

ASSESSMENT OF CO₂ EMISSIONS DURING ACIDIFICATION, STORAGE, AND AFTER INCORPORATION TO SOIL OF PIG SLURRY

Fangueiro D., Gusmão M., Surgy S., Cabral F.

UIQA-Instituto Superior de Agronomia, TU Lisbon, Tapada da Ajuda, 1349-017 Lisboa, Portugal.

Tel:+351 21 3653199. dfangueiro@isa.utl.pt

1 INTRODUCTION

Large amounts of pig slurry are produced each year in Portugal leading to environmental problems such as water and air pollution. Previous studies have reported that livestock production is the main source of anthropogenic ammonia (NH₃) emissions in Europe (Kai et al., 2008) and an important source of greenhouse gases (Weiske and Petersen, 2006). Effluent treatment has been promoted to improve slurry management and to reduce its environmental impact (Sommer and Hutchings, 2001, Fangueiro et al., 2008a). Solid-liquid separation of slurry is a useful tool at the farm level producing valuable fractions, a liquid that can be used for direct fertilisation and a solid fraction that can be composted (Fangueiro et al., 2008b). Alternatively, acidification of slurry has been proposed to reduce ammonia (NH₃) emissions during storage and field application (Kai et al., 2008). Previous works (Misselbrook et al., 2005; Fangueiro et al., 2008a) reported that higher NH₃ emissions occurred during storage of liquid fraction of slurry or manure with low dry matter content, probably due to a reduced crust formation that decreases NH₃ emissions. Hence, acidification of the liquid fraction of slurry is strongly recommended. Slurry acidification is common practice in The Netherlands and Denmark (Schils et al., 1999; Eriksen et al., 2008) but this technology still needs to be improved to avoid hazards. It is expected that this technology will be used in more countries since the European Directive (2001/81/CE) demands a decrease of atmospheric pollutants such as NH₃; targets for lower NH₃ emissions have been already set in Spain (Castrillon et al., 2009). Nevertheless, the acidification process leads to significant carbon dioxide (CO₂) emissions (Vandré and Clemens, 1997). Such CO₂ release is problematic when a closed system of slurry acidification is used (when acidified slurry is flushed back to pig houses) since it may lead to foam formation (Vandré and Clemens, 1997; Borst, 2001). Nevertheless, Fangueiro et al. (2010) reported that acidification of slurry or derived fractions led to a decrease in CO₂ emissions following soil addition relative to non acidified materials.

The aim of the present work was to measure the CO₂ emissions during the acidification process of the liquid fraction of pig slurry and its subsequent impact during storage and after soil incorporation.

2 MATERIALS AND METHODS

2.1 CO₂ emissions during acidification and storage

The slurry used in this study was taken from a lagoon of a pig farm located in Rio Maior (Portugal). The liquid fraction (LF) of pig slurry was obtained by sieving (mesh size 100 µm). Half of the screened fraction was preserved at its original pH and the second half was acidified to pH 5.5 by addition of concentrated sulphuric acid. The acidification procedure was as follows: 50 g of liquid fraction were placed into 250 ml plastic containers which were subsequently put into 1.5 l glass jars containing a separate vessel with 20 ml of 1M NaOH solution to trap any CO₂ evolved. Addition of the sulphuric acid to the liquid fraction of slurry was performed using a syringe passed through a septum located in the lid of the jars (see Figure 1). The liquid fraction was stirred during the acidification process. The non acidified liquid fraction was also stirred during the same time period. After 0.25, 0.75, 1.75, 2.75, 3.75, 4.75, 5.75, 29.75, 47.5, 77.5, 149.5 and 197.5 hours, the vessel with 20 ml of a 1M NaOH solution was removed, resealed and stored until analysis for CO₂ and replaced by another vessel with fresh NaOH. The CO₂ trapped in the NaOH was analyzed by a colorimetric method on a segmented flow autoanalyzer (Skalar, The Netherlands, sample flow = 0.16 mL min⁻¹). Each treatment was conducted in triplicate.

2.2 CO₂ emissions after soil incorporation

At the moment of soil incorporation tests, the slurry organic carbon and dry matter content were, respectively, 6.7 g C L⁻¹ and 21.3 g.L⁻¹ in the acidified slurry, and 5.5 g C L⁻¹ and 17.04 g.L⁻¹ in the non acidified slurry. Amounts of acidified and non acidified liquid fractions were applied to 60 g of dry soil equivalent at a rate of 0.8 g C kg⁻¹ dry

soil. Before the experiment, the soil moisture had been adjusted to 60% of its water holding capacity and then incubated at 25 °C for 7 days in order to slowly re-activate the microbial activity. 250 ml plastic containers containing mixtures of soil+slurry were subsequently put into 1.5 l glass jars containing a vessel with 20 ml of distilled water to avoid soil desiccation and a vessel with 20 ml of 1M NaOH solution to trap any evolved CO₂. A control (soil only) was also used. The jars were sealed with air-tight glass lids and held at 25 °C for 104 days. After 1, 3, 8, 21, 42, 56, 77 and 104 days, the vessel with 20 ml of a 1M NaOH solution was removed, resealed and stored until analysis for CO₂ and replaced by a vessel containing fresh NaOH. The CO₂ trapped in NaOH was analyzed as previously described. Each treatment was replicated 5 times.

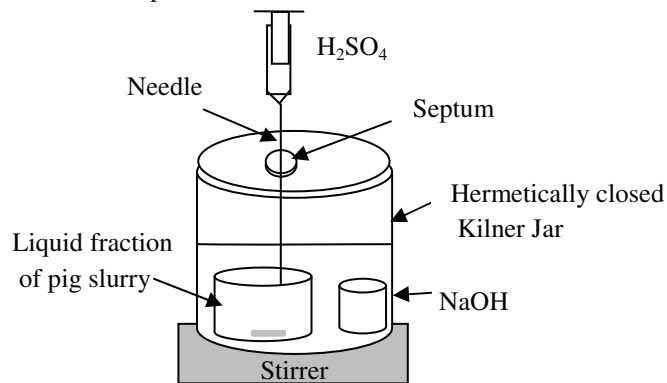


FIGURE 1 Experimental device used to measure CO₂ emissions during acidification and storage.

3 RESULTS AND DISCUSSION

3.1 CO₂ emissions during acidification and storage

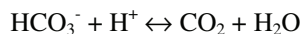
A strong CO₂ emission was observed immediately after the acidification with about 400 mg C L⁻¹ released from the acidified liquid fraction (ALF) compared to only 20 mg C L⁻¹ from the non acidified LF during the first 45 minutes of the experiment (Figure 2). However, after 4.75 h, similar CO₂ emissions rates ($P < 0.05$) were observed from the acidified and non acidified liquid fractions after which, CO₂ emissions rates decreased strongly in acidified LF whereas it increased with time in non acidified LF (Table 1). After 60 hours the amount of C released as CO₂ from non acidified LF and acidified LF were very close. Consequently, a higher CO₂ emission was observed from the non acidified LF beyond 30h until the end of the storage trial indicating that most of the CO₂ released early from the acidified LF was released later from the non acidified LF.

TABLE 1 CO₂ emissions rates (mg C L⁻¹ h⁻¹) during storage of acidified and non acidified pi slurry liquid fraction; mean of three replicates

time (h)	Acidified LF	Non acidified LF
0.25	*719.8 ^a	41.7 ^b
0.75	447.1 ^a	16.1 ^b
1.75	62.9 ^a	6.9 ^b
2.75	9.8 ^a	3.2 ^b
3.75	8.3 ^a	4.3 ^b
4.75	9.2 ^a	6.4 ^a
5.75	7.7 ^a	6.5 ^a
29.75	2.1 ^b	6.5 ^a
47.5	2.2 ^b	14.5 ^a
77.5	1.8 ^b	8.9 ^a
149.5	0.4 ^b	3.5 ^a
197.5	0.2 ^b	0.9 ^a

* Values in a same row followed by different letters are significantly different (LSD, $P \leq 0.05$).

Vandré and Clemens (1997) also observed enhanced CO₂ emissions after acidification of cattle slurry with HCl (and pronounced foaming) and attributed it mainly to a loss of bicarbonate ions (HCO₃⁻).



The carbon lost as CO₂ during acidification and subsequent storage of acidified LF represents 9% of the total carbon initially present whereas during storage of non acidified LF, the CO₂ released during storage represents more than 15% of the total carbon initially present.

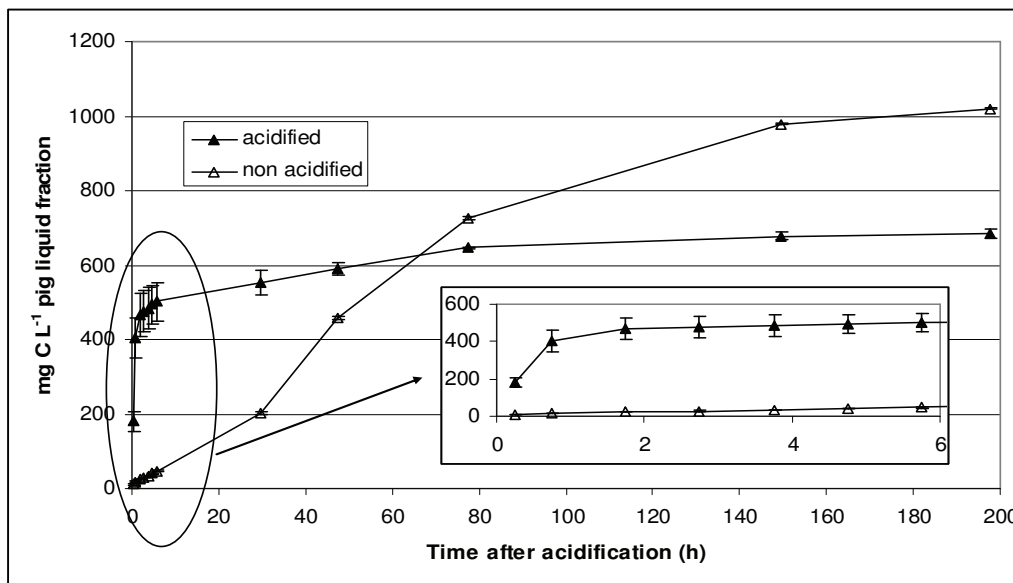


FIGURE 2 Cumulated amount of C released as CO₂ during storage of acidified and non acidified pig slurry liquid fraction – average and standard error of three replicates. The insert graph shows detail of emissions during the first 6 hours.

3.2 CO₂ emissions after soil incorporation

The addition of non acidified LF to soil led to a strong increase (more than 900%) of CO₂ emissions relative to the control (soil only) whereas in the case of the acidified LF, such increase was lower than 100% (Figure 3). The differences in terms of CO₂ emissions rates between acidified LF and non acidified LF treated soil diminished after 8 days and reached similar values to the control after 25 days. Several authors (Flessa and Beese, 2000; Fanguero et al., 2007) attributed such differences to the release of the CO₂ initially dissolved in the LF or produced by transformation of the bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions present in the slurry.

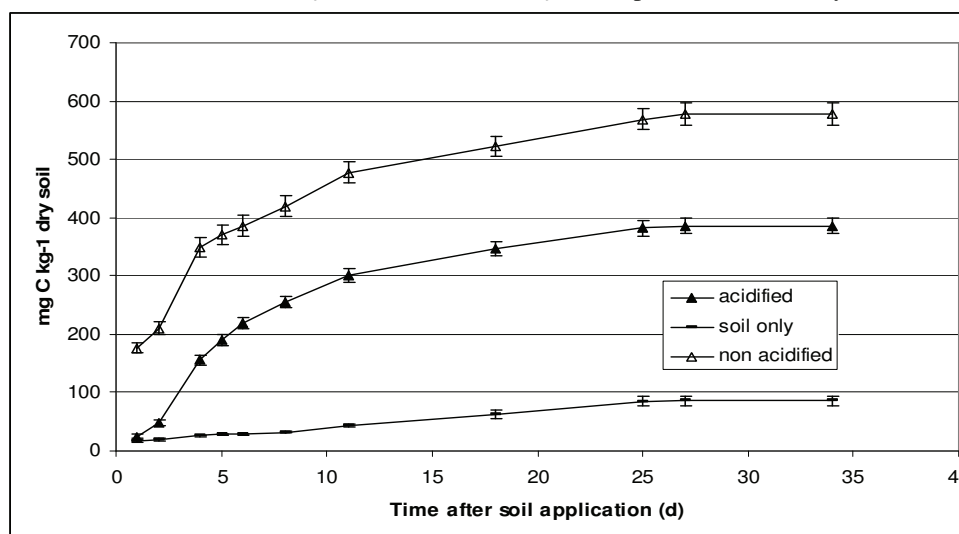


FIGURE 3 Cumulative amounts of C released as CO₂ from soil mixed with acidified and non acidified pig slurry liquid fraction following storage – average and standard error of five replicates

For the same reason, CO₂ emissions rates during the first day of the experiment were significantly lower in the acidified LF treatment than in the non acidified LF treatment, since most of the dissolved CO₂ and HCO₃⁻/CO₃²⁻ have been lost during the acidification process, prior to soil incorporation. Similarly, Fangueiro et al. (2010) also observed lower CO₂ emissions from soils amended with acidified pig slurry and derived fractions relative to soils amended with non acidified materials. After 34 days of experiment, 72 % of the applied C had been lost as CO₂ in the LF amended soil against only 48% in the ALF amended soil.

4 CONCLUSIONS

In conclusion, LF acidification led to less emissions of CO₂ during slurry storage and following mixing with soil, even if significant CO₂ emissions occurred immediately after acidification. It appears that acidification first removes all the carbonate fraction of the pig slurry liquid fraction but may also have an effect on the microbial activity responsible for organic substrate degradation, explaining the low emissions observed after soil mixing.

REFERENCES

- Borst GHA 2001. Acute intoxication of pigs with hydrogen sulphide as a result of acidification of slums. *Tijdschrift Voor Diergeneeskunde* 126,104–105
- Castrillón L, Fernández-Nava Y, Marañón E, García L, Berrueta J 2009. Anoxic–aerobic treatment of the liquid fraction of cattle manure. *Waste Management* 29, 761–766
- Eriksen J, Sorensen P, Elsgaard L 2008. The Fate of Sulfate in Acidified Pig Slurry during Storage and Following Application to Cropped Soil. *Journal of Environmental Quality* 37, 280–286.
- Fangueiro D, Chadwick D, Dixon L, Bol R 2007. Quantification of priming and CO₂ respiration sources following the application of different slurry particle size fractions to a grassland soil. *Soil Biology and Biochemistry* 39, 2608-2620.
- Fangueiro D, Coutinho J, Chadwick D, Moreira N, Trindade H 2008a. Cattle slurry treatment by screw-press separation and chemically enhanced settling: effect on greenhouse gases and ammonia emissions during storage. *Journal of Environmental Quality* 37(6), 2322-2331.
- Fangueiro D, Pereira JL, Chadwick D, Coutinho J, Moreira N, Trindade H 2008b. Laboratories estimates of the effect of cattle slurry pre-treatment on organic N degradation after soil application and N₂O and N₂ emissions. *Nutrient Cycling in Agroecosystems* 80, 107-120.
- Fangueiro D, Ribeiro H, Coutinho J, Cardenas L, Trindade H, Cunha-Queda C, Vasconcelos E, Cabral F 2010. Nitrogen mineralization and CO₂ and N₂O emissions in a sandy soil amended with original or acidified pig slurries or with the relative fractions. *Biology and Fertility of Soils* 46, 383-391.
- Flessa H, Beese F F 2000 Laboratory estimates of trace gas emissions following surface application and injection of cattle slurry. *Journal of Environmental Quality* 29, 262-268.
- Kai P, Pedersen P, Jensen JE, Hansen MN, Sommer SG 2008. A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. *European Journal of Agronomy* 28, 148–154.
- Misselbrook TH, Brookman SKE, Smith KA, Cumby T, Williams AG, McCrory DF 2005. Crusting of stored dairy cattle slurry to abate ammonia emissions: Pilot-scale studies. *Journal of Environmental Quality* 34, 411–419.
- Schils RLM, van der Meer HG, Wouters AP, Geurink JH, Sikkema K 1999. Nitrogen utilization from diluted and undiluted nitric acid treated cattle slurry following surface application to grassland. *Nutrient Cycling in Agroecosystems*. 53, 269–280.
- Sommer SG, Hutchings NJ 2001. Ammonia emission from field applied manure and its Reduction. *European Journal of Agronomy* 15, 1–15.
- Vandré R, Clemens J 1997. Studies on the relationship between slurry pH, volatilization processes, and the influence of acidifying additives. *Nutrient Cycling in Agroecosystems*. 47, 157–165.
- Weiske A, Petersen SO 2006. Mitigation of greenhouse gas emissions from livestock production. *Agriculture, Ecosystems and Environment* 112, 105–106.