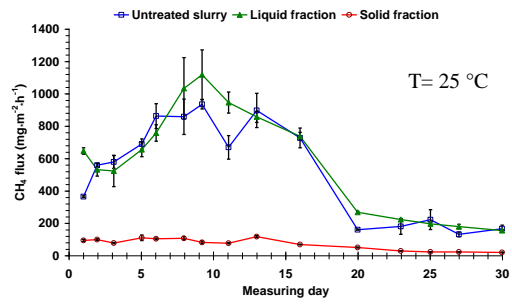
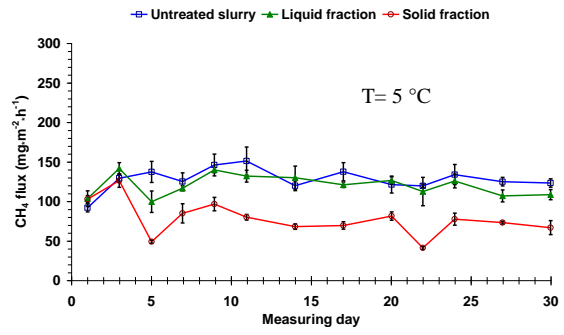
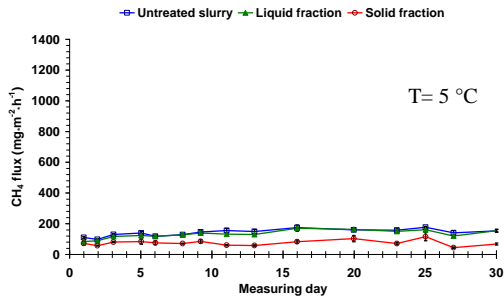


PIG

CATTLE

413 Fig. 5.

414
415
416
417

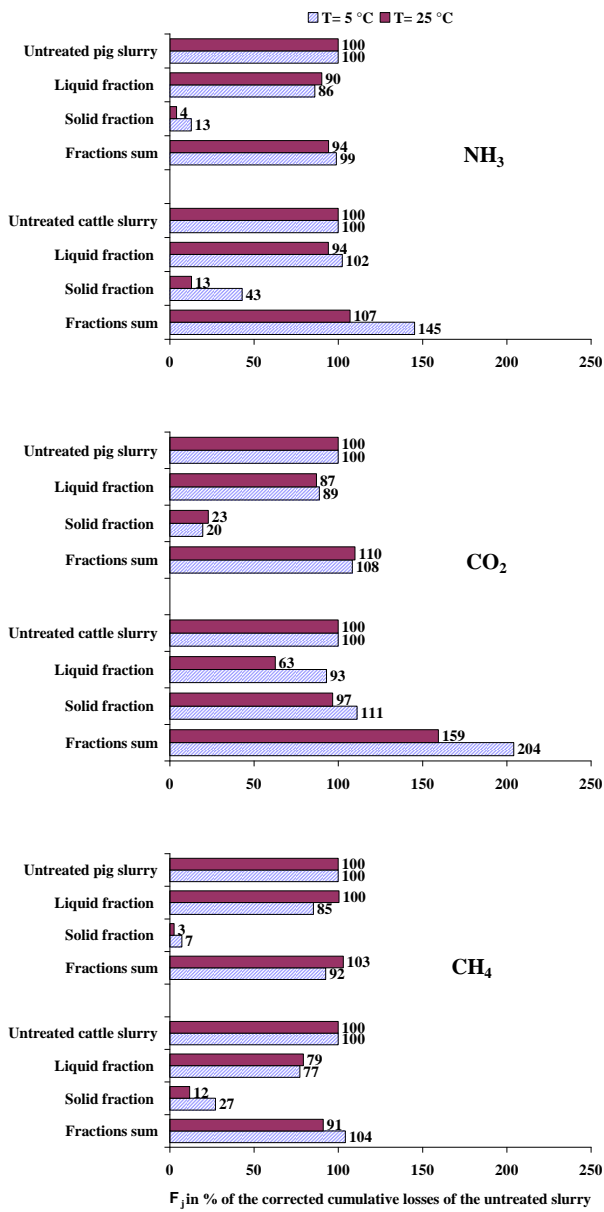


PIG

CATTLE

418 Fig. 6.

419
420
421



423 Fig. 7.

424

425

426

427

428

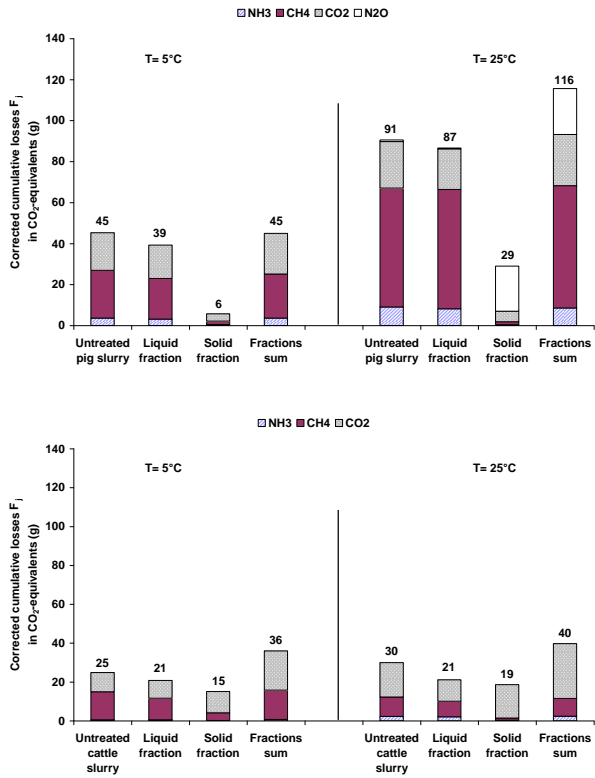
429

430

431

432

433



434 Fig. 8.

435

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_j 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
442 d of storage.

443

444

445

446

447

448 Table 1.

Type of slurry	Product	pH	TS %	VS %	TAN g kg ⁻¹	TKN g kg ⁻¹	Org. Acids %	ρ
Pig	Untreated slurry	7.79	5.90	4.21	4.31	6.40	4.78	1.00
	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
Cattle	Untreated slurry	7.11	7.46	6.02	1.47	3.58	4.48	1.00
	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

449

450

451

452 Table 2.

Type of slurry	Storage temperature °C	Product	pH	TS %	VS %	TAN g kg ⁻¹	N Kjell. g kg ⁻¹	Org. Acids %	Volume reduction %
Pig	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
	25	Solid fraction	7.25	28.6	25.0	0.28	6.63	1.29	0.00
	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
Cattle	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
	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

453

454

455

456

457

458

459

460

461

462 Table 3.

Type of slurry	Temperature °C	Untreated slurry				Liquid fraction				Solid fraction			
		N-NH ₃ (%TKN)	N-N ₂ O (%TKN)	C-CH ₄ (%VS)	C-CO ₂ (%VS)	N-NH ₃ (%TKN)	N-N ₂ O (%TKN)	C-CH ₄ (%VS)	C-CO ₂ (%VS)	N-NH ₃ (%TKN)	N-N ₂ O (%TKN)	C-CH ₄ (%VS)	C-CO ₂ (%VS)
Pig	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
		(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)
Cattle	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
		(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)

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

465

466