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

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Abstract

Effects of cattle slurry mechanical separation on CO_2, CH_4, N_2O and NH_3 emissions during slurry management under winter conditions was investigated in a laboratory study. Greenhouse gas (GHG) emissions during storage and soil application of raw cattle slurry by broadcasting of its liquid and solid fractions was assessed. Carbon dioxide was the predominant emission source during both storage and soil application of manure on a CO_2-eq basis, but CH_4 was the predominant GHG emission from stored slurries. During storage, NH_3 fluxes from liquid fractions were higher than from the solid fraction, but the solid fraction was the main source of NH_3 emissions after land application: on average, ~70% of total ammoniacal N applied to soil was lost. Combining losses during storage and after soil application of both liquid and solid fractions, total CO_2-eq emissions of the combined fractions were 11% higher than that from raw cattle slurry. Results suggest that mechanical separation of cattle slurry should not be used by farmers unless other GHG emission reduction measures are adopted.

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

Abbreviations: CO_2 eq, carbon dioxide equivalents; GHG, greenhouse gas; TAN, total ammoniacal N; TC, total carbon; TKN, total Kjeldahl N; TN, total N; TS, total solids; VS, volatile solids.

1. Introduction

Storage and handling of cattle manure contributes to emissions of CO_2, CH_4, N_2O and NH_3 to the atmosphere (FAO, 2006). A report from IPCC (2007) revealed that CH_4 and N_2O are the most important greenhouse gases (GHG) in terms of climate change because of their strong absorption of infrared radiation. Goebes et al. (2003) reported that NH_3 causes various environmental problems, such as odour, eutrophication, acidification of soils, and atmospheric particulate matter formation.

In Italy, animal manure management is responsible for ~70% NH_3 (Valli et al., 2000), ~8% CH_4 and ~9% N_2O anthropogenic emissions (APAT, 2006), and their contribution to GHG air emissions is increasing due to the growing demand for animal based foods (FAO, 2006). Italy has undertaken to reduce its GHG emissions by 6.5% by 2012 relative to 1990 levels (UNFCCC, 1997). Thus, manure management practices that minimize GHG impacts on air quality need to be investigated. Mechanical 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_3 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_2, CH_4, N_2O and NH_3 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^3 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^3 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^3.

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^3 capacity, 0.20 m height, 0.10 m base diameter and 0.095 m top

111 diameter) were filled with 1000 cm^3 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^3 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

soil moisture content was 98 g/kg. Each application experiment lasted for 7.0 d, with gaseous emission measurements immediately after manure application (t= 0) and 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 7.0 d after manure application. Net CO_2, CH_4, N_2O and NH_3 emission fluxes were calculated as the difference between emission fluxes recorded from the amended soils and those measured from the Control.

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

Gaseous losses were expressed in CO_2-eq using conversion factors of 1, 25, 298, and 2.98 respectively, for CO_2, CH_4, N_2O and NH_3 (IPCC, 2007). To estimate effects of cattle slurry mechanical separation on gaseous emissions, total CO_2, CH_4, N_2O and NH_3 losses were corrected by considering mass distribution of solid (18%) and liquid (82%) fractions to the whole separated raw cattle slurry. Afterwards, total losses (Dinuccio et al., 2008) of the gases were expressed as $kgCO_2$-eq/Mg of treated raw cattle slurry.

All data were processed with ANOVA procedures. Data distribution normality was verified using the Kolmogorov–Smirnov test. Assumption of equal variance of different groups was tested using Bartlett's test. Means were separated by Tukey test and differences were considered to be significant for $P < 0.05$. All statistical analyses were performed with SPSS 12.0 for Windows (SPSS, 2006). Due to the variability of CO_2, CH_4, N_2O and NH_3 flux intensity, variances were not homogeneous when comparing different sampling days. Therefore, independent analysis were performed for each date of sampling. Cumulative CO_2, CH_4, N_2O and NH_3 emissions were analyzed by a two-way ANOVA using manure management phase (storage, soil application) and manure type (raw cattle slurry, liquid fraction, solid fraction) as fixed factors.

3. Results and Discussion

3.1 Storage experiments

153   During the 30 d storage period, the CO_2, CH_4, N_2O and NH_3 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_2-eq, CH_4 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_4 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^2/h and were lower ($P<0.05$) than those from the raw

164   cattle slurry of 0.01 to 0.28 mg m^2/h) and from the liquid fraction of 0.02 to 0.28 mg

165   m^2/h) for most of the storage period. No N_2O was detected from all manures after 20 d

166   of storage. The lowest NH_3 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_2 and CH_4 emission rates (Figure 2) from all amended soils peaked

172   immediately following manure application, probably due to release of CO_2 and CH_4

173   dissolved in slurry (Flessa and Beese, 2000). From 2 to 4 d after manure application,

174   net CO_2 emission fluxes from all amended soils were negative, probably due to CO_2

175   consumption by soil heterotrophic microorganisms (Fangueiro et al., 2007). Soil has

176   also been shown (Figure 2) to be a sink for CH_4 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_2O 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_2O m^2/h (*i.e.,* soil amended with the solid fraction)

183   and 217 μgN_2O m^2/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_2O 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_2O 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_2O 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_2O emissions from soils. Net NH_3 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_3 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_3 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_4^+ 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_2 (Table 2). Methane also

202   contributed (*P*<0.05) to overall GHG emissions, whereas the contribution of N_2O and

203   NH_3 was very low.

204   *3.3 Effect of mechanical separation on gaseous emissions*

205   In terms of CO_2-eq, the cumulative CO_2 and NH_3 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_2O 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_4 and N_2O 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_2 and 44% higher NH_3

220   emissions during storage and application of both liquid and solid fractions than the

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

References

Amon, B., Kryvoruchko, V., Amon, T., Zechmeister-Boltenstern, S., 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agric. Ecosyst. Environ. 112, 153-162.

APAT, 2006. Italian Greenhouse Gas Inventory 1990-2004. National Inventory Report 2006. Agency for Environmental Protection and Technical Services. Rome, Italy.

Balsari, P., Dinuccio, E., Santoro, E., Gioelli, F., 2008. Ammonia emissions from rough cattle slurry and from derived solid and liquid fractions applied to alfalfa pasture. Aust. J. Exp. Agric. 48, 198-201.

Berg, W., Brunsch, R., Pazsiczki, I., 2006. Greenhouse gas emissions from covered slurry compared with uncovered during storage. Agric. Ecosyst. Environ. 112, 129-134.

Burton, C.H., 2007. The potential contribution of separation technologies to the management of livestock manure. Livest. Sci. 112, 208-216.

Chadwick, D.R., Pain, B.F., 1997. Methane fluxes following slurry applications to grassland soils: Laboratory experiments. Agric. Ecosyst. Environ. 63, 51-60.

Dinuccio, E., Berg, W., Balsari, P., 2008. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. Atmos. Environ. 42, 2448-2459.

Fangueiro, D., Chadwick, D., Dixonb, L., Bol, R., 2007. Quantification of priming and CO_2 emission sources following the application of different slurry particle size fractions to a grassland soil. Soil Biol. Biochem. 39, 2608-2620.

Fangueiro, D., Coutinho, J., Chadwick, D., Moreira, N., Trindade, H., 2008a. Effect of Cattle Slurry Separation on Greenhouse Gas and Ammonia Emissions during Storage. J. Environ. Qual. 37, 2322-2331.

Fangueiro, D., Pereira, J., Chadwick, D., Coutinho, J., Moreira, N., Trindade, H., 2008b. Laboratory assessment of the effect of cattle slurry pre-treatment on organic

254   N degradation after soil application and N_2O and N_2 emissions. Nutr. Cycl.

255   Agroecosyst. 80, 107-120.

256 FAO, 2006. Livestock's Long Shadow: Environmental Issues and Options. Rome,

257   Italy.

258 Flessa, H., Beese, F., 2000. Laboratory estimates of trace gas emissions following

259   surface application and injection of cattle slurry. J. Environ. Qual. 29, 262-268.

260 Goebes, M.D., Strader, R., Davidson, C., 2003. An ammonia emission inventory for

261   fertilizer application in the United States. Atmos. Environ. 37, 2539–2550.

262 Hao, X., Chang, C., Larney J.F., 2004. Carbon, Nitrogen Balances and Greenhouse

263   Gas Emission during Cattle Feedlot Manure Composting. J. Environ. Qual. 33, 37-

264   44.

265 Heiermann, M., Plöchl, M., Linke, B., Schelle, H., Herrmann, C., 2009. "Biogas Crops

266   – Part I: Specifications and Suitability of Field Crops for Anaerobic Digestion".

267   Agricultural Engineering International: the CIGR Ejournal. Manuscript 1087. Vol.

268   XI.

269 IPCC, 2007. Climate change 2007: The physical science basis. Contribution of

270   Working Group I to the Fourth Assessment Report of the Intergovernmental Panel

271   on Climate Change. Cambridge University Press, Cambridge, UK and New York,

272   NY, USA.

273 Misselbrook, T.H., Brookman, S.K.E., Smith, K.A., Cumby, T., Williams, A.G.,

274   McCrory, D.F., 2005. Crusting of Stored Dairy Slurry to Abate Ammonia

275   Emissions: Pilot-Scale Studies. J. Environ. Qual. 34, 411-419.

276 Møller, H.B., Hansen, J.D., Sorensen, C.A.G., 2007. Nutrient recovery by solid-liquid

277   separation and methane productivity of solids. Transactions of the ASABE 50, 193-

278   200.

279 Pattey, E., Trzcinski, M.K., Desjardins, R.L., 2005. Quantifying the reduction of

280   green-house gas emissions as a result of composting dairy and beef cattle manure.

281   Nutr. Cycl. Agroecosyst. 72 (2), 173-187.

282 Plöchl, M., Hilse, A., Heiermann, M., Suarez, T., Budde, J., Prochnow, A., 2009.

283   "Hydrolytic enzymes improve fluidity of biogas feedstock". Agricultural

284   Engineering International: the CIGR Ejournal. Manuscript 1529. Vol. IX.

285 Sahrawat, K.L., Keeney, D.R., 1986. Nitrous oxide emission from soils. Adv. Soil Sci.

286   4, 103-148.

287 SPSS, 2006. SPSS for windows: Advanced statistics, Release 12.0. SPSS, Chicago, IL.

288 UNFCCC, 1997. The Kyoto Protocol. United Nations Framework Convention on
289   Climate Change. http://unfccc.int/essential background/convention/items/2627.php
290 USDA, 1977. Keys to Soil Taxonomy. Soil Survey Staff, Soil Conservation Service
291   U.S. Dept. Of Agriculture, 7th edition. Pocahontas Press, Inc., Blacksburg, VA,
292   USA.
293 Valli, L., Fabbri, C., Bonazzi, G., 2000. A national inventory of ammonia and
294   greenhouse gas emissions from agriculture in Italy. In: Sangiorgi, F. (Ed.),
295   Technology Transfer: Proceedings of the Ninth International RAMIRAN 2000
296   Workshop, Gargnano, Italy, 6-9 September 2000, Cemagref, France, pp. 153-159.
297

298 Fig. 1.
299 Average emission fluxes of CO_2, CH_4, N_2O and NH_3 during storage of the tested materials (raw cattle
300 slurry, liquid fraction, solid fraction). The bars in the upper part of each graph represent Pooled standard
301 error of mean (SEM).
302

303
304
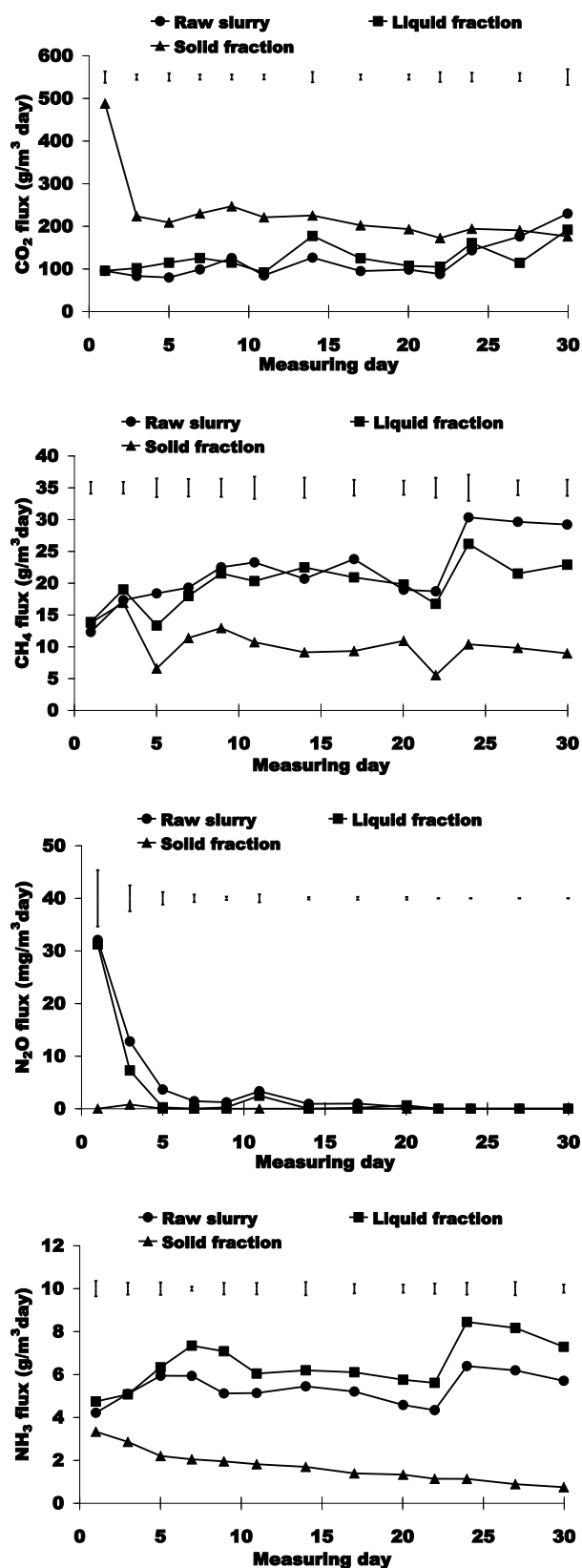
305 Fig. 2.
306 Net emission fluxes of CO_2, CH_4, N_2O and NH_3 after soil application of the tested materials (raw cattle
307 slurry, liquid fraction, solid fraction). The bars in the upper part of each graph represent Pooled standard
308 error of mean (SEM).
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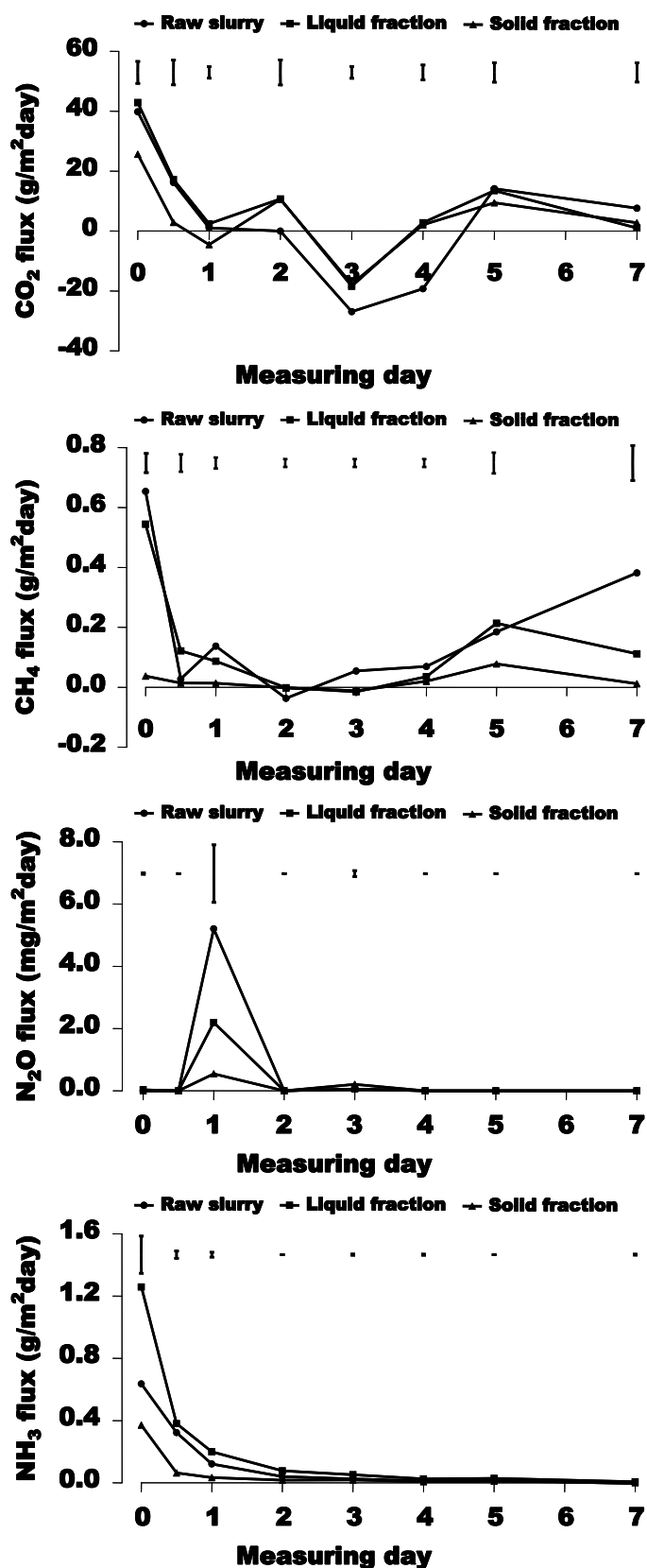
Table 1.
Composition[1] of the tested manures at the beginning of the storage and soil application experiments.

	pH	TS g/kg	VS g/kg	TKN g/kg	TAN g/kg	TAN/TKN	TC g/kg	TC/TN
STORAGE[2]								
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
SOIL APPLICATION[3]								
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[4]	0.016	0.857	0.845	0.141	0.000	0.003	1.821	0.022
P-value[5]	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	0.002

TS, Total solids; VS, volatile solids; TKN, total Kjeldahl N; TAN, total ammoniacal N; TC, total carbon; TN, total N.
[a-c] Data in a column followed by different letter differ at $P<0.05$.
[1] Data in table are based on fresh manure weight.
[2] Chemical analysis done on one sample.
[3] Chemical analysis done on four samples.
[4] SEM, Pooled standard error of mean.
[5] Significance level: P>0.05, not significant.

Table 2.
Cumulative emissions of CO_2, CH_4, N_2O and NH_3 recorded over the storage (St) and soil application (SA) experiments.

	Raw slurry St	Raw slurry SA	Liquid Fraction St	Liquid Fraction SA	Solid Fraction St	Solid Fraction SA	SEM[1]	P-value[2] Mm	P-value[2] T	P-value[2] Mn×T
C-CO$_2$										
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$_2$ eq/Mg treated raw slurry (^{A})	9.87 d	127 a	9.81 d	115 b	10.9 d	30.3 c	2.031	< 0.001	< 0.001	< 0.001
C-CH$_4$										
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$_2$ eq/Mg treated raw slurry (^{B})	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
N-N$_2$O										
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$_2$ eq/Mg treated raw slurry (^{C})	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
N-NH$_3$										
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$_2$ eq/Mg treated raw slurry (^{D})	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
Total GHG ($^A + ^B + ^C + ^D$) (kg CO$_2$ eq/Mg treated raw slurry)	27.6 c	174 a	23.0 dc	149 b	15.8 d	36.9 d	2.258	< 0.001	< 0.001	< 0.001

[a-d] Data in a row followed by different letter differ at $P<0.05$.
[1] SEM, Pooled standard error of mean.
[2] Significance level: effect of manure management phase (Mm), manure type (T), interaction (Mn $\times$ T).