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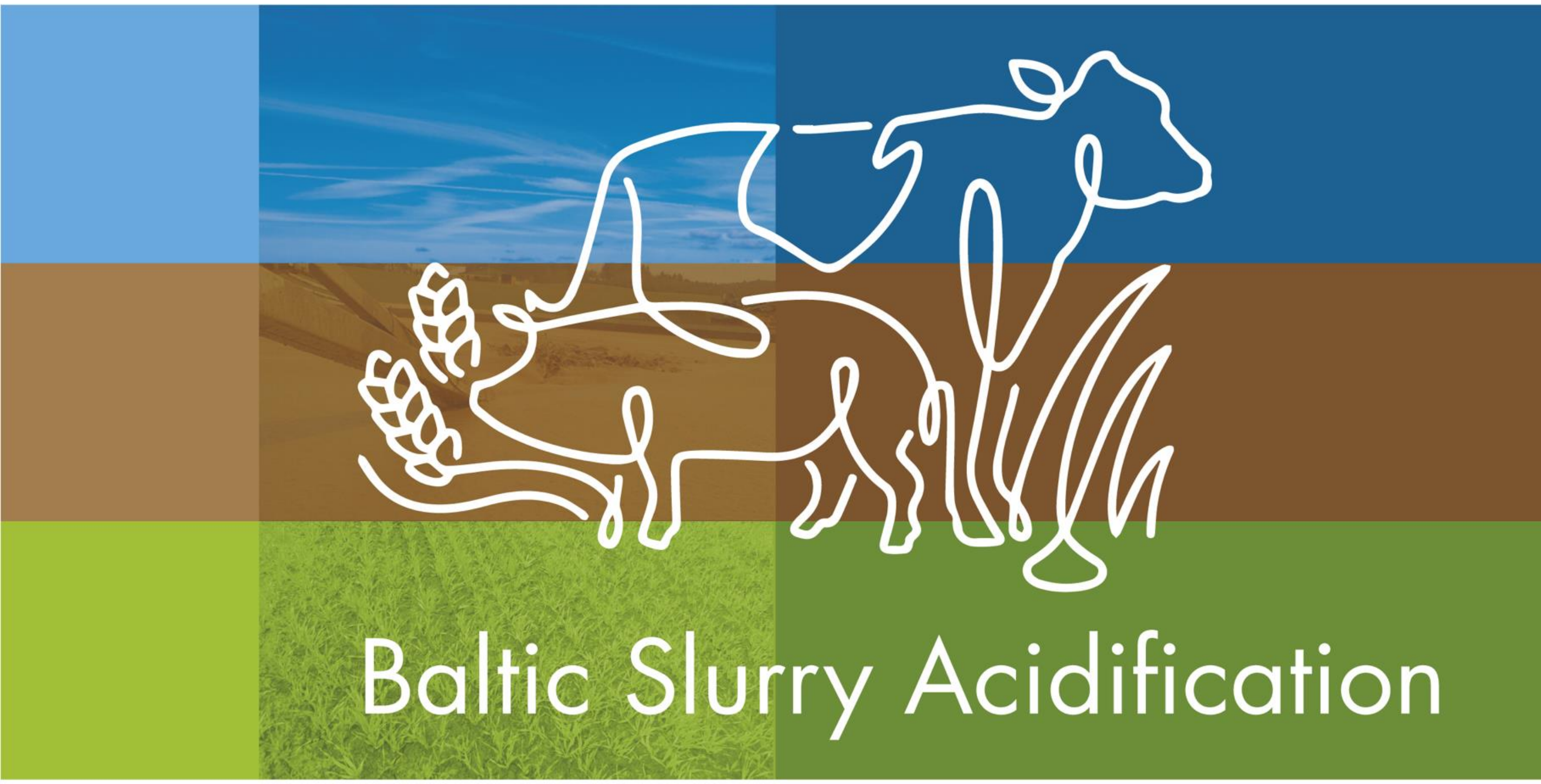
Baltic Slurry Acidification



An alternative to sulfuric acid for acidification of slurry

– A literature review

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EU STRATEGY FOR THE BALTIC SEA REGION
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Summary

In the Baltic Sea Region, livestock manure is the main source of ammonia-nitrogen emissions, which through atmospheric deposition results in a significant amount of nitrogen entering the Baltic Sea. Slurry acidification techniques can be used to reduce ammonia loss from manure in livestock housing, manure storage and from the fields during the application of manure. The commonly used acid for slurry acidification is concentrated (98% pure) sulfuric acid – H2SO4, however other acids can also be used for this purpose. This literature review summarizes some research on the acids in question.

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Background

Acidification of animal slurries aims at reducing ammonia emissions by modification of physical and biochemical properties of the slurry. Reducing these emissions is important due to the highly negative effects of NH_3 emissions have on the environment and health of the animals. Moreover, the loss of NH_4^+ via NH_3 emission reduce the fertilizer value of animal slurries.

The influence of the pH value is very significant regarding NH_3 emission and slurry composition modifications[1]. The efficiency of the acidification process as well as the composition of the resulting material depends on many parameters, such as slurry composition, acidification process or acid used. Sulphuric acid (H_2SO_4) is commonly used for acidification due to economic reasons.

The parameters to take into account when studying the economic viability of the different acids are the amount of acid required to reach the pH at which NH3 emissions are avoided, and the valuable end use of the treated slurry obtained.

Why use sulfuric acid?

The commonly used acid is concentrated (96 or 98% pure) sulfuric acid – H_2SO_4. The advantages of using sulfuric acid are as follows:

- it is a stable acid that works effectively in changing ammonia NH_3 into ammonium NH_4^+, which is a plant available N-form that does not evaporate;
- the sulphur content in sulfuric acidified slurry is useful for crops in fields;
- sulfuric acidified slurry does not damage concrete and inventory in the barn[2];
- it is available;
- it is cheap – costs about 0.25 € per kg[3].

Can other acids be used for acidification of slurry?

Sulfuric acid has in many tests proven to be the most effective acid[4]. Acidification of slurry requires great knowledge and experience of working with acid in the slurry.

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[1] Regueiro I., Coutinho J., Fangueiro D. (2013). Comparison of different approaches for ammonia emissions minimization by acidification of dairy and pig slurries. *Ramiran 2013 Recycling of Agricultural and Industrial Residues in Agriculture*.

[2] JH AGRO (http://jhagro.com/faq-slurry-acidification/)

[3] average cost in chemical wholesale in Poland, 2017

[4] JH AGRO (http://jhagro.com/faq-slurry-acidification/)

Case Study

Regueiro et al. (2016) conducted a study on alternatives to sulfuric acid for acidification of slurry. The main objective of this study was to compare the efficiency of different acids employed for slurry acidification and for this, NH_3 emissions, pH evolution, the cost related to each acid, and the composition of the slurry were considered.

Acids used for the study by Regueiro et al. (2016)

- **sulfuric acid**

- **acetic acid,** systematically named ethanoic acid, is a colourless liquid organic compound with the chemical formula CH_3COOH (also written as CH_3CO_2H
or $C_2H_4O_2$). Acetic acid has a distinctive sour taste and pungent smell. In addition to household vinegar, it is mainly produced as a precursor to polyvinyl acetate and cellulose acetate. It is classified as a weak acid since it only partially dissociates in solution, but concentrated acetic acid is corrosive and can attack the skin.

- **citric acid** is a weak organic tricarboxylic acid, having the chemical formula $C_6H_8O_7$. It occurs naturally in citrus fruits. In biochemistry, it is an intermediate in the citric acid cycle, which occurs in the metabolism of all aerobic organisms.

- **lactic acid** is an organic compound with the formula $CH_3CH(OH)CO_2H$. In its solid state, it is white and water-soluble. In its liquid state, it is clear. It is produced both naturally and synthetically.[5]

- **aluminium sulphate** is a chemical compound with the formula $Al_2(SO_4)_3$. It is soluble in water and is mainly used as a flocculating agent (causing contaminating particles to clump into larger, more easily trapped particles) in waste water treatment plants, in paper manufacturing, and in the purification of drinking water.[6]

Organic acids are widely found in nature as normal plant and animal constituents. Their use may reduce NH_3 emissions and modify slurry characteristics without affecting the health of farmers and animals. However, the use of these additives for slurry acidification has been poorly investigated. Some additives have been tested

[5] Berg W., Türk M., Hellebrand H.J. (2006). Effects of Acidifying Liquid Cattle Manure with Nitric or Lactic Acid on Gaseous Emissions. Workshop on Agricultural Air Quality.

[6] Lefcourt A.M., Meisinger J.J. (2001). Effect of adding alum or zeolite to dairy slurry on ammonia volatilization and chemical composition. Journal of Dairy Science, 84: 1814–1821.

mainly for their coagulant properties - such as aluminium sulphate ($Al_2(SO_4)_3$), referred to here as alum. Nevertheless, this additive has mostly been used in poultry litter treatment, and it proved to be efficient with regard to reducing NH_3 volatilization and improving the management of manure derived phosphorus[7].

Material and methods

Dairy and pig slurries were acidified to pH 5.5 or 3.5 using lactic acid, sulphuric acid, citric acid, acetic acid, or aluminium sulphate. Acids were added to slurry in small volumes of 0.2 mL while stirring and the pH was measured after each addition until pH value was stabilized. At the beginning and at the end of the experimental period, slurry samples were analysed for dry matter (DM), organic matter (OM), Kjedahl N, Ammoniacal Nitrogen (TAN), soluble nitrogen (Nsol), total phosphorus (Pt) and mineral phosphorus (Pmin) using standard methods.

The main findings from the study by Regueiro et al. (2016) show that

- all acids used to acidify pig and dairy slurries allowed lower NH_3 emissions in comparison with the non-acidified slurries;

- NH_3 emissions accumulation in acidified pig and dairy slurries at pH 5.5 showed to be the lowest when using sulphuric acid, aluminium sulphate and lactic acid in both pig and dairy slurries;

- the best option regarding amounts required would be aluminium sulphate followed by acetic acid for both slurries when acidifying at pH 5.5; when acidifying at pH 3.5, sulfuric acid would be the best option for both slurries;

- acidification to pH 5.5 significantly ($P < 0.05$) reduced the NH_3 emissions from both slurries compared with no acid, with H_2SO_4 and alum leading to the greatest reductions;

- the total soluble C concentration was significantly ($p < 0.05$) increased with the addition of organic acids, a change that was not observed when sulfuric acid or alum was used;

[7] Regueiro I., Coutinho J., Fangueiro D. (2016). Alternatives to sulfuric acid for slurry acidification: impact on slurry composition and ammonia emissions during storage. *Journal of Cleaner Production* 131, 296-307.

- in acidified slurries at pH 3.5, inorganic C was below the detection limit during the whole storage period, except when lactic acid was used in both slurries and citric acid in dairy slurry (which gave a significant increase in inorganic C from day 40 of the storage);

- the inorganic C concentration in acidified slurries at pH 5.5 showed a continuous increase from the beginning until the end of the storage, with values in all acidified pig and dairy slurries that were significantly ($P < 0.05$) lower than in raw slurries, except when acetic or lactic acid was used in dairy slurry and acetic or citric acid was used in pig slurry;

- the additive equivalent mass used to lower the pH to 5.5, in decreasing order, was as follows: sulfuric acid > lactic acid > citric acid > acetic acid for pig slurry, and lactic acid > sulfuric acid > acetic acid > citric acid for dairy slurry. In contrast, when the target pH was 3.5, the additive equivalent mass increased in the following order, for both slurries: sulfuric acid $<$ lactic acid $<$ citric acid $<$ acetic acid;

- acidification of pig slurry with all additives significantly ($p < 0.05$) increased the DM concentration. In contrast, for dairy slurry, a significant increase was observed only when lactic acid was used;

- acidification promoted P solubilization, except when alum was used. A high alum concentration should be avoided if slurry is intended to be used as P fertilizer, as the availability of P may be reduced;

- sulfuric acid and alum were the additives required in the lowest amounts to decrease the pH to 5.5 and were the most efficient at reducing NH_3 emissions. Therefore, alum can be considered a good alternative to H_2SO_4 when lowering the pH to 5.5;

- the use of alum or H_2SO_4 resulted in the lowest percentage losses of TN and NH_4 in both slurries (with no significant ($P > 0.05$) differences between them) followed by acetic and lactic acid (which did not differ significantly) and then citric acid, with the highest N loss;

- the highest cumulative NH_3 emissions in both slurries when citric acid was used were probably due to higher catabolic activity, as this additive gave the greatest decreases in DM concentration during storage with the corresponding highest OM degradation;

- however, the acid acquisition costs also have to be considered since values to reach pH 5.5 and pH 3.5 vary considerably depending on the acid used, and on the slurry to treat. The price of each acid varies significantly.

Baltic Slurry Acidification

www.balticslurry.eu

Summary of the project

Baltic Slurry Acidification is an agro-environmental project financed by Interreg Baltic Sea Region under the priority area Natural resources and specific objective Clear waters. The aim of the project is to reduce nitrogen losses from livestock production by promoting the use of slurry acidification techniques in the Baltic Sea Region and thus to mitigate eutrophication of the