

# Effect of mechanical separation of digested slurry on greenhouse gas and ammonia emissions during storage

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## Abstract

In our days biogas plants are more and more common at farm facilities and the management of the digestate raise some concern for the possible emissions to air. The aim of this study was to evaluate how the mechanical separation affects ammonia (NH<sub>3</sub>) and greenhouse gas (GHG) emissions from the storage of the different fractions obtained from separation of codigested slurry. Flux measurements were estimated with static and dynamic systems on untreated digestate (UDS) and the solid (SF) and liquid (LF) fractions after separation during 32 days of storage. In the static system the UDS emitted less than the treated digested slurry (TDS = SF + LF), evidencing an important role of the total solids content in the emission process. On the contrary in the dynamic system UDS emitted more than the others fraction; in this case it seems that the emission driving force is the nitrogen content. Results also demonstrated that, not always NH<sub>3</sub> emissions can be effectively measured both with photoacoustic gas analyser or the widely diffused acid trap method.

## Introduction

The storage of effluents in our days is strictly regulated and must be compatible with the time of spreading and with crop requirements. Very often this means long storage time causing substantial organic matter degradation with subsequent uncontrolled release of CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub>.

The factors that influence the emission flux are numerous: the temperature, the duration of storage, the agitation and the filling system. Mitigation options can only be proposed, if knowledge on emissions from manure management is improved. [1] already proved that anaerobic digestion is an effective means to reduce GHG emission. This study examines the effect of mechanical separation of digested slurry on GHGs and NH<sub>3</sub> emissions during storage. Furthermore it investigates different methods and techniques available for the evaluation of GHGs and NH<sub>3</sub>. The activity has been carried out in the framework of a research project aimed at finding slurry treatment options that reduce NH<sub>3</sub> and GHGs emissions during slurry storage.

## Material and Methods

The study was conducted in a room kept at  $17 \pm 0.2$  °C between September and October 2012. The different fractions of the pig codigested slurry were collected in a biogas plant (1 MWe) of located in Martinengo (BG), Italy. The untreated digested slurry (UDS) was subjected to a mechanical separation with a screw press separator generating a solid (SF) and a liquid fraction (LF). Mechanical separation took place 24 h before the beginning of the storage experiment. For each treatment, two 35 l plastic open vessels (operative volume 25 l) were filled with the effluents ( UDS, SF and LF) for a storage period of 32 days.

The samples were analysed for pH, total solid (TS), volatile solids (VS), total Kjeldhal nitrogen (TKN), total ammonia nitrogen (TAN) once week and at the end of the investigation period. The temperature of the slurry and the manure were measured continuously using temperature sensors connected to a data-logger. Gas measurements took place twice a week with a dynamic chamber method. On each sampling day the vessels were gently stirred and subsamples of one l were transferred into 2 l bottles (headspace: 1 l). To determine the correct evolution of emissions an air flow of 1 l/min was established at least 30 min before the gas sampling to reach a steady state. One air outlet, positioned in the lid of each bottle, was connected to two serial acids traps, working 24 h, filled with 1% boric acid. The NH<sub>3</sub> trapped was determined by a titration method. Between the traps and the bottle there was an empty flask connected to a gas trace analyser (P-TGA) (1302 Photoacoustic gas-monitor, Innova AirTech Instruments, Denmark) for the determination of CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub> concentrations. The TGA was run manually with corrections from cross-interferences between CO<sub>2</sub> and N<sub>2</sub>O and between CH<sub>4</sub> and N<sub>2</sub>O [2]. Net total emissions of GHGs, expressed as CO<sub>2</sub> equivalents, were estimated from CH<sub>4</sub> and N<sub>2</sub>O emissions using conversions factors of 310 and 21 for N<sub>2</sub>O and CH<sub>4</sub> respectively [3]. The sum of gas losses observed from each slurry fraction was compared with those related to the UDS to estimate the influence of slurry separation treatment on gaseous emissions. The sum of losses was calculated taking into account the proportion of each fraction relative to the UDS. Lastly two

typologies of emission factors were calculated; the first (1), calculated on the basis of chemical analyses (the lost quantity of TAN, TKN, ST of the SF, LF, TDS was compared with that one lost from the UDS), was considered representative of the vessel static system, while the second (2), calculated on the basis of the cumulative emissions, was considered representative of the dynamic bottle system. In both systems the UDS has been considered as reference and with an emission factor equal to 1.

The data were analysed and elaborated using the software packages SAS 8.2 (SAS Institute Inc, 2004). The relation between two variables was analysed by linear regression (REG SAS procedure). The differences between treatments were analysed by ANOVA using the general linear model (SAS GLM proc.). The level of significance was set at  $P < 0.05$ .

## Results and discussion

Table 1 reports the chemical characterization of the different effluents at the beginning and at the end of the storage period. The statistical analysis of the TAN, TKN and VS reductions showed that there were no significant differences for the UDS and LF, between the values recorded during the study. That means a constant (TAN e TKN) or no reduction (SV) over the time of these parameters. Contrarily the SF and consequently the TDF showed significant differences concerning the TAN. As can be seen from the fourth week the TAN concentration falls down, from 2.0 g/kg to 0.2 g/kg (Table 1).

**Table 1. UDS, SF, LF compositions at the beginning and at the end of the storage period (mean  $\pm$  standard deviation)**

Untreated digested slurry (UDS)	TS (g/kg)	VS (g/kg)	TKN (g/kg)	TAN (g/kg)	TAN/TKN %	PH
START	5.09 $\pm$ 0.06	3.63 $\pm$ 0.39	3.11 $\pm$ 0.06	1.95 $\pm$ 0.04	63%	8.02 $\pm$ 0.02
END	5.25 $\pm$ 0.03	3.89 $\pm$ 0.03	2.65 $\pm$ 0.01	1.34 $\pm$ 0.02	50%	8.05 $\pm$ 0.08
<b>Solid fraction (SF)</b>						
START	22.68 $\pm$ 0.06	20.17 $\pm$ 0.15	5.66 $\pm$ 0.04	2.03 $\pm$ 0.16	36%	
END	23.20 $\pm$ 0.67	20.39 $\pm$ 0.61	4.38 $\pm$ 0.34	0.17 $\pm$ 0.02**	4%	
<b>Liquid fraction (LF)</b>						
START	3.41 $\pm$ 0.31	2.39 $\pm$ 0.27	3.11 $\pm$ 0.04	1.86 $\pm$ 0.04	60%	7.99 $\pm$ 0.01
END	3.70 $\pm$ 0.03	2.40 $\pm$ 0.01	2.49 $\pm$ 0.01	1.29 $\pm$ 0.02	52%	8.11 $\pm$ 0.01

For UDS and the LF a good correlation ( $R_{DS}^2=0,74$ ;  $R_{LF}^2=0,90$ ) between the  $NH_3$  emissions and TAN was found. Thus when the TAN decreased also the  $NH_3$  flux ( $mg\ m^{-2}h^{-1}$ ) decreased.

To establish a relation between the emissions and the TAN the fluxes were corrected for a coefficient that takes into account the  $NH_3$  concentration variation in time. The new fluxes ( $g\ t^{-1}\ d^{-1}$ ) obtained, between the days, were similar ( $P > 0.05$ ) for the UDS and LF, while SF and TSD fluxes were significantly different: SF reported a marked reduction of  $NH_3$  flux (from 165 to 0  $g\ t^{-1}d^{-1}$ ) from the third week, a characteristic that can be considered representative of the superficial layer of a heap of a SF [4]. It is evident in the TSD the influence of the SF trend. On average TDS and UDS are statically different ( $P < 0.001$ ). Between the days the mains are similar for the first two weeks and then they begin to be different, with TDS (average flux:  $63.1 \pm 2.7\ g\ t^{-1}d^{-1}$ ) characterized by lower  $NH_3$  emissions than UDS ( $72.4 \pm 0.5\ g\ t^{-1}d^{-1}$ ) (Figure 1).

Slurry stored in the vessels are predominantly anaerobic, thus there is little or no oxidation [5]. That's the reason why, observing Table 2, the emission factors calculated on TKN basis can be considered indicative of the real  $NH_3$  emitted from the sample: the SF emitted almost 3 times more than the UDS. Also the LF in the vessel emits more than UDS (+ 34%). Contrarily observing the factors obtained from the cumulative emission of the bottle, the separated fractions (SF = 0.96; LF = 0.89; TDS = 0.90) emitted less than the UDS; in the bottles, filled with disturbed samples, the emissions are mainly affected by the TAN. Thus the samples (UDS) characterized by a higher ammonia concentration and a higher value of the TAN/TKN ratio emitted more than the others (TDS). Instead in the vessels, systems which can be considered only partially disturbed (these are mixed for few seconds only twice a week), other factors are important in the emission process. It seems that UDS, characterized by a major TS contents, even if a crust was not developed, shows higher resistance to the  $NH_3$  diffusion from the liquid to the atmosphere; thus in the vessel the UDS emitted less than the TDS.

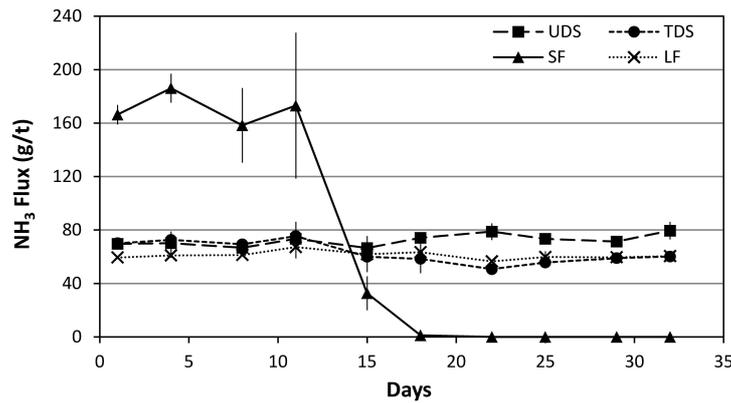


Figure 1. Net emission fluxes of NH<sub>3</sub> (related to the TAN) from the untreated (UDS) and the treated digested slurry (TDS). Errors bars represent the 1.96 standard error.

The reduction of total carbon in the vessels was limited and the differences not detectable with the methodology used. On the contrary the emission factors (Table 2), derived by the cumulative emissions (2), can be considered representative of what can happen in a disturbed system like the bottles are. In this case it was observed the carbon emissions were strictly related to TS content. The SF (22 - 25% TS) and the LF (3.1 - 2.5% TS) emitted almost 5 time more and half less, respectively, compared to the UDS.

Table 2. Emission factors calculated by the analyses (1) and by the fluxes measured in the bottle (2)

	1				2			
	UDS	SF	LF	TDS	UDS	SF	LF	TDS
TAN	1	3.03	0.93	1.14	1	0.95	0.89	0.90
TKN	1	2.75	<b>1.34</b>	<b>1.48</b>	<b>1</b>	<b>0.96</b>	<b>0.89</b>	<b>0.90</b>
C tot	1	nd	nd	nd	1	<b>4.67</b>	<b>0.50</b>	<b>0.91</b>

Table 3. Cumulative emissions of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> from untreated and treated digested slurry, solid fraction, over the storage experiment obtained from the dynamic chamber method (mean ± standard deviation)

	UDS	SF	LF	TDS
NH <sub>3</sub> (kg t <sup>-1</sup> )	1.9 ± 0.01	1.81 ± 0.05	1.69 ± 0.011	1.7 ± 0.02
<b>GHGs emissions ( kg CO<sub>2</sub> eq.t<sup>-1</sup>)</b>				
CO <sub>2</sub>	15.8 ± 5.75	74.2 ± 17.34	7.86 ± 2.34	14.49 ± 0.39
CH <sub>4</sub>	1.10 ± 0.093	1.45 ± 0.98	0.52 ± 0.03	0.61 ± 0.12
N <sub>2</sub> O	5.4 ± 0.005	25.42 ± 2.74	4.73 ± 1.65	6.81 ± 1.76
tot	22.35 ± 5.85	101.104 ± 21.1	13.12 ± 4.04	21.92 ± 2.27
% CO <sub>2</sub> /tot	70.7	73.4	59.9	66.122
% CH <sub>4</sub> /tot	4.9	1.4	3.9	2.8
% N <sub>2</sub> O/tot	24.3	25.1	36.2	31.1

Further Table 3 shows that the treatment permitted a 11% reduction of NH<sub>3</sub> emissions. On the basis of CO<sub>2</sub> eq. CH<sub>4</sub> (40%) and CO<sub>2</sub> (8%) emissions reductions were also observed in the TDS. On the contrary the treatment increased the N<sub>2</sub>O emissions; this gas has very high weight (310) in terms of CO<sub>2</sub> eq. This increase was in particular caused by the SF, were dry condition, together with the air-filled porosity, may explain the occurrence of N<sub>2</sub>O production from pig SF samples. Thus the treatment did not mean a significant reduction of total GHGs emission. In any case, during the storage period the predominant carbon emission was in the form of CO<sub>2</sub>.

Concerning the comparison between the two techniques (P-TGA and acid trap) for the NH<sub>3</sub> flux estimation, the measurements were significantly different, confirmed by the low determination coefficient (R<sup>2</sup> = 0.36)

(Figure 2B), with fluxes greater than  $50 \text{ mg m}^{-2} \text{ h}^{-1}$ : those ones derived from the acid traps were always higher than those calculated by the TGA. This difference might be explained by the different measurement period but can be also affected by the instrument. With fluxes concentration inferior to  $50 \text{ mg m}^{-2} \text{ h}^{-1}$  (Figure 2A) no significant differences were found resulting in high determination coefficient ( $R^2 = 0.90$ ).

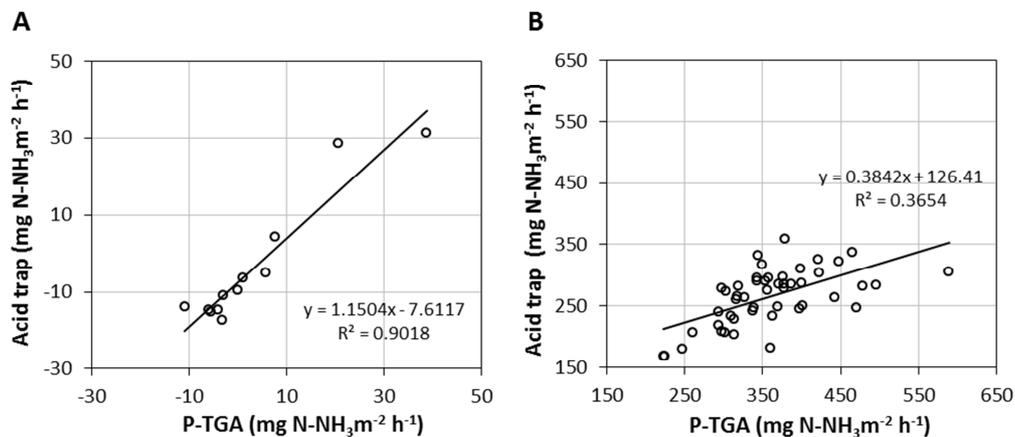


Figure 2. Linear regression between net NH<sub>3</sub> emissions estimated by dynamic chamber method using acid traps (y) and P-TGA (x) methods, with fluxes <  $50 \text{ mg m}^{-2} \text{ h}^{-1}$  (A) and fluxes >  $50 \text{ mg m}^{-2} \text{ h}^{-1}$  (B)

### Conclusions and perspectives

The experiment compared the emissions (NH<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>) of the same effluent in a dynamic system (bottle) and in a static system (vessel). The effects of the solid-liquid separation on the emissions gave contrasting results with the two systems. It was found that when the effluents are disturbed (in the bottle system), the main factor in the nitrogen emission seems to be the NH<sub>3</sub> concentration, while in undisturbed system, like the vessels, the TS content can play an important role. Thus in the bottle, on CO<sub>2</sub>-eq basis the treatment did not affect significantly the GHG, while NH<sub>3</sub> emissions were reduced by up to 15%. On the contrary, in the static system the UDS has reported the lowest nitrogen emission, almost 50% less than the treated effluent. However to confirm these observations, more investigations are necessary to understand the emission behaviour in a static and in a dynamic system.

This study gave operational guidelines, useful for the digested slurry management of biogas plants, which will play a major role in the reduction of GHG emissions as they generate renewable energy and reduce NH<sub>3</sub> and GHGs emissions during manure storage.

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