ALUM AS ACIDIFICATION ALTERNATIVE

During storage of dairy slurry

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Situation in Portugal

No treatment to minimize gaseous emissions: namely NH₃

Slurry is stored for 5 months and applied directly to the soil

N loss from NH₃ emissions results in decrease of manure fertilizer value

Need for solution to minimize NH₃ emissions
Acidification:

- **Known**
  - To reduce NH$_3$ emissions

- **Studied in past with**
  - H$_2$SO$_4$
  - HNO$_3$

- **Current usage**
  - Applied in Denmark with H$_2$SO$_4$

**BUT**

- Limited Implementation in many countries
Need for alternatives

Acidification with $\text{H}_2\text{SO}_4$

- Acid Hazards
- Foam Formation
- Costs

Need for alternatives
Objectives

Optimization of acidification approach

- Low cost
- No NH$_3$ emissions & stable pH
- Decrease additive hazards & minimize foam
- Decrease additive hazards & minimize foam
Dairy slurry initial pH 7.2

Pig slurry initial pH 7.4

Additives

- H$_2$SO$_4$
- CH$_3$COOH
- Al$_2$(SO$_4$)$_3$
- C$_6$H$_8$O$_7$
- C$_3$H$_6$O$_3$

pH values

- pH 5.5
- pH 3.5
Incubate samples for 60 days
Follow NH₃ emissions and pH evolution
Calculate final costs of acidification
Previous Experiment Results

- Control
- Sulfuric
- Lactic
- Acetic
- Citric
- Alum

pH vs t (d)

Left graph: pH change over time for different treatments.

Right graph: pH change over time for different treatments.
Previous Experiment Results

- **Cumulated NH₃ emissions**
  - **t (d)**: Time in days
  - **mg N-NH₄ * L slurry⁻¹**

- **pH**
  - **€ Equiv.⁻¹ m⁻³ slurry**

- **Graphs**
  - Blue line: Sulfuric acid
  - Red line: Lactic acid
  - Green line: Acetic acid
  - Purple line: Citric acid
  - Orange line: Aluminium sulfate
  - Black line: Control
Dairy slurry initial pH 6.8

Acidification Approaches
- Constant pH
- Raising pH

Additives
- \(H_2SO_4\)
- \(CH_3COOH\)
- \(Al_2(SO_4)_3\)

pH values
- pH 5
- pH 3.5

Experiment
Incubate samples for 45 days
Follow NH₃ emissions by traps with H₃PO₄ and pH evolution
Add fresh slurry every week

Maintain pH constant by acid addition

Cost calculation of acids used
Results

Evolution of pH

- Control
- Sulfuric Acid
- Acetic acid
- Aluminium sulphate

**Constant pH 3.5**

**Constant pH 5**
Results

Cumulated NH₃ emissions at Constant pH

- Sulfuric acid
- Acetic acid
- Aluminium sulphate
- control

- pH 3.5
- pH 5

Cumulated NH₃ emissions (mg N-NH₄ * Kg slurry⁻¹)

t (d)
pH evolution & Cumulated NH₃ emissions

Raised pH 3.5
Results

Average pH

NH₃ emission
(mg N_NH₄ Kg slurry⁻¹)

Acid amount
(g Equiv. Kg slurry⁻¹)
**Discussion**

**pH evolution & Acid addition**

- **Constant pH 5**
  - $\text{H}_2\text{SO}_4$: pH rapidly increased to pH 6

- **Constant pH 3.5**
  - $\text{H}_2\text{SO}_4$: pH 4.4 was reached easily
  - $\text{CH}_3\text{COOH}$ and $\text{Al}_2(\text{SO}_4)_3$: Always below pH 4

- **Raised pH 3.5**
  - $\text{H}_2\text{SO}_4$: Fastest and highest increase to pH 6
  - $\text{CH}_3\text{COOH}$ and $\text{Al}_2(\text{SO}_4)_3$: Low increase pH 4.2

- **Constant $\text{H}_2\text{SO}_4$ addition is required to keep low pH**

- **CH$_3$COOH and Al$_2$(SO$_4$)$_3$ addition intervals could be more spaced**

- **Addition is required with $\text{H}_2\text{SO}_4$, but not for $\text{CH}_3\text{COOH}$ and Al$_2$(SO$_4$)$_3$**
NH₃ emissions are reduced with all approaches

- Highest: 5 mg NH₃ Kg slurry⁻¹ with CH₃COOH followed by H₂SO₄ at raised pH
- Control: 17 mg NH₃ Kg slurry⁻¹

pH remained constant with CH₃COOH and Al₂(SO₄)₃

- H₂SO₄ showed the fastest pH increase

Acid addition over storage to keep pH<4 is not required with CH₃COOH and Al₂(SO₄)₃

- At raised pH 3.5 the amount of Al₂(SO₄)₃ required was 3 times higher than H₂SO₄ but a pH below 4 was maintained
• At constant pH 5: Maintains a low pH using similar amounts as with $\text{H}_2\text{SO}_4$

• At constant pH 3.5: extra acid addition is not necessary to keep pH<4

• At raised pH 3.5: was required 3 times more Alum than $\text{H}_2\text{SO}_4$ BUT the final pH differs from pH 3.9 to 5.2: Longer period is required to compare acid costs

**Aluminium sulphate** is a good alternative to sulfuric acid
Thank you for your attention

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