



## UNIVERSITÀ DEGLI STUDI DI TORINO

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**Effects of mechanical separation on GHG and ammonia emissions from cattle  
slurry under winter conditions**

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51 **Abstract**

52 Effects of cattle slurry mechanical separation on CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> emissions  
53 during slurry management under winter conditions was investigated in a laboratory  
54 study. Greenhouse gas (GHG) emissions during storage and soil application of raw  
55 cattle slurry by broadcasting of its liquid and solid fractions was assessed. Carbon  
56 dioxide was the predominant emission source during both storage and soil application  
57 of manure on a CO<sub>2</sub>-eq basis, but CH<sub>4</sub> was the predominant GHG emission from stored  
58 slurries. During storage, NH<sub>3</sub> fluxes from liquid fractions were higher than from the  
59 solid fraction, but the solid fraction was the main source of NH<sub>3</sub> emissions after land  
60 application: on average, ~70% of total ammoniacal N applied to soil was lost.  
61 Combining losses during storage and after soil application of both liquid and solid  
62 fractions, total CO<sub>2</sub>-eq emissions of the combined fractions were 11% higher than that  
63 from raw cattle slurry. Results suggest that mechanical separation of cattle slurry  
64 should not be used by farmers unless other GHG emission reduction measures are  
65 adopted.

66 *Keywords:* greenhouse gases, ammonia, cattle, slurry separation.

67 *Abbreviations:* CO<sub>2</sub> eq, carbon dioxide equivalents; GHG, greenhouse gas; TAN, total  
68 ammoniacal N; TC, total carbon; TKN, total Kjeldahl N; TN, total N; TS, total solids;  
69 VS, volatile solids.

70

71 **1. Introduction**

72 Storage and handling of cattle manure contributes to emissions of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O  
73 and NH<sub>3</sub> to the atmosphere (FAO, 2006). A report from IPCC (2007) revealed that  
74 CH<sub>4</sub> and N<sub>2</sub>O are the most important greenhouse gases (GHG) in terms of climate  
75 change because of their strong absorption of infrared radiation. Goebes et al. (2003)  
76 reported that NH<sub>3</sub> causes various environmental problems, such as odour,  
77 eutrophication, acidification of soils, and atmospheric particulate matter formation.

78 In Italy, animal manure management is responsible for ~70% NH<sub>3</sub> (Valli et al.,  
79 2000), ~8% CH<sub>4</sub> and ~9% N<sub>2</sub>O anthropogenic emissions (APAT, 2006), and their  
80 contribution to GHG air emissions is increasing due to the growing demand for animal  
81 based foods (FAO, 2006). Italy has undertaken to reduce its GHG emissions by 6.5%  
82 by 2012 relative to 1990 levels (UNFCCC, 1997). Thus, manure management practices  
83 that minimize GHG impacts on air quality need to be investigated. Mechanical  
84 separation of animal slurry into solid and liquid fractions is currently becoming a

85 common practice in Italy, due to the ability to improve the flexibility of slurry  
86 application and reduce environmental risks (Burton, 2007). On farms where land area  
87 is insufficient for disposal of N in slurry, separation of the solids can also reduce  
88 manure transport costs (Balsari et al., 2008), thereby making it easier for producers to  
89 conform to the manure N limits set by the Nitrates Directive (91/676/EC). However,  
90 mechanical separation of slurry has the potential to increase GHG and NH<sub>3</sub> emissions  
91 compared to traditional slurry management (Amon et al., 2006; Dinuccio et al., 2008;  
92 Fangueiro et al., 2008a), mainly due to high emissions during storage of the solid  
93 fraction. In contrast, the effect of mechanical separation of slurry on gaseous emissions  
94 on overall slurry management (*i.e.*, storage + land application) is not yet clear due to  
95 the lack of experimental data. With the aim to cover this knowledge gap, a laboratory  
96 scale study was completed in order to assess CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> emissions from  
97 storage and soil application of raw cattle slurry by broadcasting separated liquid and  
98 solid fractions.

99

## 100 **2. Materials and methods**

101 The experiment was a randomised block design with three treatments being: (1)  
102 raw cattle slurry, (2) separated liquid and (3) separated solid manure and four  
103 replicates per treatment. Raw cattle slurry (~21 kg) was separated using a lab scale  
104 mechanical separator as described by Dinuccio et al. (2008). Samples of 1000 cm<sup>3</sup> of  
105 each manure type were stored at 5 ± 0.5 °C for a period of 30 d in an open vessel with  
106 1500 cm<sup>3</sup> capacity and gas samples were collected and analyzed at 2 to 3 d intervals.  
107 The bulk density of the solid fraction was estimated at 0.40 kg 1000 cm<sup>3</sup>.

108 After storage, replicate samples were collected and used in a soil application  
109 experiment which was in a climate controlled room at 10 ± 0.5 °C. Open glass vessels  
110 with 1500 cm<sup>3</sup> capacity, 0.20 m height, 0.10 m base diameter and 0.095 m top  
111 diameter) were filled with 1000 cm<sup>3</sup> of soil. The soil was a loamy sand soil (USDA,  
112 1977) with 837 g/kg sand, 143 g/kg silt, 19.4 g/kg clay; pH = 7.43, total C = 8.79 g/kg,  
113 total N = 1.18 g/kg. After collection, the soil was sieved through a 4 mm screen and  
114 stored in moist form, in the dark, at 4°C prior to the start of the experiments. The bulk  
115 density of 1.16 g cm<sup>3</sup> of the undisturbed soil was achieved by shaking the vessels until  
116 the required soil volume was reached. The tested manures were homogeneously  
117 applied on the soil surface at a rate of 70 kg/ha of total Kjeldahl N (TKN). Non-  
118 fertilized soil was used as a Control. At the time of manure application the gravimetric

119 soil moisture content was 98 g/kg. Each application experiment lasted for 7.0 d, with  
120 gaseous emission measurements immediately after manure application ( $t= 0$ ) and 0.5,  
121 1.0, 2.0, 3.0, 4.0, 5.0 and 7.0 d after manure application. Net CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub>  
122 emission fluxes were calculated as the difference between emission fluxes recorded  
123 from the amended soils and those measured from the Control.

124 Flux measurements from both storage and soil application were collected by  
125 dynamic chamber method using a gas trace analyzer (1312 Photoacoustic Multi-gas  
126 Monitor and Multipoint Sampler, Innova Air Tech Instruments, Ballerup, Denmark)  
127 following the protocol described by Dinuccio et al. (2008). Additionally, at the  
128 beginning of each experiment, materials from each replicate were characterized for pH,  
129 total solids (TS), volatile solids (VS), TKN, total ammoniacal N (TAN), total carbon  
130 (TC) and total N (TN; Table 1) according to procedures described by Heiermann et al.  
131 (2009) and Plöchl et al. (2009).

132 Gaseous losses were expressed in CO<sub>2</sub>-eq using conversion factors of 1, 25, 298,  
133 and 2.98 respectively, for CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> (IPCC, 2007). To estimate effects  
134 of cattle slurry mechanical separation on gaseous emissions, total CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and  
135 NH<sub>3</sub> losses were corrected by considering mass distribution of solid (18%) and liquid  
136 (82%) fractions to the whole separated raw cattle slurry. Afterwards, total losses  
137 (Dinuccio et al., 2008) of the gases were expressed as kgCO<sub>2</sub>-eq/Mg of treated raw  
138 cattle slurry.

139 All data were processed with ANOVA procedures. Data distribution normality was  
140 verified using the Kolmogorov–Smirnov test. Assumption of equal variance of  
141 different groups was tested using Bartlett’s test. Means were separated by Tukey test  
142 and differences were considered to be significant for  $P < 0.05$ . All statistical analyses  
143 were performed with SPSS 12.0 for Windows (SPSS, 2006). Due to the variability of  
144 CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> flux intensity, variances were not homogeneous when  
145 comparing different sampling days. Therefore, independent analysis were performed  
146 for each date of sampling. Cumulative CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> emissions were  
147 analyzed by a two-way ANOVA using manure management phase (storage, soil  
148 application) and manure type (raw cattle slurry, liquid fraction, solid fraction) as fixed  
149 factors.

150

### 151 **3. Results and Discussion**

#### 152 *3.1 Storage experiments*

153 During the 30 d storage period, the CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> emission fluxes  
154 measured from the raw cattle slurry and its liquid fraction showed similar trends  
155 (Figure 1). Carbon dioxide was the main GHG (Table 2) emitted during storage of the  
156 solid fraction, in agreement with findings of Hao et al., (2004) and Pattey et al., (2005).  
157 In term of CO<sub>2</sub>-eq, CH<sub>4</sub> emission was the predominating GHG from stored liquid  
158 manures, a finding supported by Berg et al. (2006). After 30 d of storage, the amount  
159 of C lost by CH<sub>4</sub> emissions (Table 2) from the liquid fraction was higher ( $P<0.05$ ) than  
160 that lost from the raw cattle slurry, suggesting that mechanical separation of the solids  
161 reduced the amount of carbon that was available for methanogenesis (Amon et al.,  
162 2006; Møller et al., 2007). Nitrous oxide fluxes (Figure 1) from the solid fraction  
163 ranged from 0.001 to 0.007 mg m<sup>2</sup>/h and were lower ( $P<0.05$ ) than those from the raw  
164 cattle slurry of 0.01 to 0.28 mg m<sup>2</sup>/h) and from the liquid fraction of 0.02 to 0.28 mg  
165 m<sup>2</sup>/h) for most of the storage period. No N<sub>2</sub>O was detected from all manures after 20 d  
166 of storage. The lowest NH<sub>3</sub> emission rates (Figure 1) were from the solid fraction, but  
167 were higher from the liquid fraction ( $P<0.05$ ) compared to the raw cattle slurry for  
168 most of the storage period. This was mainly due its lower TS content (Table 1), which  
169 reduced development of a natural surface crust (Misselbrook et al., 2005).

### 170 3.2 Application experiments

171 Net CO<sub>2</sub> and CH<sub>4</sub> emission rates (Figure 2) from all amended soils peaked  
172 immediately following manure application, probably due to release of CO<sub>2</sub> and CH<sub>4</sub>  
173 dissolved in slurry (Flessa and Beese, 2000). From 2 to 4 d after manure application,  
174 net CO<sub>2</sub> emission fluxes from all amended soils were negative, probably due to CO<sub>2</sub>  
175 consumption by soil heterotrophic microorganisms (Fangueiro et al., 2007). Soil has  
176 also been shown (Figure 2) to be a sink for CH<sub>4</sub> during the first few h after manure  
177 application, probably due to the increased amount of easily degradable organic  
178 compounds (*e.g.*, carbohydrates and volatile fatty acids) and available N that stimulate  
179 activity of methanotrophs (Chadwick et al., 1997).

180 Net N<sub>2</sub>O emissions from all amended soils peaked 24 h after manure application,  
181 but then decreased to Control levels until the end of the investigation period. Peak rates  
182 (Figure 2) ranged from 22.8 µgN<sub>2</sub>O m<sup>2</sup>/h (*i.e.*, soil amended with the solid fraction)  
183 and 217 µgN<sub>2</sub>O m<sup>2</sup>/h (*i.e.*, soil with the raw cattle slurry). Such values are lower with  
184 respect to those obtained in a recent laboratory scale experiment by Fangueiro et al.  
185 (2008b) under conditions favourable to N<sub>2</sub>O formation. Factors such as manure type, N  
186 application rate, temperature, soil type, moisture and water holding capacity of the soil

187 have been suggested by Sahrawat and Keeney (1986) to affect N<sub>2</sub>O production after  
188 manure application to soil. The low air temperature (10°C) and soil moisture content  
189 (98 g/kg), which are typical environmental conditions in many Italian areas in winter,  
190 could be the reason for low N<sub>2</sub>O emissions from soil applied manures. However, due to  
191 the short 7 d time period of flux data collection, our results should not be used for  
192 national inventory of N<sub>2</sub>O emissions from soils. Net NH<sub>3</sub> emission rates (Figure 2)  
193 from all amended soils peaked immediately following manure application and rapidly  
194 declined to Control levels after 5 d. After soil application of the liquid fraction (Table  
195 2), NH<sub>3</sub> emissions increased by about 60% compared to raw cattle slurry, probably due  
196 to its higher pH and TAN/TKN ratio ( $P<0.05$ , Table 1). Mechanical separation  
197 decreased NH<sub>3</sub> emissions after manure application (Amon et al., 2006; Balsari et al.,  
198 2008), as the low TS content of the liquid fraction may enable more rapid infiltration  
199 of NH<sub>4</sub><sup>+</sup> into soil. In this study, removal of solids from the raw cattle slurry was likely  
200 not extensive enough to improve soil infiltration of the liquid fraction. After soil  
201 application, the main GHG emitted from all manures was CO<sub>2</sub> (Table 2). Methane also  
202 contributed ( $P<0.05$ ) to overall GHG emissions, whereas the contribution of N<sub>2</sub>O and  
203 NH<sub>3</sub> was very low.

### 204 *3.3 Effect of mechanical separation on gaseous emissions*

205 In terms of CO<sub>2</sub>-eq, the cumulative CO<sub>2</sub> and NH<sub>3</sub> emissions from storage and soil  
206 application of liquid and solid fractions of mechanical separation raw cattle slurry  
207 increased by 104% and 37% from storage and by 14% and 48% with soil application,  
208 respectively. In contrast, N<sub>2</sub>O emissions from storage and soil application were  
209 reduced by 41% and 60%, respectively. Methane emissions were 14% lower from the  
210 soil application phase only. Combined CH<sub>4</sub> and N<sub>2</sub>O emissions from storage and soil  
211 application of liquid and solid fractions (Table 2) were 9% and 59% lower than those  
212 from raw cattle slurry. Nevertheless, considered as a whole, storage and soil  
213 application of separated liquid and solid fractions resulted in a net increase of 11% in  
214 GHG emissions compared with the storage and soil application of raw cattle slurry.

215

## 216 **5. Conclusions**

217 Under the conditions of this laboratory scale study, storage and soil application of  
218 both liquid and solid fractions resulted an 11% increase in GHG emissions compared  
219 to mixed raw cattle slurry. This was due to the 20% higher CO<sub>2</sub> and 44% higher NH<sub>3</sub>  
220 emissions during storage and application of both liquid and solid fractions than the

221 storage and soil application of the raw cattle slurry. Mechanical separation of cattle  
222 slurry is not recommended unless other GHG emission reduction measures are  
223 adopted. Since natural environments differ from the laboratory, results obtained from  
224 our study should be validated at under field conditions.

225

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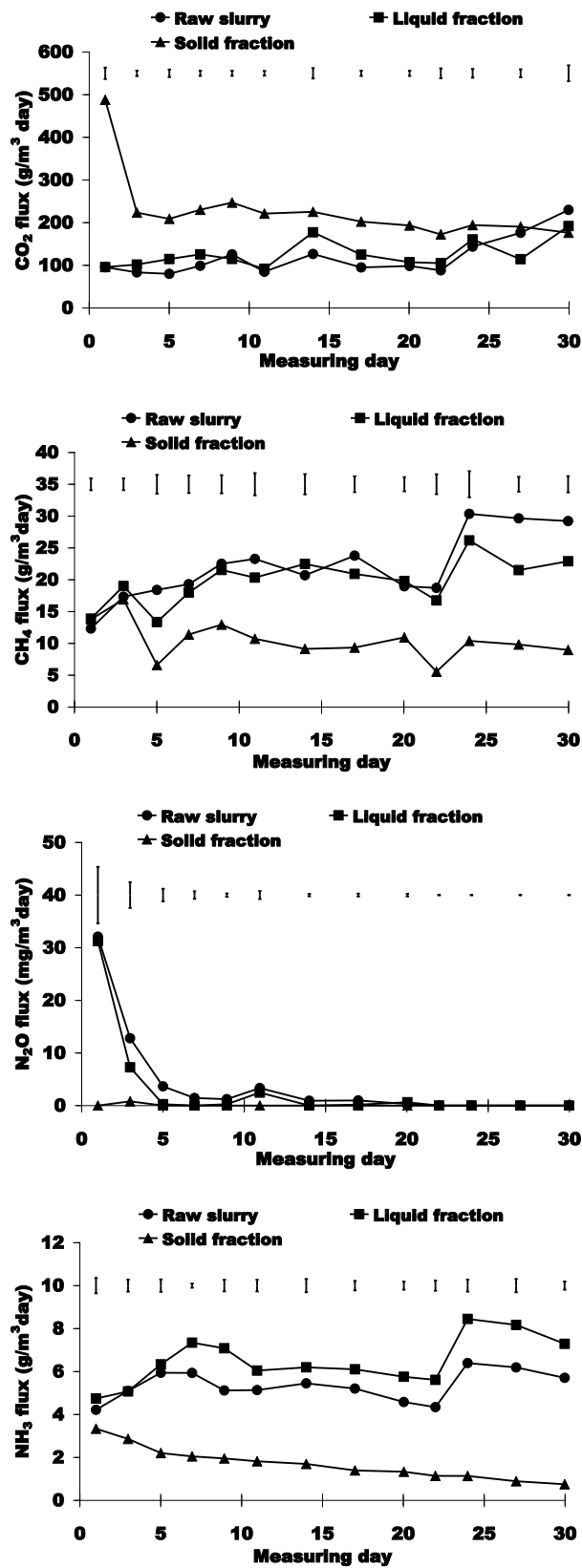
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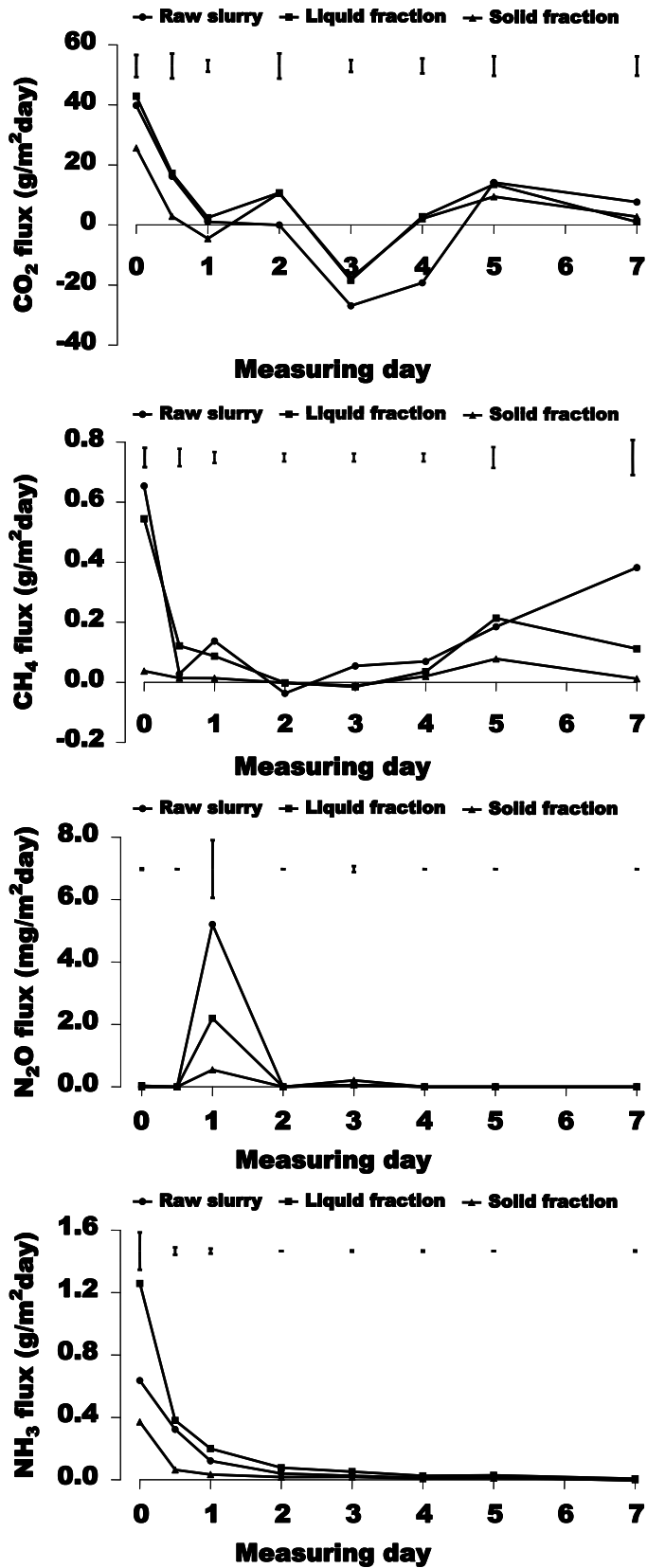
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Fig. 1.  
Average emission fluxes of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> during storage of the tested materials (raw cattle slurry, liquid fraction, solid fraction). The bars in the upper part of each graph represent Pooled standard error of mean (SEM).



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304

305 Fig. 2.  
 306 Net emission fluxes of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> after soil application of the tested materials (raw cattle  
 307 slurry, liquid fraction, solid fraction). The bars in the upper part of each graph represent Pooled standard  
 308 error of mean (SEM).  
 309



311 Table 1.

312 Composition<sup>1</sup> of the tested manures at the beginning of the storage and soil application experiments.

	<i>pH</i>	<i>TS</i> g/kg	<i>VS</i> g/kg	<i>TKN</i> g/kg	<i>TAN</i> g/kg	<i>TAN/TKN</i>	<i>TC</i> g/kg	<i>TC/TN</i>
<b>STORAGE<sup>2</sup></b>								
Raw cattle slurry	7.10	74.6	60.2	3.58	1.47	0.41	31.1	13.6
Liquid fraction	7.10	51.2	38.1	3.29	1.49	0.45	19.8	11.0
Solid fraction	8.30	192	173	5.59	1.16	0.21	83.1	27.4
<b>SOIL APPLICATION<sup>3</sup></b>								
Raw cattle slurry	6.80 c	76.7 b	61.7 b	3.32 b	1.38 a	0.42 b	32.6 b	16.0 b
Liquid fraction	7.00 b	49.9 c	36.4 c	3.23 b	1.43 a	0.44 a	18.5 c	14.2 b
Solid fraction	8.50 a	186 a	163 a	3.57 a	0.20 b	0.06 c	71.6 a	19.3 a
SEM <sup>4</sup>	0.016	0.857	0.845	0.141	0.000	0.003	1.821	0.022
P-value <sup>5</sup>	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	0.002

313 TS, Total solids; VS, volatile solids; TKN, total Kjeldahl N; TAN, total ammoniacal N; TC, total  
314 carbon; TN, total N.

315 <sup>a-c</sup> Data in a column followed by different letter differ at P<0.05.

316 <sup>1</sup> Data in table are based on fresh manure weight.

317 <sup>2</sup> Chemical analysis done on one sample.

318 <sup>3</sup> Chemical analysis done on four samples.

319 <sup>4</sup> SEM, Pooled standard error of mean.

320 <sup>5</sup> Significance level: P>0.05, not significant.

321

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323

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325

326 Table 2.

327 Cumulative emissions of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> recorded over the storage (St) and soil application  
328 (SA) experiments.

	Raw slurry		Liquid Fraction		Solid Fraction		SEM <sup>1</sup>	P-value <sup>2</sup>		
	St	SA	St	SA	St	SA		Mm	T	Mn×T
<b>C-CO<sub>2</sub></b>										
g/kg TC	91.5 c	51.2 d	155 b	246 a	204 a	41.9 d	10.92	0.032	0.011	0.009
kg CO <sub>2</sub> eq/Mg treated raw slurry ( <sup>A</sup> )	9.87 d	127 a	9.81 d	115 b	10.9 d	30.3 c	2.031	< 0.001	< 0.001	< 0.001
<b>C-CH<sub>4</sub></b>										
g/kg TC	6.40 c	13.1 a	9.01 b	12.5 a	3.48 d	0.98 e	1.094	0.013	< 0.001	0.003
kg CO <sub>2</sub> eq/Mg treated raw slurry ( <sup>B</sup> )	17.3 c	45.3 a	13.3 c	32.7 b	4.65 d	6.47 d	0.911	< 0.001	< 0.001	< 0.001
<b>N-N<sub>2</sub>O</b>										
g/kg TKN	0.03 c	0.48 a	0.02 c	0.21 b	< 0.01 c	0.07 c	0.029	< 0.001	0.006	0.014
kg CO <sub>2</sub> eq/Mg treated raw slurry ( <sup>C</sup> )	0.05 c	0.78 a	0.03 c	0.29 b	< 0.01 c	0.03 c	0.049	< 0.001	0.001	0.003
<b>N-NH<sub>3</sub></b>										
g/kg TAN	102 e	140 c	128 c	225 b	123 dc	681 a	7.748	< 0.001	< 0.001	< 0.001
kg CO <sub>2</sub> eq/Mg treated raw slurry ( <sup>D</sup> )	0.46 c	0.70 b	0.47 c	0.94 a	0.17 d	0.09 d	0.027	< 0.001	< 0.001	< 0.001
<b>Total GHG (<sup>A</sup> + <sup>B</sup> + <sup>C</sup> + <sup>D</sup>) (kg CO<sub>2</sub> eq/Mg treated raw slurry)</b>	27.6 c	174 a	23.0 dc	149 b	15.8 d	36.9 c	2.258	< 0.001	< 0.001	< 0.001

329 <sup>a-d</sup> Data in a row followed by different letter differ at P<0.05.

330 <sup>1</sup> SEM, Pooled standard error of mean.

331 <sup>2</sup> Significance level: effect of manure management phase (Mm), manure type (T), interaction (Mn × T).

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