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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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Abstract

Effects of cattle slurry mechanical separation on CO₂, CH₄, N₂O and NH₃ 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 CO₂-eq basis, but CH₄ was the predominant GHG emission from stored slurries. During storage, NH₃ fluxes from liquid fractions were higher than from the solid fraction, but the solid fraction was the main source of NH₃ 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 CO₂-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: CO₂ 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 CO₂, CH₄, N₂O and NH₃ to the atmosphere (FAO, 2006). A report from IPCC (2007) revealed that CH₄ and N₂O 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 NH₃ 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% NH₃ (Valli et al., 2000), ~8% CH₄ and ~9% N₂O 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

common practice in Italy, due to the ability to improve the flexibility of slurry application and reduce environmental risks (Burton, 2007). On farms where land area is insufficient for disposal of N in slurry, separation of the solids can also reduce manure transport costs (Balsari et al., 2008), thereby making it easier for producers to conform to the manure N limits set by the Nitrates Directive (91/676/EC). However, mechanical separation of slurry has the potential to increase GHG and NH₃ emissions compared to traditional slurry management (Amon et al., 2006; Dinuccio et al., 2008; Fangueiro et al., 2008a), mainly due to high emissions during storage of the solid fraction. In contrast, the effect of mechanical separation of slurry on gaseous emissions on overall slurry management (*i.e.*, storage + land application) is not yet clear due to the lack of experimental data. With the aim to cover this knowledge gap, a laboratory scale study was completed in order to assess CO₂, CH₄, N₂O and NH₃ emissions from storage and soil application of raw cattle slurry by broadcasting separated liquid and solid fractions.

2. Materials and methods

The experiment was a randomised block design with three treatments being: (1) raw cattle slurry, (2) separated liquid and (3) separated solid manure and four replicates per treatment. Raw cattle slurry (~21 kg) was separated using a lab scale mechanical separator as described by Dinuccio et al. (2008). Samples of 1000 cm³ of each manure type were stored at 5 ± 0.5 °C for a period of 30 d in an open vessel with 1500 cm³ capacity and gas samples were collected and analyzed at 2 to 3 d intervals. The bulk density of the solid fraction was estimated at 0.40 kg 1000 cm³.

After storage, replicate samples were collected and used in a soil application experiment which was in a climate controlled room at 10 ± 0.5 °C. Open glass vessels with 1500 cm³ capacity, 0.20 m height, 0.10 m base diameter and 0.095 m top diameter) were filled with 1000 cm³ of soil. The soil was a loamy sand soil (USDA, 1977) with 837 g/kg sand, 143 g/kg silt, 19.4 g/kg clay; pH = 7.43, total C = 8.79 g/kg, total N = 1.18 g/kg. After collection, the soil was sieved through a 4 mm screen and stored in moist form, in the dark, at 4°C prior to the start of the experiments. The bulk density of 1.16 g cm³ of the undisturbed soil was achieved by shaking the vessels until the required soil volume was reached. The tested manures were homogeneously applied on the soil surface at a rate of 70 kg/ha of total Kjeldahl N (TKN). Non-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

During the 30 d storage period, the CO₂, CH₄, N₂O and NH₃ emission fluxes measured from the raw cattle slurry and its liquid fraction showed similar trends (Figure 1). Carbon dioxide was the main GHG (Table 2) emitted during storage of the solid fraction, in agreement with findings of Hao et al., (2004) and Pattey et al., (2005). In term of CO₂-eq, CH₄ emission was the predominating GHG from stored liquid manures, a finding supported by Berg et al. (2006). After 30 d of storage, the amount of C lost by CH₄ emissions (Table 2) from the liquid fraction was higher ($P<0.05$) than that lost from the raw cattle slurry, suggesting that mechanical separation of the solids reduced the amount of carbon that was available for methanogenesis (Amon et al., 2006; Møller et al., 2007). Nitrous oxide fluxes (Figure 1) from the solid fraction ranged from 0.001 to 0.007 mg m²/h and were lower ($P<0.05$) than those from the raw cattle slurry of 0.01 to 0.28 mg m²/h and from the liquid fraction of 0.02 to 0.28 mg m²/h for most of the storage period. No N₂O was detected from all manures after 20 d of storage. The lowest NH₃ emission rates (Figure 1) were from the solid fraction, but were higher from the liquid fraction ($P<0.05$) compared to the raw cattle slurry for most of the storage period. This was mainly due its lower TS content (Table 1), which reduced development of a natural surface crust (Misselbrook et al., 2005).

3.2 Application experiments

Net CO₂ and CH₄ emission rates (Figure 2) from all amended soils peaked immediately following manure application, probably due to release of CO₂ and CH₄ dissolved in slurry (Flessa and Beese, 2000). From 2 to 4 d after manure application, net CO₂ emission fluxes from all amended soils were negative, probably due to CO₂ consumption by soil heterotrophic microorganisms (Fangueiro et al., 2007). Soil has also been shown (Figure 2) to be a sink for CH₄ during the first few h after manure application, probably due to the increased amount of easily degradable organic compounds (*e.g.*, carbohydrates and volatile fatty acids) and available N that stimulate activity of methanotrophs (Chadwick et al., 1997).

Net N₂O emissions from all amended soils peaked 24 h after manure application, but then decreased to Control levels until the end of the investigation period. Peak rates (Figure 2) ranged from 22.8 µgN₂O m²/h (*i.e.*, soil amended with the solid fraction) and 217 µgN₂O m²/h (*i.e.*, soil with the raw cattle slurry). Such values are lower with respect to those obtained in a recent laboratory scale experiment by Fangueiro et al. (2008b) under conditions favourable to N₂O formation. Factors such as manure type, N application rate, temperature, soil type, moisture and water holding capacity of the soil

have been suggested by Sahrawat and Keeney (1986) to affect N₂O production after manure application to soil. The low air temperature (10°C) and soil moisture content (98 g/kg), which are typical environmental conditions in many Italian areas in winter, could be the reason for low N₂O emissions from soil applied manures. However, due to the short 7 d time period of flux data collection, our results should not be used for national inventory of N₂O emissions from soils. Net NH₃ emission rates (Figure 2) from all amended soils peaked immediately following manure application and rapidly declined to Control levels after 5 d. After soil application of the liquid fraction (Table 2), NH₃ emissions increased by about 60% compared to raw cattle slurry, probably due to its higher pH and TAN/TKN ratio ($P<0.05$, Table 1). Mechanical separation decreased NH₃ emissions after manure application (Amon et al., 2006; Balsari et al., 2008), as the low TS content of the liquid fraction may enable more rapid infiltration of NH₄⁺ into soil. In this study, removal of solids from the raw cattle slurry was likely not extensive enough to improve soil infiltration of the liquid fraction. After soil application, the main GHG emitted from all manures was CO₂ (Table 2). Methane also contributed ($P<0.05$) to overall GHG emissions, whereas the contribution of N₂O and NH₃ was very low.

3.3 Effect of mechanical separation on gaseous emissions

In terms of CO₂-eq, the cumulative CO₂ and NH₃ emissions from storage and soil application of liquid and solid fractions of mechanical separation raw cattle slurry increased by 104% and 37% from storage and by 14% and 48% with soil application, respectively. In contrast, N₂O emissions from storage and soil application were reduced by 41% and 60%, respectively. Methane emissions were 14% lower from the soil application phase only. Combined CH₄ and N₂O emissions from storage and soil application of liquid and solid fractions (Table 2) were 9% and 59% lower than those from raw cattle slurry. Nevertheless, considered as a whole, storage and soil application of separated liquid and solid fractions resulted in a net increase of 11% in GHG emissions compared with the storage and soil application of raw cattle slurry.

5. Conclusions

Under the conditions of this laboratory scale study, storage and soil application of both liquid and solid fractions resulted an 11% increase in GHG emissions compared to mixed raw cattle slurry. This was due to the 20% higher CO₂ and 44% higher NH₃ 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.

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Fig. 1.
Average emission fluxes of CO₂, CH₄, N₂O and NH₃ 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).

Fig. 2.
Net emission fluxes of CO₂, CH₄, N₂O and NH₃ after soil application 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).

Table 1.

Composition¹ 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>
STORAGE²								
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 APPLICATION³								
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 CO₂, CH₄, N₂O and NH₃ recorded over the storage (St) and soil application (SA) experiments.

	Raw slurry		Liquid Fraction		Solid Fraction		SEM ¹	P-value ²		
	St	SA	St	SA	St	SA		Mm	T	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 c	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 × T).