Acidifications effect on transformations in and composition of animal slurry

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Abstract
Animal slurry is to an increasing extend being treated with acid to reduce ammonia emission. This has an impact on all subsequent applications of the manure, hence the acidifications effect on the manures chemical equilibriums and composition needs to be clarified. Thus, at full-scale conditions was two finishing pig stables operated simultaneously, with traditional manure treatment and with daily acidification to pH 5.5. The composition of the two manures was analysed. Compared to the non-acidified manure, increased hydrolysis was observed in the acidified manure, and a reduced rate of acetogenesis, acidogenesis, methanogenesis and sulphate reduction. Less minerals were precipitated in the acidified slurry. The particles were increasingly aggregated in the acidified manure. Hence, the acidified manure contained larger particles and more organic and inorganic dissolved compounds. Thus, the acidification may affect separation treatment, biogas production and plant fertilizer value.

Introduction
Ammonia emission causes eutrophication of natural ecosystems and reduced fertilizer value of animal manure. Lowering the pH of animal slurry under pH 6 can minimizes the ammonia emission by more than 65% [1]. In 2012 approximately 10% of Danish manure was therefore acidified within the stable or upon soil application [2].

The chemical and physical composition of the manure will change upon lowering the pH value, because the chemical and microbial processes and transformations are pH dependent. This is exemplified by previous observations of increased dry matter content [1,3]. Manure is a significant source of energy, fertilizer, greenhouse gases and odour; hence the production of these will change upon acidification.

Microbial degradation of organic matter occurs through hydrolysis, acidogenesis, acetogenesis, methanogenesis and sulphate reduction. Composition and activity of microorganisms depend on the surrounding conditions. This is changed significantly by acidification, which will affect the organic degradation pathways. Relative to non-acidified manure, acidification treatment has previously been observed to cause increased butanoic acid content [4], indicating a changed degradation pattern. And lowered CH_4 and H_2S emission have been observed [5-7], and expected to be due to inhibition of methanogenesis and sulphate reduction.

Two dominant precipitates in manure are struvite and hydroxyapatite. Many precipitation reactions of inorganics are controlled by pH value. An example of side-reactions to the precipitation, causing dissolution, is magnesium and calcium with hydroxide at high pH, and reaction of PO_4^{3-} with protons at low pH.

To be able to predict the manures particulate and liquid composition, it is necessary to asses specifically, which of all dominating organic and inorganic reactions are reversed, decelerated or accelerated by the pH change. This study therefore aims to analyze the effect of continuous acidification on the organic and inorganic reactions under full-scale conditions.

Material and Methods

Manure treatment

One typical finishing pig manure and one acidified finishing pig manure were produced. To produce the two manures, two batches of 64 finishing pigs were raised simultaneously at similar full-scale housing conditions for 77 days. The manure pits at the control conditions was emptied twice during the growth period. The acidification treatment was carried out daily, to pH 5.5 by adding H_2SO_4. To the approx. 25 m3 of acidified manure was added 317 kg 96% H_2SO_4.The manure level in the pit was adjusted daily, and the remaining was emptied to the manure storage.

Chemical analyses

The two manures were analyzed for pH and conductivity. The particle size distributions and zeta potentials were measured with a Zetamaster (Malvern, Worcestershire). The total and dissolved content of Ca, Mg, P and S were measured using ICP-OES. Total nitrogen and NH4-N was measured using Kjeldahl. The 2-5 carbon containing carboxylic acids were measured using gas chromatography (Hewlett Packard 6850A). The carbohydrate content was measured using a glucose standard and coloration with 3,5-dinitrosalicylic acid. Cellulose was determined with Van Soest. In the animal house, the concentration of NH_3 in the air emitted from the animal house was measured using an INNOVA (Lumasence, CA) and H_2S using a Jerome 631-XE (Arizona Instrument LLC, AZ). Gas production during storage was measured in 0.5 L bottles containing 0.3 L manure, being control manure, acidified manure and acidified manure added 5 mg acetic acid per L; after 5 weeks was the gas production measured using gas chromatography (Hewlett Packard, CA). Measurement of storage gas production and Ca, Mg and P were measured in manure samples from a later manure treatment, but operated at comparable conditions.

Results and discussion

Manure reactions

The acidification of animal manure from pH 7 to pH 5.5 could potentially have an effect on all the chemical and microbial mediated equilibriums: organic degradation, inorganic dissolution and particle aggregation.

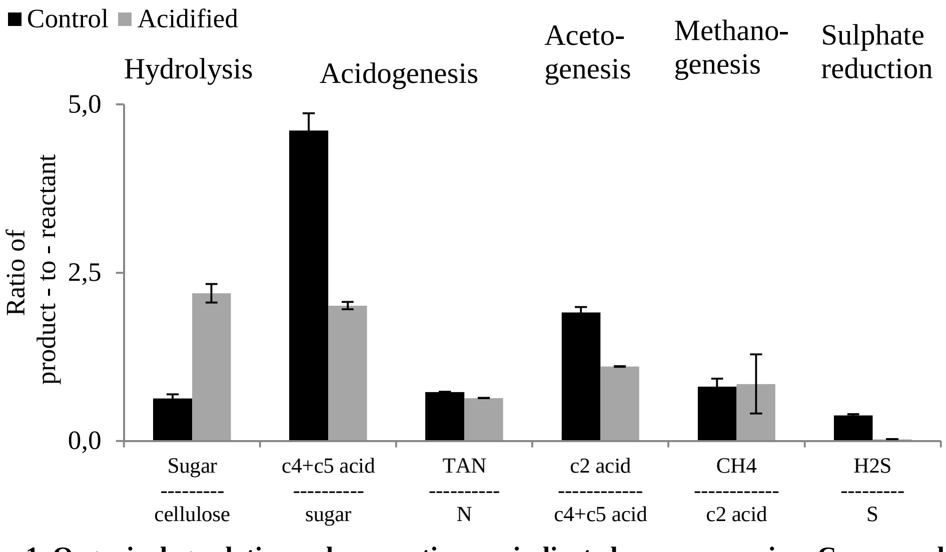

Figure 1. Organic degradation; a lower ratio may indicate lower conversion. Compound-units are in mg/g manure, except for sugar in µg glucose eq/g, and H_2S and CH_4 is in µl/L air.

Organic degradations are microbial mediated. Because the activities of microorganisms are highly dependent on the surrounding medium, a response to pH changes can be expected. Previously, the methanogenesis and the sulphate reduction have been observed to occur at lower rate upon acidification [5-7]. The ratio between the equilibriums reactants and products (figure 1) for the non-acidified and acidified manure did in this study indicate inhibition of acidogenesis, acetogenesis and sulphate reduction. The hydrolysis was by the ratio sugar/cellulose indicated to be accelerated (figure 1), but this was partly due to the inhibited secondary acidogenesis. However, the cellulose concentration was 30% (± 10%) lower in the acidified manure than in the non-acidified; hence the hydrolysis was indeed accelerated. The methanogenesis appeared unaffected by the acidification (figure 1), but measurement were performed of methane emission from acidified manure added extra c2 acid and this treatment did not increase methane production; hence the methanogenesis proved inhibited. Overall, the initial organic degradation to organic monomers proved accelerated upon manure acidification, while all subsequent degradations proved decelerated.

Inorganic precipitation-dissolution equilibriums are chemically mediated. Because the majority has acid-base side reactions, an effect of pH changes are expected. Dominant precipitates in animal slurry is struvite ($MgNH_4PO_4$ x $6H_2O$) and calcium-phosphates as hydroxyapatite ($Ca_5(PO_4)_3OH$). In the manure, the acidification was observed to cause an increasing amount of Mg, Ca and P to be dissolved (figure 2), supported by findings in a previous short-term acidification study [3]. Side-reactions of the minerals include reaction of Mg and Ca with hydroxide and reaction of PO_4^{3-} with protons. Combining these equilibriums, it is determined that both minerals are increasingly dissolved from pH 8 to pH 5 under standard chemical conditions. This supports the observed dissolutions upon the non-standard chemical condition in the acidified manure. Hence, the minerals proved dissolved upon acidification.

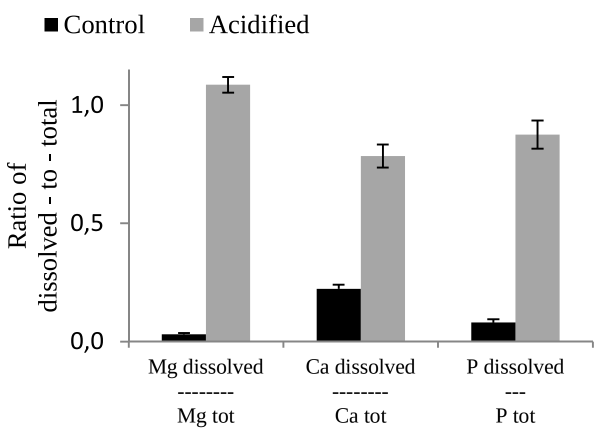

Figure 2. Inorganic degradation; a lower higher amount of dissolved indicates less precipitation. Compound-units are mol/mol.

Particle aggregation is chemically controlled by the ionic charges. The composition of manure is pH dependent as already observed, and the charges of the liquid and particle surfaces are pH dependent; hence the pH is expected to affect the clustering of particles. Measured as the immobile charge on the particle surface, i.e. the zeta potential, the surface attached groups were in average less negative (table 1). The ionic strength of the solution, measured as the conductivity, was increased. Both observations were in agreement with the observed inorganic dissolution of divalent cations (figure 2), and with pH caused protonation of negatively charged compounds. The zeta potential effect causes minimized surface charge, while the increased ionic strength and the dissolved divalent ions cause a thinner electrostatic layer around the particles. The consequence is less repulsion between the particles, and thus expectedly an increased coagulation and particle agglomeration upon the acidification treatment.

Table 1. Particle aggregation characteristics.

	Control	Acidified
Zeta potential (mV)	-13,6 (± 1,2)	-9,6 (± 0,7)
Conductivity (mS/cm)	26,6 (± 0,6)	28,0 (± 0,4)

Manure composition

Acidification of animal manure from pH 7 to pH 5.5 proved to have an effect on the chemical and microbial mediated equilibriums, and will therefore change the composition of the manure.

Gaseous losses from the manure were observed to be lower from the acidified manure, i.e. NH_3, CH_4, and H_2S (data not shown).This was due to the observed lowered production of the dissolved precursors, and the pH caused protonation of acids. In consequence, more of the slurry compounds remained in the manure upon acidification treatment.

The liquid composition was controlled by the increased inorganic dissolution, the increased rate of hydrolysis and the lowered rate of all subsequent organic degradations (figure 1 and 2). Hence, the liquid contained more multivalent metal-ions from mineral dissolution. Due to the changed organic degradation pattern, the liquid contained more of the organic monomers sugar and amino acid, more of the large carboxylic acids and less of the small carboxylic acids, unchanged ammonium amount and less hydrogen sulphide. And in addition it contained more sulphate as the acid added in the treatment. These indications were supported by the observed increased conductivity (table 1), that is an increasing amount of ions are dissolved in the liquid upon acidification treatment.

The particles in manure were observed to be larger upon acidification treatment. The average particle size (between 0.1 µm and 1 mm) was 50 µm (± 5µm) for the non-acidified manure and 140 µm (± 15 µm) for the acidified manure, with the smallest particles containing the majority of the inorganic. The mineral precipitate content was observed to be lowered, and the lignocellulose content was also lowered however to a lesser degree. This contrasts the observed particle size increases. Hence, the coagulation resulting in particle aggregation must be responsible for the particle size increase. The compounds in the aggregates could consist of a mixture of ion reactive species including Mg and Ca, amino acids, phosphate, carbohydrate and lignocellulose. Thus, the manure particles were less dominated by minerals upon acidification treament, but instead larger sized organic aggregations.

Conclusion and perspectives

The decelerated acidogenesis, acetogenesis, methanogenesis and sulphate reduction and the mineral dissolution resulted in increased particle aggregation. Compared to untreated manure, the acidified manure contained more organic and inorganic dissolved compounds, and larger aggregated particles. Consequently, the acidified manure will have a changed impact on the environment. In addition to a reduced NH_3 emission, the effect of the manure changes include an increased fertilizer N content, increased plant availability of P and some micronutrients, a more rapidly available carbon pool for soil amendment and biogas production, a higher content of the precursor for the biogas inhibiting sulphide, larger particles affecting solid-liquid separation, and likely a changed chemical composition of odourous compounds.

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