Animal slurry acidification: more than a solution for ammonia emissions abatement?

D. Fangueiro, S. Surgy, I. Regueiro, F. Gioelli, M. Hjorth, J. Coutinho
Structure of the presentation

1) Introduction
2) Slurry composition and separation
3) Gaseous emissions during storage
4) N, P and C dynamics after soil application
5) Agronomic value
✓ pH lowering of animal manure: logical and direct solution to minimize ammonia emissions.

\[ \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \]

✓ Additives used: nitric and sulfuric acid with liquid manure and aluminium sulfate with solid manure
Introduction

Restrict utilization due to some limitations

Acid hazard

Foam formation in barns and storage

And costs depending on:
- which acid is used (\( \text{H}_2\text{SO}_4 \) is one of the cheapest)
- at which stage is acidification performed (in barn, storage, field)
Today, safe and efficient solutions are proposed to farmers for slurry acidification in barn, in slurry store or immediately before soil application.

But such service is still limited to Denmark where 15% of slurry was acidified in 2013 with an expected increase to 20% in 2014.

More information is needed to export such technology to countries from South Europe.
Introduction

• Strong focus of research on efficiency to decrease NH$_3$ but few data on other gas emissions neither on N, P and C dynamics in soil;

• Most studies performed in North Europe and few available information on the applicability of this technique in Mediterranean countries where pedo-climatic conditions are very different from North Europe.
Provide an overview about the potential for slurry acidification application as a slurry management tool in Mediterranean countries.
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## Slurry composition and separation

<table>
<thead>
<tr>
<th></th>
<th>Pig slurry</th>
<th>Acidified pig slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry matter content (g kg(^{-1}))</strong></td>
<td>49.6</td>
<td>62.6</td>
</tr>
<tr>
<td>Total N (g kg(^{-1}))</td>
<td>4.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Total P (g kg(^{-1}))</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Total C (g kg(^{-1}))</td>
<td>14.9</td>
<td>13.3</td>
</tr>
<tr>
<td>Inorganic C (g kg(^{-1}))</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Ca (g kg(^{-1}))</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Mg (g kg(^{-1}))</td>
<td>1.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Slurry composition

Possible dissolution of the dominants mineral P species in manure (struvite and di-calcium phosphate)

Influence of pH target storage time
## Slurry composition and separation

<table>
<thead>
<tr>
<th></th>
<th>Slurry</th>
<th>Acidified Slurry</th>
<th>Liquid fraction</th>
<th>Acidified Liquid fraction</th>
<th>Solid fraction</th>
<th>Acidified Solid fraction</th>
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</thead>
<tbody>
<tr>
<td><strong>Dry matter content</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(g kg⁻¹)</td>
<td>49.6</td>
<td>62.6</td>
<td>10.2</td>
<td>30.9</td>
<td>194.8</td>
<td>195.5</td>
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<tr>
<td><strong>Total N</strong></td>
<td>4.2</td>
<td>4.3</td>
<td>2.8</td>
<td>2.9</td>
<td>10.4</td>
<td>9.9</td>
</tr>
<tr>
<td>(g kg⁻¹)</td>
<td></td>
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<tr>
<td><strong>Total P</strong></td>
<td>1.1</td>
<td>1.0</td>
<td>0.04</td>
<td>0.69</td>
<td>4.7</td>
<td>2.1</td>
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<tr>
<td>(g kg⁻¹)</td>
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<tr>
<td><strong>Total C</strong></td>
<td>14.9</td>
<td>13.3</td>
<td>2.7</td>
<td>1.9</td>
<td>72.4</td>
<td>67.6</td>
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<tr>
<td>(g kg⁻¹)</td>
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<tr>
<td><strong>Inorganic C</strong></td>
<td>0.8</td>
<td>0.0</td>
<td>0.4</td>
<td>0</td>
<td>2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>(g kg⁻¹)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ca</strong></td>
<td>2.4</td>
<td>2.4</td>
<td>0.1</td>
<td>0.9</td>
<td>10.6</td>
<td>6.7</td>
</tr>
<tr>
<td>(g kg⁻¹)</td>
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<td></td>
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<tr>
<td><strong>Mg</strong></td>
<td>1.1</td>
<td>1.0</td>
<td>0.05</td>
<td>0.5</td>
<td>4.7</td>
<td>2.8</td>
</tr>
<tr>
<td>(g kg⁻¹)</td>
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Methane Emissions

- Slurry acidification can decrease CH$_4$ emissions during storage (Berg et al., 2003)

- Acidification efficiency to decrease CH$_4$ emissions depends strongly on the acid used (Berg et al., 2003; Petersen et al. 2012):
  - >90% with lactic acid
  - 40-65% with HCl
  - 17-75% with nitric acid

- Below pH 5, this decrease does not depend on the target pH.
Gaseous emissions during storage

Carbon dioxide emissions

✓ CO$_2$ emission occurred mainly during the acidification process and can be 2-10 times higher than during subsequent storage (Fangueiro et al., 2013; Dai and Blanes Vidal, 2013).

✓ A stronger and faster decay of CO$_2$ emissions is observed in acidified slurry relative to non acidified during the first days of storage.

✓ Over the whole storage period, differences between acidified and non acidified slurry in terms of CO$_2$ emissions were generally not significant.
Gaseous emissions during storage

Storage of acidified and original cattle slurry with different DM content

Gaseous emissions during storage

Hydrogen sulfide emissions

✓ As occurred with CO$_2$ emissions, a strong burst of H$_2$S emissions may happened during the acidification process followed by a strong decrease over the first days of subsequent storage.

✓ BUT acidification has no significant effect on H$_2$S emissions over the whole storage period (Dai and Blanes-Vidal (2012))

✓ More than the pH effect, the slurry mixing that was performed in all treatments strongly influence H$_2$S emissions.
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Influence of slurry acidification on N mineralization and nitrification

Increase of NO$_3^-$ content in raw slurry after 7 days but only after 14 days in acidified slurry

Higher NH$_4^+$ contents in soil during longer periods in Acidified slurry

Influence of slurry acidification on N mineralization and nitrification

Delay and decrease of nitrification with acidification: effect more intense in low DM slurry

Soil application of acidified and non acidified cattle slurry with different DM content
Influence of slurry acidification on N$_2$O after soil application – pig slurry

Fangueiro D., Ribeiro H., Coutinho J., Cardenas L., Trindade H., Cunha-Queda C., Vasconcelos E., Cabral F. 2010 Nitrogen mineralization and CO$_2$ and N$_2$O emissions in a sandy soil amended with original or acidified pig slurries or with the relative fractions. Biology and Fertility of Soil, 46 (4): 383-391.
Influence of slurry acidification on CO$_2$ emissions after soil application – pig slurry

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 Soil, 46 (4): 383-391.
Influence of slurry acidification on P availability

Slurry acidification increases P availability for plants

Soil application of acidified and non acidified cattle slurry and derived liquid fraction
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Acidified slurry may act as a starter for maize (Petersen et al., 2013)
Agronomic Value

Dry yield Oat
Sandy soil

Dry yield Oat
Sandy loam soil

Dry matter yield (ton ha\(^{-1}\))

control
Raw slurry
Acidified slurry

control
Raw slurry
Acidified slurry
## Conclusions

<table>
<thead>
<tr>
<th>Slurry composition</th>
<th>Soluble P</th>
<th>Inorganic C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage</td>
<td>CO₂</td>
<td>➔ (initial burst)</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>➔</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>➔ (initial burst)</td>
</tr>
<tr>
<td>Soil application</td>
<td>Nitrification</td>
<td>➔ (delay)</td>
</tr>
<tr>
<td></td>
<td>N₂O</td>
<td>➔</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>➔</td>
</tr>
<tr>
<td></td>
<td>P availability</td>
<td>➔</td>
</tr>
<tr>
<td></td>
<td>Crop yields</td>
<td>➔</td>
</tr>
</tbody>
</table>
Conclusions

YES, slurry acidification can be used as a slurry management tool in Mediterranean countries
Acknowledgements

Co-authors: S. Surgy, I. Regueiro, F. Gioelli, M. Hjorth, J. Coutinho

Funders:

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Thank you for your attention.