Performance of Additives in Reducing Ammonia Emissions from Cow Slurry

by
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(Revised edition)

preface

The emission of ammonia from manure contributes substantially to environmental pollution and causes acidification in certain areas of Sweden. The National Board of Agriculture in Sweden has therefore set the goal to reduce the total ammonia emission from agriculture with 50 % before 2000 with the respect to 1990. In Sweden, 20 - 25 % of the total ammonia emissions derive from manure in livestock buildings. The need to reduce ammonia emissions from livestock buildings is therefore urgent. During the last years, several additives for manure have been introduced on the swedish market. However, the efficiencies of these additives have not been determined, and those additives which have been evaluated have been difficult to compare due to different test methods.

The objective of this study has therefore been to determine the efficiencies of different manure additives in reducing ammonia emissions. The ammonia emissions from manure treated with different additives have been analysed in an ammonia measuring chamber developed at JBT (Dept. of Agricultural Biosystems and Technology). Seven different additives were evaluated in this investigation. The investigation has been conducted by Mr. Mats Andersson, research assistant at the Division of Buildings-, Energy- and Environmental Technology. Mr. Andersson has also compiled the data and has written this report. The investigation has been financially supported by the National Board of Agriculture in Sweden.

Lund in September 1994

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summary

Ammonia emissions contribute substantially to environmental pollution and cause severe acidification. In Sweden, 20-25 % of the total ammonia emission derives from manure in animal buildings. Different measures can be applied to decrease emissions in animal buildings, but they are usually costly and/or cause unsatisfactory living conditions for the animals. Simple techniques can be used which would not interfere with the living conditions for the animals if emission-reducing additives were applied in the manure. The efficiencies of many of the manure additives on the market has not been determined, and those additives that have been evaluated are difficult to compare due to different test methods and methods of evaluation.

The objectives of this study were to investigate the abilities of different manure additives in reducing ammonia emission, for how they would be efficient, and to which cost the additives can be used. To be able to measure the ammonia emission from manure treated with additives, an ammonia measuring chamber was used. The chamber is designed as a climate chamber for manure and with this technique it is possible to measure under controlled conditions.

Seven different additives were evaluated in this study; Add A, Penac G, Kemira No. 2, Kemira No. 5, Kemira No. 15, fly ash and Stalosan. Two concentrations of fly ash were evaluated. Three cow slurry samples per treatment, except for Kemira No. 5, were used in the study. The ammonia emission from the slurry samples were measured one day after, one week after and six weeks after the application of the additives. Once every week the slurry samples were stirred by hand and the crust formations were studied.

One day after the application of the additives in the slurry samples the treatment with Kemira No. 2 and Stalosan resulted in lower ammonia emission than from the control ($p < 0.001$). The emissions from the slurries treated with these two additives were approximately 40 % and 50 % lower than from the untreated slurries, respectively. At $p < 0.01$, no significant differences were found between the treatments with Kemira No. 15, fly ash (low), Penac G and the control. At this significance level, the treatments with Add A and fly ash (high) resulted in higher emissions than from the control. The Kemira No. 5 treatment was not replicated and therefore hard to evaluate. However, this single treatment indicated that this additive can reduce the ammonia emission.

One week after the application of the additives the treatment with Kemira No. 2 resulted in lower emission than from the control ($p < 0.001$). The Stalosan treatment gave even better effect and the emissions were significantly lower than from the treatment with Kemira No. 2 ($p < 0.001$). Treatments with these two additives resulted in approximately 40 % and 60 % lower emission than from the untreated slurries, respectively. At $p < 0.05$ and $p < 0.01$, no significant differences were found between the control and the other treatments except with fly ash (high), which resulted in higher emissions than from the control. The Kemira No. 5 treatment also seemed to have an emission-reducing effect.

Six weeks after application of the additives, Stalosan still reduced the ammonia emission compared with the emission from the untreated slurries ($p < 0.05$). The approximate reduction was 30 %. At this significance level the treatment with Add A resulted in a higher emission than from the untreated slurries. All the other slurries treated with the different additives emitted ammonia at the same rate as the control.

Specimens for Kjeldahl analyses were taken from all the slurry samples on all the measuring occasions. Correlation analyses between the emission results and the results from the Kjeldahl analyses were conducted. No good correlations were found between the emission values and total-N, ammonium-N, ammonium-N / total-N, total solids and pH-values, and the ammonia emission values could thus not be explained by the results from the Kjeldahl analyses.

Crust was formed on all the slurries during all of the six weeks of the experiment. The thicknesses of the crusts were the same on all the slurries on all the occasions, except on the one treated with Kemira No. 5 which was about two times thicker.

A rough economic evaluation of the two best performing additives in this study (Kemira No. 2 and Stalosan) was also conducted. If an emission-reducing effect only is expected in the livestock buildings when applying the additives Kemira No. 2 and Stalosan, the cost would be 780 SEK/kg saved nitrogen and 260 SEK/kg saved nitrogen respectively. If a reduction of the emission from the slurry storages (two weeks) can also be expected, the costs will be reduced to 740 SEK/kg saved nitrogen and 240 SEK/kg saved nitrogen. This economic evaluation is approximate and should only be used as an indication of the cost levels of using these two additives.

1 background and purpose of the study

Nitrogen is the macronutrient taken up most by plants. It is, for instance, a part of the protein and the chlorophyll of the plants. A good supply of nitrogen in balance with other nutrients leads to strong vegetative growth. Small changes in nitrogen supply usually have large influences on the vegetation.

In Sweden during the last half century an increased nitrogen deposition, due to atmospheric ammonium sulphate, has been detected. This has had a stimulating effect on vegetative growth until recent years. Moderate supplies of easy accessible nitrogen usually have a positive effect on plants and to a certain degree also on fungus and micro-organisms. However, in some parts of the country the nitrogen deposition has increased so much that nitrogen saturation has occurred. A symptom of nitrogen saturation is the increased nitrate leaching from the forest lands located in southern parts of Sweden.

According to Jordbruksverket (1994), the average nitrogen deposition in Sweden is approximately 2.2 kg/ha. However, local deposition figures vary widely, with extreme values of up to 25 kg/ha in the southwest of Sweden (Jordbruksverket, 1991). As the critical load limits for lakes, water courses, soils and plants throughout the country range between 5 and 15 kg/ha (Luft -90, 1990), measures have to be taken to prevent an environmental catastrophe.

The nitrogen deposition in Sweden is made up of nitrogen oxides (60%) and am-monia (40 %). Different combustion processes in motor vehicles and in energy production contribute to most of the nitrogen oxides, while animal manure is the main source of the ammonia (80-90 %). The ammonia emission from animal manure is divided between animal buildings (20-25 %), manure storages (25-30 %) and manure spreading (50 %).

Different measures can be applied to decrease the ammonia emission in animal buildings, but they are usually costly and/or cause unsatisfactory living conditions for the animals. To decrease ammonia emission by applying additives to the manure, simple techniques can be used which would not interfere in the living conditions for the animals. The efficiencies of many of the manure additives on the market have not been determined, and those additives that have been evaluated are difficult to compare due to different test methods and methods of evaluation.

The objectives of this study were to investigate the abilities of different manure additives in reducing ammonia emission, for how long they would be efficient, and to which cost the additives can be used

2 literature review

In the literature review in this report the processes with which the ammonia is emitted from manure in animal buildings are described. Some of the more promising manure additives according to Witter (1991 a), with emphasis on the principles of their mode of action in reducing ammonia emission, are also described.

2.1 Ammonia emissions from animal buildings
2.1.1 A description of ammonia
At normal pressure and temperature ammonia is a gas, which easily reacts with protons, metals or acid components and forms ions or complexes with different stabilities (Rank, 1988). It has a strong affinity to water and in the reaction an ammonium ion is formed. The equilibrium equation according to Vlek & Craswell (1981) is:
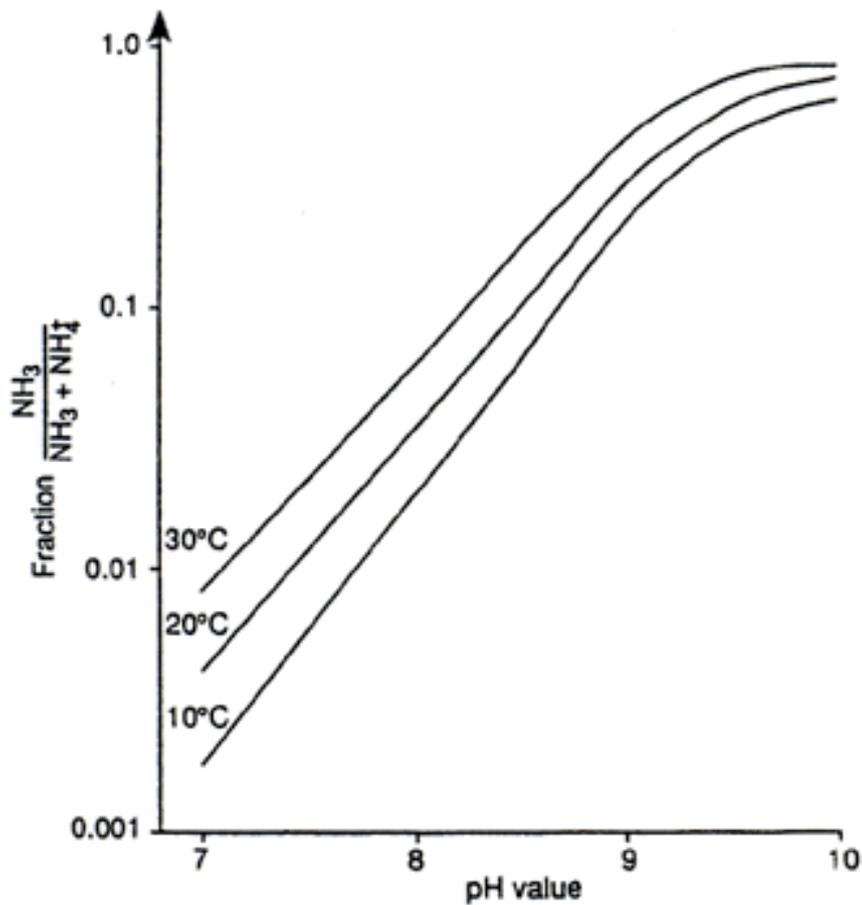
(1)

The volatilization rate of ammonia depends on the evaporation of ammonia into the atmosphere, changes in concentration of NH_4^+ or NH_3 in the solution, or any other displacement of the equilibrium equation (Rank, 1988). The equilibrium equation is displaced to the right as the temperature is raised and/or the pH-value is increased (Jordbruksverket, 1991; Rank, 1988). The driving force of the ammonia volatilization from a solution is differences in the partial pressure of ammonia between the liquid phase and the atmosphere (Denmead et al., 1982; Freney et al., 1981; Svensson, 1993).

2.1.2 Conversion of nitrogen to ammonia in faeces and urine

Nitrogen is excreted by animals both in the form of urine and in the form of faeces. Most of the nitrogen in faeces is present in organic forms, while in urine 65-90 % of the nitrogen is present as urea (Witter, 1991 a). In fowl, about 60-70 % of the nitrogen excreted is in the form of uric acid. The ratio of nitrogen excreted in faeces to that excreted in the urine varies between species, but also depends on the protein level of the feed. On average, 50-60 % of the nitrogen is excreted in the urine by pigs and cows.

Ammonia emissions from livestock buildings originate from ammonia formed by two processes. Organic forms of nitrogen present in the faeces may decompose and hydrolysis of urea, mainly in the urine, may occur. Because hydrolysis of urea proceeds at a fast rate compared with mineralization of nitrogen from the faeces, urine is generally the main source of ammonia emissions from livestock buildings. According to Hartung (1992) less than 1 % of the total ammonia emission from stored cattle slurry originates from the faeces (Table 1). Table 1 also shows that a decrease in ammonia release is possible if water is added to the manure. However, huge amounts of water are required. The ord-inary composition of faeces and urine in cow slurry is 2:1 (Frank, 1993).

Table 1.
Volatilization of ammonia from stored bovine faeces and urine with and with-out added water kept at 30 °C (after Kellems et al., 1979).

Volatilization of ammonia from stored bovine faeces and urine with and with-out added water kept at 30 °C (after Kellems et al., 1979).

Composition of manure	[%]		Ammonia release [µ NH$_3$/h]
Faeces	Urine	Water	
100	-	-	3.1
-	100	-	426.0
50	50	-	120.0
75	25	-	16.0
75	-	25	3.4
50	-	50	6.6
25	-	75	9.7
5	-	95	2.2

Urea hydrolysis is mediated by the enzyme urease and yields ammonium and carbonate, as follows:

$$CO(NH_2)_2 + 3H_2O \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^- + OH^- \qquad (2)$$
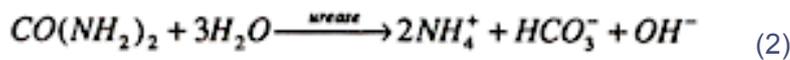
As soon as urine comes into contact with faeces, which contain urease, the conversion of urea starts (Elzing et al., 1992). The conversion rate of urea into ammonia is temperature dependent, and is greatly decreased at temperatures below 5-10 °C (Witter, 1991 a). Depending on the pH-value of the system, gaseous ammonia and/or carbon dioxide may be formed. The optimum pH-value for urease activity is usually between 6.5 and 7.0. Urea hydrolysis can take place both under aerobic and anaerobic conditions.

Hydrolysis of uric acid is thought to proceed via the intermediates allantoin, allantoic acid and urea (Witter, 1991 a). According to Witter (1991 a) and Demmers et al. (1992), the hydrolysis of uric acid proceeds at a somewhat slower rate than urea hydrolysis. This means that for fowl, which contains uric acid, there is adequate time to dry the manure as an effective measure to prevent formation of urea, and consequently of ammonia.

2.2 Different types of manure additives
There is an abundance of manure additives of different types on the market. The most common (and effective) ones can be divided into five groups as follows:

* pH-regulators (acids)

* pH-regulators (soluble Ca- and Mg-salts)

* Urease inhibitors

* Adsorbents

* Biological immobilization of ammonium

There are some other interesting additives, besides those mentioned above, which can not be sorted into specific groups. In this report these additives are presented as "Other additives to reduce ammonia emission from animal manure".

2.2.1 pH-regulators (acids)
Because the balance between ammonium and ammonia in solution is highly pH-dependent, reduction of the pH value to below 7 is a very effective way in reducing ammonia losses (Hartung, 1992; Witter, 1991 a), see Figure 1.

Pure acids such as nitric, sulphuric or phosphoric acid are more cost effective than acidic salts such as superphosphate or calcium sulphate (gypsum) due to their greater solubility (Witter, 1991 a). The amount of these chemicals that needs to be added to achieve a certain reduction in ammonia emission is dependent on the solubility and reaction of the chemical added and the pH-value and buffer capacity of the manure. Because

ammonia is alkaline, ammonia volatilization results in net acidification of the manure. In an unbuffered system, ammonia volatilization is therefore self-restricting. In a system where ammonia emissions occur from urea, the carbonate formed upon urea hydrolysis provides the necessary alkalinity to sustain ammonia volatilization (Witter, 1991 a). The carbonate must thus be neutralized to prevent ammonia volatilization.

During the decomposition of organic forms of nitrogen, ammonia is formed upon deamination of amino acids. Witter (1991 a) claims that it is likely that this ammonia formation is the main source of alkalinity during the decomposition of fresh faeces, and thus explains the increase in pH-value observed in the initial stages of the decomposition. Hence, the calculation of the amount of acid required in solid manures is different from the one of the required amount of acid in liquid manures.
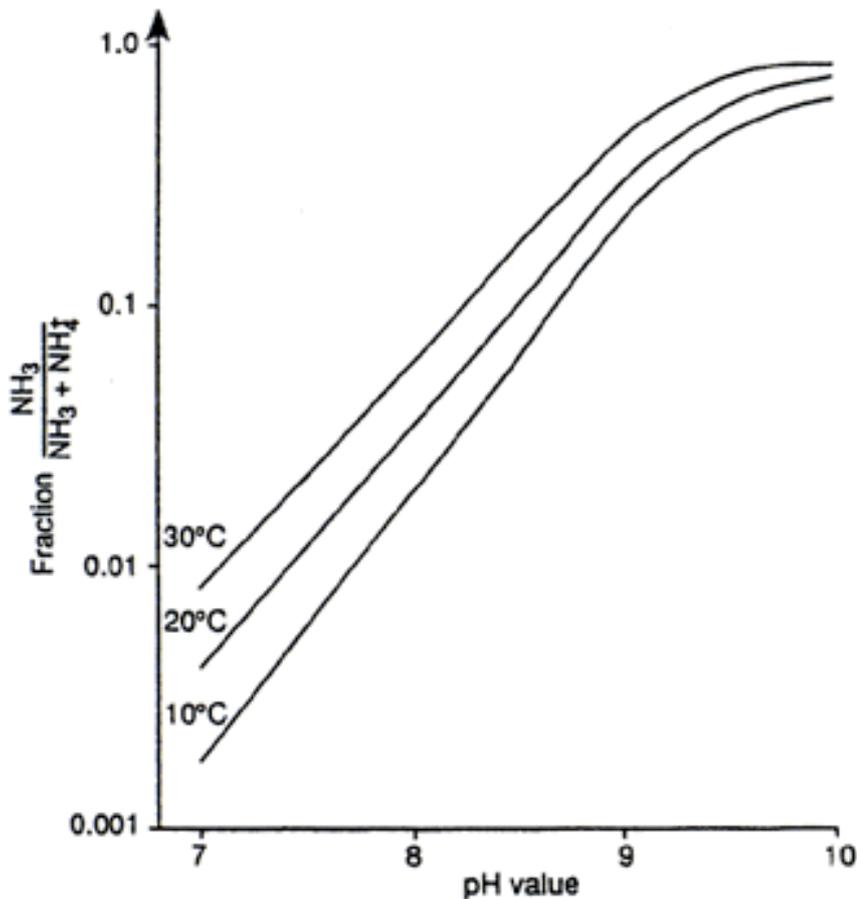
Figure 1.
The balance between ammonium and ammonia depending on the pH-value (Miner, 1974).

The advantages with the use of acids in reducing ammonia emission from manure are that virtually 100 % reduction in emission can be achieved and when the acid is in the form of phosphoric or nitric acid, the fertilizer value of the manure is increased.

The disadvantages with the use of acids are that they are highly corrosive and hazardous to use, unless diluted with water. According to Witter (1991 a) the concentrated acids may violently react with the organic matter in the manure, which probably results in the production of noxious gases. Due to this fact, the use of acids is probably only realistic with slurries, and not in the environment of livestock buildings. Spreading of acidified slurry on soil will result in an acidification of the soil, and problems with scorching of crops after application of slurries with nitric acid have also been reported (Witter, 1991 a).

2.2.2 pH-regulators (soluble Ca- and Mg- salts)

Soluble magnesium or calcium salts have been added to manure since the early part of this century with the purpose of reducing smell, and in some cases in order to reduce ammonia emissions from the manure. The chloride and nitrate salts of magnesium and calcium are mostly used, although any soluble magnesium or calcium salt is suitable (Witter, 1991 a). The sulphate salts of magnesium and calcium are not sufficiently soluble and considerably less effective. Fenn et al. (1981) have, according to Witter (1991 a), proposed a reaction mechanism for how the magnesium and calcium salts work:

$$CO(NH_2)_2 + 3H_2O \xrightarrow{\text{urease}} (NH_4)_2CO_3 \cdot H_2O \qquad (3)$$

$$(NH_4)_2CO_3 \cdot H_2O + CaX_2 \longrightarrow CaCO_3 + 2NH_4X + H_2O \qquad (4)$$
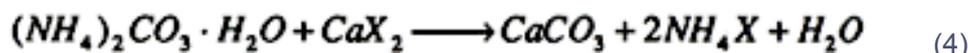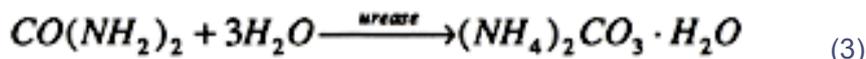
where
X = Cl- or NO$_3$-

Precipitation of $CaCO_3$ reduces ammonia volatilization as it reduces the $(NH_4)_2CO_3$ concentration, which easily decomposes to NH_3, CO_2 and water (Fenn & Kissel, 1973):

$$(NH_4)_2CO_3 + H_2O \longrightarrow 2NH_3 + 2H_2O + CO_2$$
$$\uparrow\downarrow$$
$$2NH_4OH \qquad (5)$$

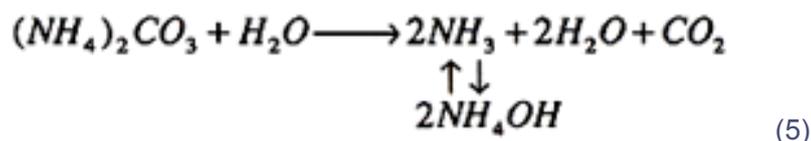Magnesium and calcium salts are effective in reducing ammonia volatilization from manures whenever carbonate is an important source of alkalinity driving the ammonia volatilization. Little is known, however, about the different sources of alkalinity of man-ures.

Witter & Kirchmann (1989) achieved up to 50 % reduction in ammonia emission during aerobic decomposition of chicken manure through the addition of $CaCl_2$ and $MgCl_2$. Because of resolubilization of the $CaCO_3$ formed, the efficiency in reducing ammonia emissions is reduced over time. Witter (1991 b) found that addition of $CaCl_2$ to fresh chicken manure applied to soil reduced peak rates of ammonia emission after three days by 70 %, but after two weeks the reduction in ammonia emission was less than 40 %.

The advantages with chloride and nitrate salts of magnesium and calcium are that they are non-hazardous and inexpensive. Nitrate salts have the advantage of improving the fertilizer value of the manure.

The chloride salts have the disadvantage of increasing the chloride content of the manure and hence also the chloride content in the soils on which the manure is spread. The magnesium and calcium salts are effective in reducing ammonia emission only during a couple of weeks, and are therefore restricted to use in animal buildings.

2.2.3 Urease inhibitors

Urease inhibitors have been developed in order to reduce ammonia emissions from urea fertilizers after application to soil. Some of these urease inhibitors may also be effective in reducing ammonia emissions from manures where the emission is associated with urea hydrolysis such as occurs in animal buildings.

Witter (1991 a) claims that of the known urease inhibitors only one group, phosphoramides, appears to be sufficiently effective in reducing ammonia emission. Beyrouty et al. (1988) tested some phosphoramide compounds in the field and found that urea hydrolysis could be reduced by up to 70 % over a time period of 4 -10 days after application of the urea to the soil. The compounds differed in effectiveness and were differently affected by the pH-value in the soil. Most of the compounds were more effective under acidic rather than alkaline conditions.

Investigations concerning the effects of urease inhibitors on ammonia emissions in animal buildings are scarce (Witter, 1991 a). According to Kemme et al. (1993), research on pigs on the effects of urease inhibitors has mainly been focused on performance.

Additives which have attracted great interest lately are those which are based on an extract (sarsaponin) from the Yucca palm (Yucca schidigera). The Yucca schidigera plant grows almost exclusively in the south-western deserts of the USA. Its ability to grow under such adverse conditions is due to the plant´s capability of binding ammonia (Headon & Walsh, 1993). The Yucca extract is used either as a feed additive or an additive for manure. As a feed additive, the product is claimed to improve feed conversion efficiencies in pigs and chickens, and because of its residual urease inhibitory properties, to reduce ammonia emission from manure in animal buildings (Witter, 1991 a). As an additive for manure, ammonia emission reductions have been obtained in some investigations carried out in the USA (Headon & Walsh, 1993; Kemme et al., 1993). However, in other studies conducted by Kemme et al. (1993) ammonia emission from manure was not reduced when recommended doses of the Yucca extract were added (Microaid). At higher doses the maximal reduction in ammonia emission was 22 %. In this trial it was asserted that the mode of action of the Yucca additive relies on binding or converting ammonia rather than on inhibiting the enzyme urease.

Use of urease inhibitors may be an effective way to reduce ammonia emissions from animal buildings. They will probably have less effect on emissions from manure storages, because there the ammonia is derived from ammonification of organic matter. If the urease inhibitor used improves the feed conversion efficiency in the animals there is an added incentive for farmers to use the compound.

A disadvantage with urease inhibitors is the temporary effect of reduction, which makes them suitable only for animal buildings (Witter, 1991 a). Further, little is known about the persistence and possible side-effects of these additives in the environment.

2.2.4 Adsorbents of ammoniacal nitrogen
There is a variety of substances which are effective in adsorbing either ammonia, ammonium or both. Adsorption of ammoniacal nitrogen reduces the ammonium content in the manure, and thereby ammonia volatilization. Of the different materials, clay minerals and peat seem to be the most efficient ones. Neither bilaminar (e.g. kaolinite) nor multilayer clay minerals (e.g. montmorillonite) have shown an increased binding activity for ammonium ions (Krieger et al., 1993). Clinoptilolites, which are three-dimensionally constructed natural zeolites, on the other hand, seem to work (Krieger et al., 1993; Witter, 1991 a). Clinoptilolites are used as either feed additives or manure additives. In some investigations, clinoptilolites have improved the feed conversion efficiency (Airoldi et al., 1993), while in other investigations the feed conversion efficiency has not been improved at all (Witter, 1991 a). Pond & Yen (1980) reported, according to Krieger et al. (1993), that the effect depends on concentration, particle size and the geographical origin of the clinoptilolite used. In an experiment conducted by Airoldi et al. (1993), a zeolite content of 10 % in the ration was required to reduce ammonia emission from the manure. Witter & Kirchmann (1989) have tested clinoptilo-lite as an additive for manure and they showed that the additive is mainly effective in adsorbing ammonium and not ammonia. Its ammonium adsorption capacity was about 18 mg NH_4^+ -N/g.

Peat (in particular Sphagnum fuscum derived peat) is, in contrast to clinoptilolite, more effective in adsorbing ammonia than ammonium. The ammonia adsorption capacity of peat is 23 mg NH_3 -N/g (Witter, 1991 a), and increases as the pH-value decreases (Kapuinen, 1992). Whereas most of the ammonium adsorbed by zeolites is held in an exchangeable form, and may hence be available for plant uptake or may be removed from the zeolites by ion-exchange, less than 40 % of the ammonia adsorbed by peat is held in an exchangeable form (Witter & Kirchmann, 1989).

The advantages with zeolites and peat are that they are effective in reducing ammonia emissions by adsorbing ammoniacal nitrogen and they are also non-toxic, non-hazardous and valuable soil conditioners when added to the soil with the manure.

A disadvantage with these additives is that they are costly to use. Peat is native to Sweden, whereas zeolites have to be imported which in most cases makes the use of the former more economical.

2.2.5 Biological immobilization

The microbial activity in the manure is often limited by a lack of suitable substrates. Addition of such an substrate will therefore result in increased microbial activity and the decomposition of the added material. By adding carbon-rich organic materials to manure, the ammonium nitrogen may be converted into organic forms of nitrogen during decomposition of the added material. Of the carbon (energy) utilized by the microorganisms about half is used for maintenance requirements, and under aerobic conditions, the used carbon is respired as carbon dioxide. The rest of the carbon in the added organic material is used in synthesis of new microbial cells, thus increasing the microbial population (Witter, 1991 a). Not only carbon is used in the synthesis but also nitrogen, amongst other macro- and micronutrients. If the added substrate has a low nitrogen content, for instance due to a high C/N-ratio, the microorganisms may use the inorganic forms of nitrogen (ammonium and nitrate) in the manure. These inorganic forms of nitrogen have thus become biologically immobilized by the incorporation into new microbial tissue.

The added substrate will eventually become exhausted, and the newly formed microorganisms will die and serve as substrates for the remaining microorganisms. The previously immobilized nitrogen will then be remineralized, and hence increase the ammonium content of the manure which may lead to ammonia volatilization. To enhance microbial immobilization of nitrogen and reduce ammonia volatilization, the added substrates must therefore have the following characteristics (Witter, 1991 a):

* High C/N-ratio.

* The carbon must be in a form that can be readily metabolized by microorganisms.

* The substrate should ideally provide both rapidly and slowly available forms of carbon. If the carbon is readily available the substrate must be added gradually in small doses.

Biological immobilization of nitrogen is an effective method of reducing ammonium levels in manures, given that a suitable carbon substrate is available. There are no environmental side-effects associated with this method, and the initially immobilized nitrogen will later be remineralized when the manure is applied in the field.

There are some disadvantages connected with this method of reducing ammonia volatilization from manure. According to Kirchmann & Witter (1989), no nitrogen immobilization occurs during anaerobic storage of manures. This means that the method is suitable for solid manures during storage under aerobic and semi-aerobic conditions as well as in deep-litter systems, but is less suitable for slurries. Furthermore, the effective-ness of this method is highly dependent on the characteristics of the substrate added, the application rate, ammonium content and nitrogen mineralization pattern of the manure. There has been too little research in this field yet to be able to come up with firm recommendations on the suitability of this method to reduce ammonia emissions from manure. At JBT, investigations concerning different types of substrates are in progress, which will yield results during 1995.

2.2.6 Other types of additives to reduce ammonia emissions from animal manure

There are some other additives on the market which are effective in reducing ammonia volatilization from manure, but they are less interesting due to the cost of using them or the environmental impacts associated with them.

Formaldehyde. When formaldehyde reacts with ammonia a stable organic complex is formed. Furthermore, the anti-microbial properties of formaldehyde may inhibit urease and ammonification (Witter, 1991 a). The additive is hazardous to use and may have negative side-effects after spreading of the manure.

Lime. Ammonia volatilization from manure can be reduced by liming to a pH-value above 10, thereby inhibiting the urease. It is difficult to maintain such a high pH-value in the manure, and the fact that a somewhat lower pH-value (8-9) will favour ammonia volatilization gives little scope for this method to reduce ammonia volatilization.

MAP-method. By adding phosphoric acid and magnesium oxide to the manure (slurry), it is possible to remove the ammonium from the slurry through precipitation of ammonium as $MgNH_4PO_4$ x $6H_2O$, a salt with low solubility at an alkaline pH. This new technique (the MAP-method) has been developed by a German company, Moderne Abwasser-Prozesstechnik GMBH. The precipitated salt can be sedimented out and can be used as a NPMg-fertilizer. Using this technique, up to 95 % of the ammonium from the slurry can be removed. The MAP-method was originally developed for waste water treatment, and to use it with animal slurries the slurries first have to be separated into a solid and a liquid phase. The ammonium in the liquid phase is then removed. Even though the MAP-method is very effective in reducing ammonia volatilization from slurries, the method will probably not become widespread due to high costs.

3 material and methods

3.1 The additives used in the study
The additives that were evaluated in the study were:

* Add A

* Penac G

* Kemira No. 2

* Kemira No. 5

* Kemira No. 15

* Fly ash

* Stalosan

Add A is a product marketed by the company Biosolv located in Stockholm. The additive consists of optional anaerobic bacteria, and the bacterias are of many different species, e.g. a microbial consortium (Biosolv, 1993). The price of the product is about 105 SEK/l (1992).

Penac G is marketed by the company Penac located in Trelleborg. The product consists of silicon dioxide which is ground to a fine texture (= 0.05 mm), and "oxygen treated" (Penac, 1993). The price is about 200 SEK/kg (1993).

Kemira No. 2 consists mainly of superphosphate Ca(H2PO4)2 and gypsum CaSO4 . 2H2O. The price is about 2.50 SEK/kg (1993).

Kemira No. 5 consists of peat impregnated of calcium chloride CaCl2 and superphosphate Ca(H2PO4). The price of the product is about 1 SEK/kg (1993).

Kemira No. 15 consists mainly of hydrogen peroxide H2O2, calcium chloride CaCl2 and propionic acid CH2CH2COOH. The price is about 3.20 SEK/kg (1993). All the Kemira-additives are marketed by Kemira AB, located in Helsingborg (Kemira, 1993).

Fly ash is a rest product from burning of fossil fuels. Fly ash consists mainly of three components; silicon dioxide SiO2, calcium chloride CaCl2 and dialuminum trioxide Al2O3. The price is lower than 1 SEK/kg (1994) when imported in large quantities from Denmark. Fly ash is no longer marketed in Sweden due to excessively high sulphur contents.

Stalosan consists mainly of superphosphate Ca(H2PO4)2 and copper sulphate CuSO4. Stalosan is marketed in Sweden by Hygrisan AB, located in Malmö (Hygrisan, 1993). The price of the product is about 5.80 SEK/kg (1993).

3.2 The measuring chamber

3.2.1 Design

To be able to measure the ammonia emission from manure treated with the additives an ammonia measuring chamber was used, which was described by Andersson (1994).

The measuring chamber is designed as a climate chamber for manure. The chamber consists of a container (bottom area 0.25 m2) in which the manure (0.010 m3) is kept, and a hood equipped with a ventilation system and placed on top of the container (Figure 2). The manure temperature is controlled by an electrically heated waterbath (0.045 m3) in which the container is immersed. To be able to to keep a uniform water temperature, the water tank is insulated and the water is circulated by an aquarium pump. The ventilation hood on the container is equipped with an air intake duct in the rear (Ø = 0.07 m), an air outlet with an exhaust fan in the front, a dust filter in front of the exhaust fan and an air mixing fan. The intake air is either cooled by a heat exchanger, untreated, or heated by a heating fan. The following parameters can be steplessly varied or may be kept constant; air flow rate, inlet air temperature and manure temperature.

The temperatures in the waterbath, the manure, the inlet air and the outlet air are measured using PT 1000 sensors and the relative humidity in the inlet air is measured using capacitive sensors (Rotronic). The air flow rate is measured using an orifice plate and a pressure gauge. Through the dust filter, exhaust air is sucked into an infrared-ana-lyser (Miran 203) to measure the ammonia concentration. All the parameters mentioned are continuously recorded by a personal computer via data loggers.
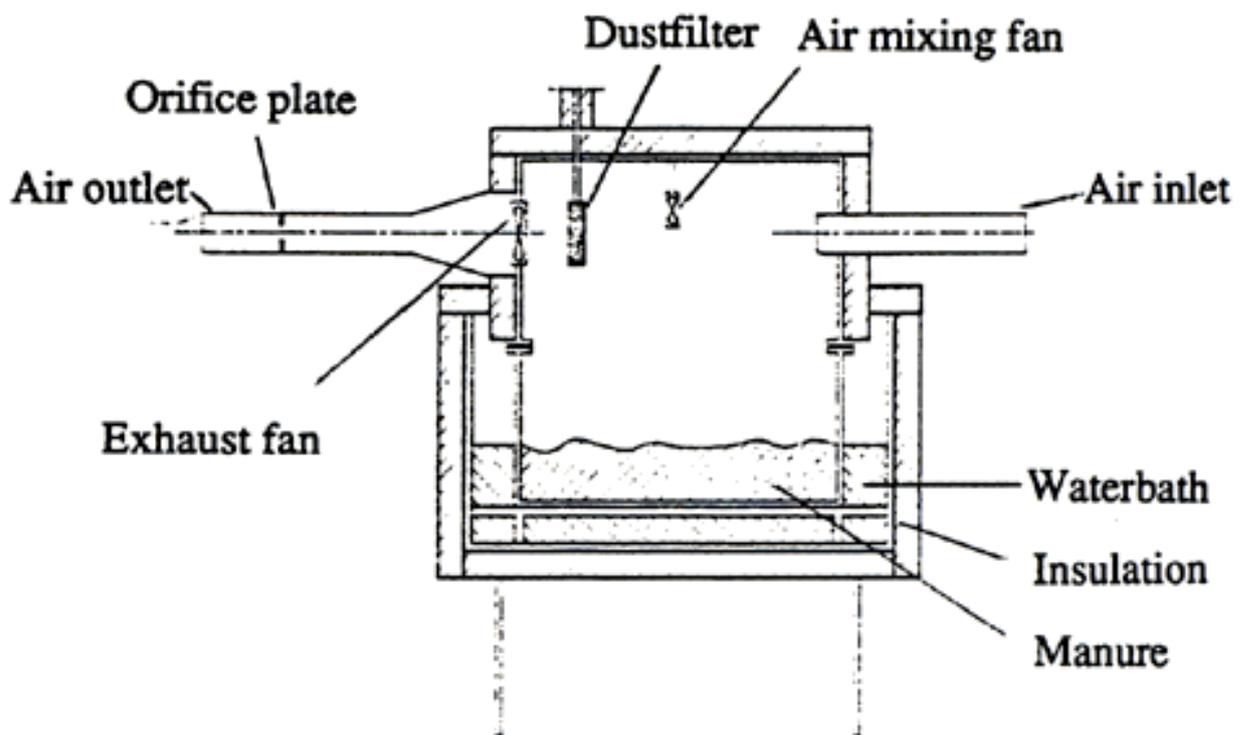

Figure 2. A section of the measuring chamber.

3.2.2 Performance characteristics

The air flow rate through the measuring chamber is steplessly variable between 30 and 200 m3/m2 h. At the lowest and the highest level the coefficient of variation (C.V.) of the air flow rate is calculated to 4.1 % and 1.9% respectively. As the air flow rate is changed the ammonia volatilization reaches a constant level after approximately 20 minutes.

The stirring fan in the measuring chamber mixes the inlet air by blowing it diagonally backwards. In one experiment, the air mixing efficiency was measured by sucking in samples of air over a cow slurry surface through a thin metal tube from 24 evenly distributed different spots in the chamber. In Figure 3 each pillar represents an average value of the samples collected from the three spots sideways in the chamber. The sample spots were arranged at three levels; high, medium and low. The air flow rates were 60 m3/m2 h and 140 m3/m2 h. The air at the high level in the chamber was found to be thoroughly mixed (C.V. = 7.1 % at 60 m3/ m2 h and C.V. = 6.4 % at 140 m3/m2 h). At the medium level and the low level in the chamber the concentration of ammonia tended to increase close to the chamber gable with the exhaust fan, which is in accordance with the results found by van Beek (1990) in his investigations on poultry houses. The C.V. of the ammonia concentration at the medium level were calculated to 16.2 % and 10.7 % respectively.
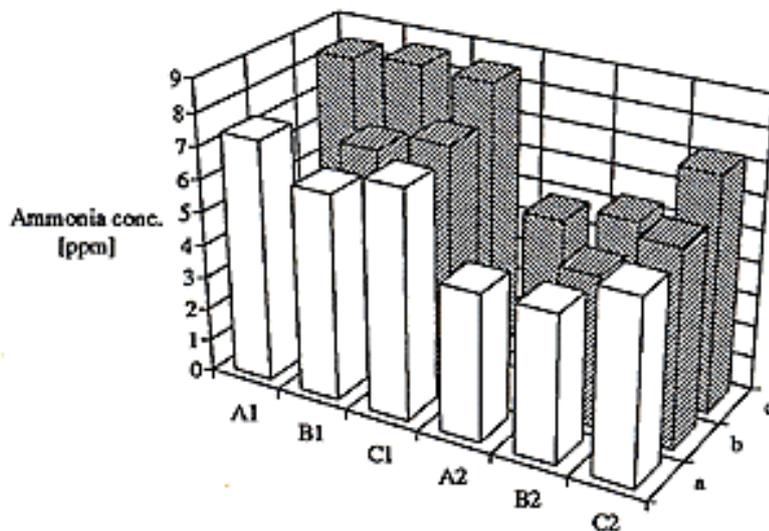
Figure 3.

Ammonia concentrations in different spots in the chamber over a cow slurry surface. A1 = High level 60 m3/m2 h, B1 = Medium level 60 m2/m2 h, Cl = Low level 60 m3/2 h, A2 = High level 140 m3/m2 h, B2 = Medium level 140 m3/m2 h, C2 = Low level 140 m3/m2 h, a = Close to air inlet duct, B = Middle of the chamber, C = Close to exhaust fan.

In another experiment, the decline of ammonia emission was investigated. Preheated (30 °C) and room temperated (15 °C) cow slurry was used and the air flow rate was 140 m3/m2 h. The ammonia concentration and the air flow rate were continuously recorded. Two and five hours of operation resulted in a 7 % and a 20 % decrease in ammonia emission from preheated slurry, respectively. The corresponding figures with room temperated slurry were 2 % and 7 %. These results show the importance of quickly conducted ammonia emission experiments, especially at high temperatures.

Measurement accuracy of the measuring chamber was calculated to 1.7 % as the C.V. of duplicate determinations of the ammonia volatilization. Six samples of thoroughly mixed cow slurry were used in this study.

3.3 The measuring procedure with the chamber
The measuring procedure with the chamber consisted of three parts:

* Treatments of the manure samples.

* Ammonia emission measurements with the chamber.

* Treatments of the manure between the measuring occasions.

3.3.1 Treatments of the manure samples

The manure that was used in the study was fresh (one day old) homogeneous cow slurry. The slurry was distributed in 0.005 m^3 portions in 0.010 m^3 buckets, so that three slurry samples per treatment were obtained. Two doses of fly ash and one dose of each other additive were to be evaluated, which gives 27 slurry samples all together (including three untreated) that would be portioned. However, the additive Kemira No. 5 was only sufficient for one slurry sample, and hence 25 slurry samples were used. The doses of the additives in the slurry samples (0.005 m^3) were in accordance with the recommendations of the different companies:

* Add A, 50.0 x 10-6 m3
* Penac G, 4 x 10-4 kg in 3.0 x 10-6 m3 water
* Kemira No. 2, 135.0 x 10-3 kg
* Kemira No. 5, 68.0 x 10-3 kg
* Kemira No. 15, 1.0 x 10-6 m3
* Fly ash, 5.0 x 10-3 kg (Low)
* Fly ash, 50.0 x 10-3 kg (High)
* Stalosan, 25.0 x 10-3 kg
* Control, untreated

In the calculations of the amounts of substances that were to be added to the slurry samples, a content of 4 x 10-3 kg nitrogen / kg slurry, of which 2 x 10-3 kg / kg slurry was ammonium nitrogen, was assumed. It was also assumed that all the ammonium nitrogen would be converted into ammonia, and hence the doses of additives were calculated for 2 10-3 kg nitrogen / kg slurry. The additives were thoroughly mixed by hand in the buckets with slurry, which then were stored uncovered in a place with the same climate conditions as in the place with the measuring chamber.

3.3.2 Ammonia emission measurements with the chamber

The ammonia emission from the treated slurry samples were measured with the chamber on three occasions; one day after, one week after, and six weeks after the application of the additives.

On each measuring occasion the slurry samples were poured one by one into the container of the measuring chamber. Specimens for Kjeldahl analyses (total-N, ammonium-N, total solids and pH) were taken from the slurry samples. The hood, which is equipped with the ventilation system, was placed on the manure container, and the measurements were started. Each measuring period lasted for 20 minutes, which has been found to be sufficient for the ammonia emission to reach a constant level (Andersson, 1994).

Between the measuring periods, the manure container was thoroughly washed and dried to prevent any influence from other slurry samples. The total time required for the measuring period, washing and change of slurry sample was 40 minutes per slurry sample. The ammonia emission from 25 slurry samples was measured, which required two days of work on each measuring occasion. To avoid systematic errors, like daily variations in inlet air temperature, relative humidity in the inlet air etc, the start order of the slurry samples was randomized. After each measuring period, the slurry samples were poured back into the bucket and put in the store room.

A sampling interval of two minutes between measurements of slurry temperature, inlet air temperature and relative humidity in the inlet air was used. The experiments were conducted at a air flow rate of 60 m3/m3 h.

3.3.3 Treatments of the manure between the measuring occasions

The slurry samples were mixed by stirring them by hand once a week during the storage period in order to ensure a uniform ammonia emission, which otherwise would be pre-vented by crust on top of the slurry. The three measuring occasions were all conducted one day after a mixing occasion. The mixing results in a oxygen supply in the slurry, which to some extent leads to aerobic conditions. The fatty acids in the slurry will then break down which results in an increase in the pH-value at which ammonia volatilization becomes greater (Jordbruksverket, 1991).

This emission peak lasts for a couple of hours, after which the emission of ammonia stabilises. By mixing the slurry the day before a measuring occasion, the influence of the emission peak which may be expected when pouring the slurry samples in the manure container of the measuring chamber will be reduced. The ammonia emission from the different slurry samples will thus be easier to determine.

4 results

4.1 Statistical analyses
To be able to evaluate the abilities of the additives in reducing ammonia emission from manure, comparisons of the means of the emission values were made by employing the GLM (General Linear Model) model data processing system. Tukey´s range test was used, and this test controls the Type 1 experimentwise error rate. The significance levels were $p<0.05$, $p<0.01$ and $p<0.001$. In order to attempt to explain the emission results with the results from the Kjeldahl analyses, correlation analyses (Pearson´s correlation coefficient) between the variables were conducted at the significance level $p<0.05$.

All the climate parameters recorded during the emission experiments are presented as means with standard deviations.

4.2 The first measuring occasion
In Table 2 the climate conditions with variations during the two days of the first measuring occasion are presented. As can be seen in the table, the variations during each day as well as during the two days together were relatively small. The variations were considered so small that they would not influence the ammonia emission levels. The climate conditions and the ammonia emissions at each measurement are presented in Table 3.

Table 2. The climate variations during the two days of measuring on the first occasion.

Day	Slurry temperature [°C]		Inlet air temperature [°C]		Relative humidity in the inlet air [%]	
	x	S	x	S	x	S
1	11.36	0.53	9.51	0.38	59.0	2.0
2	10.82	0.51	8.99	0.31	57.6	1.7
1+2	0.52	11.10	9.26	0.35	58.3	1.9

x = Mean value, s = Standard deviation

Table 3.
The ammonia emissions from the slurry samples and the climate conditions during each measuring period on the first measuring occasion.

Treat-ment No.	Additive	Ammonia emission [mg/m² h]	Slurry tem-perature [°C]		Inlet air tem-perature [°C]		Relative humi-dity in the inlet air [%]	
			x	S	x	S	x	S
1	Add A	354	10.84	0.09	9.52	0.22	60.0	0
1	Add A	354	11.27	0.13	9.84	0.16	54.0	0.8
1	Add A	358	11.32	0.50	9.67	0.13	59.6	0.5
2	Penac G	354	10.60	0.01	9.30	0.35	55.3	0.8
2	Penac G	339	10.27	0.22	8.73	0.09	57.0	0
2	Penac G	324	10.54	0.20	9.51	0.23	58.3	0.5
3	Kemira No. 2	200	10.88	0.04	9.42	0.29	60.5	0.5
3	Kemira No. 2	177	10.94	0.15	9.29	0.22	57.8	0.4
3	Kemira No. 2	193	10.50	0.20	8.97	0.17	58.0	0
4	Kemira No. 5	247	11.04	0.29	9.70	0.07	60.0	0
5	Kemira No. 15	339	11.02	0.22	9.74	0.10	60.0	0
5	Kemira No. 15	339	10.28	0.49	8.63	0.05	56.1	0.3
5	Kemira No. 15	347	10.74	0.18	9.03	0.49	60.1	0.4
6	Fly ash (Low)	327	10.40	0.43	8.93	0.41	57.8	0.4
6	Fly ash (Low)	362	11.03	0.30	9.69	0.17	60.0	0
6	Fly ash (Low)	347	10.32	0.44	8.82	0.04	55.0	0
7	Fly ash (High)	347	10.52	0.20	8.86	0.23	58.9	0.0
7	Fly ash (High)	370	10.91	0.33	9.63	0.25	60.0	0
7	Fly ash (High)	362	10.89	0.26	9.17	0.64	59.0	0.6
8	Stalosan	146	10.35	0.11	8.77	0.27	55.7	0.5
8	Stalosan	154	10.60	0.01	8.90	0.01	55.3	0.5
8	Stalosan	150	10.98	0.35	9.60	0.23	60.0	0
9	Control	308	10.60	0.16	9.28	0.06	59.4	0.5
9	Control	308	10.71	0.25	9.20	0.08	60.0	0
9	Control	327	10.70	0.14	9.29	0.02	60.0	0

x = Mean value, s = Standard deviation

Table 4 shows the results from the statistical evaluation of the manure additives. Means of the emission values of each treatment with the same grouping letter are not significantly different. The treatment with Kemira No. 2 and Stalosan showed good effect and were significantly different from the control ($p < 0.001$). The emissions from the manures treated with these additives were approximately 40 % and 50 % lower than from the untreated slurry, respectively. At $p < 0.01$, no significant differences were found between the treatments with Kemira No. 15, fly ash (low), Penac G and the control. At this significance level, the treatments with Add A and fly ash (high) resulted in higher emissions than from the control. The Kemira No. 5 treatment was not replicated and therefore hard to evaluate. However, this single treatment indicated that this additive can reduce the ammonia emission.

Table 4.
Means of the ammonia emission values of each treatment on the first measur-ing occasion. Means with the same grouping letter are not significantly dif-ferent ($p < 0.05$, $p < 0.01$ and $p < 0.001$).

Treatment	Ammonia emission [mg/m² h]		Grouping letters at each significance level		
	x	s	p<0.05	p<0.01	p<0.001
1. Add A	355	2	A	A	A
2. Penac G	339	15	A,B	A,B	A
3. Kemira No. 2	190	14	C	C	B
4. Kemira No.5*	247	-	-	-	-
5. Kemira No. 15	342	5	A,B	A,B	A
6. Fly ash (low)	345	25	A,B	A,B	A
7. Fly ash (high)	360	12	A	A	A
8. Stalosan	150	4	D	D	B
9. Control	314	16	B	B	A
* The treatment with Kemira No. 5 was not replicated. x = Mean value, s = Standard deviation					

In appendix 9.1 the results from the Kjeldahl analyses are presented. In the correlation analysis, no good correlations were found between the emission values and total-N, ammonium-N, ammonium-N / total-N, total solids and pH-values (Table 5). The ammonia emission values could thus not be explained by the results from the Kjeldahl analyses.

Table 5.
The correlation coefficients (r2) between the ammonia emissions and total-N, ammonium-N, ammonium-N / total-N, total solids and pH.

	Ammonia emission
Total-N	0.14
Ammonium-N	-0.04
Ammonium-N / total-N	-0.15
Ammonia emission	1.00
Total solids	-0.21
pH	0.10

4.3 The second measuring occasion
In Table 6 the climate variations during the two days of the second measuring occasion (one week after the application of the additives) are presented. As can be seen in the table, the variations during each day as well as during the two days together were relatively small. The variations were considered so small that they would not influence the ammonia emission levels. The climate conditions and the ammonia emissions at each measurement are presented in Table 7.

Table 6.
The climate variations during the two days of measuring on the second occasion.

	Slurry temperature [°C]		Inlet air temperature [°C]		Relative humidity in the inlet air [%]	
Day	x	s	x	s	x	s
1	9.63	0.39	7.69	0.24	61.1	1.0
2	9.10	0.34	7.12	0.30	65.9	1.3
1+2	9.37	0.37	7.41	0.27	63.4	1.2
x = Mean value, s = Standard deviation						

Table 7.
The ammonia emissions from the slurry samples and the climate conditions during each measuring period on the second measuring occasion.

Treat-ment No.	Additive	Ammonia emission [mg/m2 h]	Slurry tem-perature [°C]		Inlet air tem-perature [°C]		Relative humi-dity in the inlet air [%]	
			x	S	x	S	x	S
1	Add A	236	9.27	0.07	7.60	0.10	61.3	0.5
1	Add A	247	9.53	0.22	7.58	0.06	59.3	0.5
1	Add A	239	9.33	0.23	7.75	0.32	62.5	0.5
2	Penac G	254	9.26	0.06	7.75	0.17	59.7	0.5
2	Penac G	227	8.76	0.07	7.07	0.15	65.0	0
2	Penac G	227	8.95	0.03	7.35	0.12	67.5	0.5
3	Kemira No. 2	166	9.16	0.16	7.72	0.19	61.0	0
3	Kemira No. 2	166	9.39	0.17	7.74	0.22	60.0	0
3	Kemira No. 2	154	8.88	0.04	7.20	0.21	66.4	0.5
4	Kemira No. 5	204	9.26	0.05	7.78	0.33	62.0	0
5	Kemira No. 15	243	9.31	0.29	7.72	0.37	62.0	0
5	Kemira No. 15	235	8.68	0.04	7.03	0.23	65.0	0
5	Kemira No. 15	239	9.13	0.10	7.67	0.22	61.0	0
6	Fly ash (Low)	239	8.74	0.14	7.10	0.22	65.3	0.5
6	Fly ash (Low)	243	9.42	0.12	7.76	0.30	62.0	0
6	Fly ash (Low)	231	8.67	0.10	7.00	0.24	64.8	0.4
7	Fly ash (High)	243	8.90	0.02	7.40	0.21	67.0	0
7	Fly ash (High)	262	9.28	0.14	7.64	0.08	62.0	0
7	Fly ash (High)	270	9.26	0.12	7.74	0.29	60.8	0.4
8	Stalosan	100	8.60	0.02	7.00	0.19	65.0	0
8	Stalosan	108	8.80	0.01	6.69	0.04	64.0	0
8	Stalosan	112	9.22	0.04	7.68	0.20	62.0	0
9	Control	223	8.91	0.02	7.30	0.01	67.5	0.5
9	Control	227	8.90	0.01	7.27	0.22	67.0	0
9	Control	227	8.98	0.04	7.38	0.17	67.8	0.4

x = Mean value, s = Standard deviation

Table 8 shows the results from the statistical evaluation of the manure additives. Means of the emission values of each treatment with the same grouping letter are not significantly different. The treatment with Kemira No. 2 still showed good effect and resulted in significantly lower ammonia emission than from the control (p<0.001). The treatment with Stalosan resulted in significantly lower emission than from the Kemira No. 2 treatment (p<0.001). Treatments with these two additives resulted in approximately 40 % and 60 % lower emission than from the untreated slurry, respectively. At p<0.05 and p<0.01, no significant differences were found between the control and the other treatments except with fly ash (high), which resulted in higher emissions than from the control. The treatment with Kemira No. 5 may also have had an effect.

Table 8.
Means of the ammonia emission values of each treatment on the second mea-suring occasion. Means with the same grouping letter are not significantly different (p<0.05, p<0.01 and p<0.001)

Treatment	Ammonia emission [mg/m2 h]		Grouping letters at each significance level		
	x	s	p<0.05	p<0.01	p<0.001
1. Add A	241	6	A,B	A,B	A
2. Penac G	236	22	A,B	A,B	A
3. Kemira No. 2	162	7	C	C	B
4. Kemira No. 5*	204	-	-	-	-
5. Kemira No. 15	239	4	A,B	A,B	A
6. Fly ash (low)	238	6	A,B	A,B	A
7. Fly ash (high)	258	14	A	A	A
8. Stalosan	107	9	D	D	C
9. Control	226	2	B	B	A
* The treatment with Kemira No. 5 was not replicated.					
x = Mean value, s = Standard deviation					

In appendix 9.2 the results from the Kjeldahl analyses are presented. In the correlation analysis, no good correlations were found between the emission values and total-N, ammonium-N, ammonium-N / total-N, total solids and pH-values (Table 9). The ammonia emission values could thus not be explained by the results from the Kjeldahl analyses.

Table 9.
The correlation coefficients (r2) between the ammonia emissions and total-N, ammonium-N, ammonium-N / total-N, total solids and pH.

	Ammonia emission
Total-N	-0.04
Ammonium-N	0.02
Ammonium-N / total-N	0.05
Ammonia emission	1.00
Total solids	-0.12
pH	0.36

4.4 The third measuring occasion

In Table 10 the climate variations during the two days of the third measuring occasion (six weeks after the application of the additives) are presented. The variations during the first day of measurement were the highest, but they were considered so small that they would not influence the ammonia emission levels. The climate conditions and the ammonia emissions at each measurement on the third measuring occasion are presented in Table 11.

Table 10.
The climate variations during the two days of measuring on the third occasion.

	Slurry temperature [°C]		Inlet air temperature [°C]		Relative humidity in the inlet air [%]	
Day	x	s	x	s	x	s
1	9.97	0.72	7.51	1.15	62.3	6.4
2	7.69	0.49	6.02	0.44	58.0	3.1
1+2	8.73	0.61	6.70	0.84	60.0	4.9
x = Mean value, s = Standard deviation						

Table 12 shows the results from the statistical evaluation of the manure additives. At p<0.05 Stalosan was still effective six weeks after application of the additive (approximately 30 % lower emission than from the control). At this significance level the treatment with Add A resulted in a higher emission than from the untreated slurries. All the other slurries treated with the different additives emitted ammonia at the same rate as the control.

Table 11.
The ammonia emissions from the slurry samples and the climate conditions during each measuring period on the third measuring occasion.

Treat-ment No.	Additive	Ammonia emission [mg/m2 h]	Slurry tem-perature [°C]		Inlet air tem-perature [°C]		Relative humi-dity in the inlet air [%]	
			x	S	x	S	x	S
1	Add A	231	9.71	0.37	7.41	0.46	67.8	0.6
1	Add A	247	11.25	0.60	10.22	0.72	45.5	2.3
1	Add A	200	11.62	0.55	7.50	0.65	64.0	0
2	Penac G	200	9.85	0.71	8.31	0.72	53.2	2.1
2	Penac G	181	7.38	0.24	5.96	0.10	55.7	0.5
2	Penac G	189	7.78	0.19	6.65	0.30	60.8	0.4
3	Kemira No. 2	193	9.36	0.37	7.60	0.63	65.2	0.9
3	Kemira No. 2	177	9.68	0.56	7.61	0.35	61.1	2.1
3	Kemira No. 2	158	6.99	0.30	5.73	0.34	57.6	0.5
4	Kemira No. 5	177	9.37	0.48	6.73	0.53	64.9	1.0
5	Kemira No. 15	200	11.67	11.05	6.20	0.52	65.0	0
5	Kemira No. 15	189	7.07	0.23	5.92	0.18	55.0	0
5	Kemira No. 15	223	9.66	0.30	7.82	0.51	65.6	0.8
6	Fly ash (Low)	196	7.12	0.33	6.22	0.33	56.6	0.5
6	Fly ash (Low)	208	9.35	0.35	6.24	0.69	63.4	0.5
6	Fly ash (Low)	177	7.20	0.38	5.75	0.28	54.5	0.5
7	Fly ash (High)	181	7.03	0.20	5.61	0.38	59.7	1.3
7	Fly ash (High)	216	11.66	12.30	5.96	0.57	63.0	0
7	Fly ash (High)	216	9.66	0.40	7.60	0.47	64.0	1.2
8	Stalosan	119	7.21	0.10	5.84	0.21	55.0	0
8	Stalosan	123	7.66	0.08	5.70	0.03	54.0	0
8	Stalosan	131	9.66	0.30	7.14	0.73	68.7	0.6
9	Control	169	7.55	0.15	6.52	0.32	61.3	0.5
9	Control	181	7.15	0.14	5.87	0.44	62.4	0.9
9	Control	185	7.42	0.15	6.24	0.33	62.0	0

x = Mean value, s = Standard deviation

Table 12.
Means of the ammonia emission values of each treatment on the third measuring occasion. Means with the same grouping letter are not signi-ficantly different (p<0.05, p<0.01 and p<0.001)

Treatment	Ammonia emission [mg/m2 h]		Grouping letters		
	x	s	p<0.05	p<0.01	p<0.001
1. Add A	226	24	A	A	A
2. Penac G	190	10	A,B	A	A,B
3. Kemira No. 2	176	18	B	A,B	A,B
4. Kemira No. 5*	277				
5. Kemira No. 15	204	17	A,B	A	A
6. Fly ash (low)	194	16	A,B	A	A,B
7. Fly ash (high)	204	20	A,B	A	A
8. Stalosan	124	6	C	B	B
9. Control	178	8	B	A,B	A,B
* The treatment with Kemira No. 5 was not replicated. x = Mean value, s = Standard deviation					

In appendix 9.3 the results from the Kjeldahl analyses are presented. In the correlation analysis, no good correlations were found between the emission values and total-N, ammonium-N, ammonium-N / total-N, total solids and pH-values (Table 13). The ammonia emission values could thus not be explained by the results from the Kjeldahl analyses.

Table 13.
The correlation coefficients (r2) between the ammonia emissions and total-N, ammonium-N, ammonium-N / total-N, total solids and pH.

	Ammonia emission
Total-N	-0.29
Ammonium-N	0.01
Ammonium-N / total-N	0.28
Ammonia emission	1.00
Total solids	-0.20
pH	0.10

4.5 Crust formation in the slurries
During the six weeks of experiment the slurries in the buckets were mixed thoroughly once every week. On each mixing occasion the crust formation in the slurries was examined visually. Crust had formed on all the slurries during all of the six weeks. The crusts in the slurries grew at approximately the same rate and the thicknesses of the crusts were the same in all the slurries, except in the one treated with Kemira No. 5 which was twice as thick.

4.6 Economic evaluation
A rough economic evaluation of the two best performing additives in this study (Kemira No. 2 and Stalosan) was made. The following conditions were used:

* The doseages of the additives were those used in the laboratory experiments; 135.0 x 10-3 kg Kemira No. 2 / 5 kg slurry and 25.0 x 10-3 kg Stalosan / 5 kg slurry.

* The nitrogen content of the cow slurry was 0.35 %.

* The ammonium-N release in per cent of the total-N in cow slurry in livestock buildings was 6 % and from cow slurry storages 8 % (Jordbruksverket, 1991).

* The ammonia emissions used were the mean emission values recorded in the laboratory test on the first and second measuring occasion: Kemira No. 2; 185 mg/m2 h and 162 mg/m2 h; Stalosan 150 mg/m2 h and 107 mg/m2 h; control 314 mg/m2 h and 226 mg/m2 h.

* The prices of the products were 2.50 SEK/kg for Kem-ira No 2 and 5.80 SEK/kg for Stalosan.

* The storage time for the cow slurry was 8 months

In the economic evaluation of the additives, following formulas were used:

In the economic evaluation of the additives, following formulas were used:

$$a = b \cdot c \cdot d \qquad (6)$$

$$e = \frac{(f - g)}{f} \cdot h \cdot i \cdot b \cdot 100^{-2} \qquad (7)$$

By dividing equation (6) by equation (7) the costs of using the additives can be calculated:

$$j = \frac{a}{e} = \frac{c \cdot d \cdot f \cdot 100^2}{(f - g) \cdot h \cdot i} \qquad (8)$$

a = the cost of using the additives [SEK/year]

b = the amount of cow slurry produced [kg/year]

c = the doseage of the additives [kg additive/kg slurry]

d = the prices of the additives [SEK/kg additive]

e = the saved amount of nitrogen [kg N/year]

f = the ammonia emission from untreated slurry on the first measuring occasion [mg/m2 h]

g = the ammonia emission from slurry treated with the additives on the first measuring occasion [mg/m2 h]

h = the ammonium-N release in per cent of the total-N in the slurry in animal buildings [%] i = the nitrogen content in the slurry [%]

j = the costs of using the additives [SEK/kg saved nitrogen]

The costs of using Kemira No. 2 and Stalosan were calculated to 780 SEK/kg saved nitrogen and 260 SEK/kg saved nitrogen, respectively.

A reduction of the ammonia emission from the slurry storages was included in the calculations, and then the following formula was used:

$$k = e + \frac{l}{m} \cdot \frac{(n-o)}{n} \cdot p \cdot i \cdot b \cdot 100^{-2}$$

(9)

where k = the saved amount of nitrogen [kg/year]

l = the time period during which the additives reduce the ammonia emission; 2 weeks

m = the storage period of the slurry

n = the ammonia emission from untreated slurry on the second measuring occasion [mg/m2 h]
o = the ammonia emission from slurry treated with the additives on the second measuring occasion [mg/m2 h]

p = the ammonium-N release in per cent of the total-N in the slurry from slurry storages [%]

By dividing equation (6) by equation (9) the costs of using the additives were calculated. The costs of using Kemira No. 2 and Stalosan decreased slightly to 740 SEK/kg saved nitrogen and 240 SEK/kg saved nitrogen, respectively.

These calculations were based on laboratory results and assumptions, and they can only be used as indications of the cost levels of using the additives. Even though no costs associated with the spreading of the additives were used in the calculations, it is clear that the use of slurry additives is a fairly expensive method of reducing the ammonia emission from livestock buildings.

5 discussion

Why did the additives Kemira No. 2 and Stalosan reduce the ammonia emissions from the cow slurries so effectively, and why did the other additives fail to work satisfactory? One answer might be that both the additives are based upon superphosphate $Ca(H_2PO_4)_2$, and according to equations (3), (4) and (5) the concentration of $(NH_4)_2CO_3$ in the slurry formed in the urea hydrolysis is reduced due to the precipitation of $CaCO_3$. The pH-value decreases and the ammonia emission is reduced. This could be the cause of the ammonia emission reductions, even though no correlations between the pH-values and the ammonia emissions were detected.

It is more difficult to explain why additions to the slurries of the substances based upon silicon dioxides, Penac G and fly ash, resulted in the same, or slightly higher emissions, as those from the untreated slurries. Witter (1994) reached similar results with finely ground rock, and his explanation is that additions of these substances result in pH-value increases.

The treatment with the additive Kemira No. 5 was not replicated and thus hard to evaluate. However, the treatment seemed to decrease the ammonia emission, which can be explained by the contents of calcium chloride and superphosphate in the formulation.

The treatment with the additive Kemira No. 15 did not result in a emission decrease, which is hard to explain due to the contents of salts and acids in the formulation.

On the first and the third measuring occasions the treatments with Add A resulted in statistically higher ammonia emissions than from the controls ($p<0.01$ and $p<0.05$, respectively). According to the company that markets Add A, Biosolv, the population of bacteria requires certain living conditions, e.g. that the livestock are fed with "the right type of feed". Biosolv also claims that the time period required for the additive to reduce the ammonia emission with full effect is a couple of months. Whether the lack of effect in reducing ammonia emission is due to unsuitable feed, too short a measuring period, an inability to work under laboratory conditions, or simply an inability to reduce ammonia emission from cow slurry, is hard to tell. In this experiment, however, the treatment with Add A resulted in an increased ammonia emission at the first and the third measuring occasion.

No good correlations were found between the emission values and the values from the Kjeldahl analyses. Applications of the additives Kemira No. 2 and Stalosan in manure were expected to result in decreases in pH, but these decreases were not detected in the analyses. Rank (1988) reports that very small decreases in pH are required to lower the ammonia emission substantially. One reason could be that the pH may have increased during the storage (four weeks in a freezer) and the thawing period of the specimens from the slurry samples prior to the analyses. Another reason might be that the precision of the pH-measuring was not sufficiently accurate, but this hypothesis fails when considering that the contents of ammonium-N should then have been much lower than what was detected.

6 conclusions

One day after the application of the additives in the slurry samples the treatment with Kemira No. 2 and Stalosan resulted in lower ammonia emission than from the control ($p<0.001$). The emissions from the slurries treated with these two additives were approximately 40 % and 50 % lower than from the untreated slurries, respectively. At $p<0.01$, no significant differences were found between the treatments with Kemira No. 15, fly ash (low), Penac G and the control. At this significance level, the treatments with Add A and fly ash (high) resulted in higher emissions than from the control. The Kemira No. 5 treatment was not replicated and therefore hard to evaluate. However, this single treatment indicated that this additive can reduce the ammonia emission.

One week after the application of the additives the treatment with Kemira No. 2 resulted in lower emission than from the control ($p<0.001$). The Stalosan treatment gave even better effect and the emissions were significantly lower than from the treatment with Kemira No. 2 ($p<0.001$). Treatments with these two additives resulted in approximately 40 % and 60 % lower emission than from the untreated slurries, respectively. At $p<0.05$ and $p<0.01$, no significant differences were found between the control and the other treatments except with fly ash (high), which resulted in higher emissions than from the control. The Kemira No. 5 treatment also seemed to have an emission-reducing effect.

Six weeks after application of the additives, Stalosan still reduced the ammonia emission compared with the emission from the untreated slurries ($p<0.05$). The approximate reduction was 30 %. At this significance level the treatment with Add A resulted in a higher emission than from the untreated slurries. All the other slurries treated with the different additives emitted ammonia at the same rate as the control.

The probable cause of Kemira No. 2 and Stalosan, both of which based on superphosphate, reducing the ammonia emission is that the carbonate ions present in the slurries are precipitated as calcium carbonate. The pH then decreases, which results in a lower ammonia emission.

In the correlation analyses of the results from all three of the measuring occasions no good correlations were found between the emission values and total-N, ammonium-N, ammonium-N / total-N, total solids and pH-values. Thus, in neither of the cases could the ammonia emission values be explained by the results from the Kjeldahl analyses.

The climate variations during each day, as well as during the two days together, of each measuring occasion were relatively small, and were considered so small that they would not influence the ammonia emission levels.

Crust had formed on all the slurries throughout the six weeks of the experiment. The crusts on the slurries grew at approximately the same rate and the thicknesses of the crusts were the same on all the slurries, except on the one treated with Kemira No. 5, which was about two times thicker.

The economic evaluation showed that if a reduction in ammonia emission is only expected in livestock buildings when applying the additives Kemira No. 2 and Stalosan, the cost would be 780 SEK/kg saved nitrogen and 260 SEK/kg saved nitrogen respec-tively. If a reduction of the emission from the storages (two weeks) also can be expected the costs will be reduced to 740 SEK/kg saved nitrogen and 240 SEK/kg saved nitrogen. This economic evaluation is approximate and should only be used as an indication of the cost levels of using these two additives.

7 future research and development

Application of manure additives as a means to decrease ammonia emissions from animal buildings is very interesting due to the generally simple application techniques required and the low interference in the living conditions of the animals. More research must be conducted in this field to develop the technique and to investigate its limits. The research and development should be aimed in the following directions:

* Most of the tested additives on the market have been evaluated with different test methods which makes the effects of these additives hard to compare. Also, new additives are being continuously introduced into the market. Therefore standardized test procedures must be developed.

* To be able to determine the absolute ammonia emis-sion reducing effect of the additives tested in this study they have to be tested in full-scale trials.

* Inexpensive additives have to be developed.

* Additives with long effects have to be developed. The main reason why manure additives are expensive to use is the limited time they are effective. The largest ammonia emissions occur during storage and spreading of the manure.

* The application techniques of the additives must be developed. When, where and how should the additives be spread?

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9 appendices

9.1 Appendix 1: Results from the Kjeldahl analyses of the slurry samples on the first measuring occasion.

Treatm. No.	Additive	Total-N [%]	Amm.-N (%)	Amm.-N / Total-N [%]	Total solids [%]	pH
1	Add A	0.31	0.16	51	7.6	8.1
1	Add A	0.31	0.13	43	7.9	8.1
1	Add A	0.35	0.16	47	8.4	8.1
2	Penac G	0.28	0.14	51	8.8	8.0
2	Penac G	0.37	0.17	45	8.4	7.9
2	Penac G	0.32	0.17	54	-	8.1
3	Kemira No. 2	0.34	0.16	46	10.1	8.0
3	Kemira No. 2	0.34	0.16	47	10.8	7.9
3	Kemira No. 2	0.29	0.16	57	10.2	7.9
4	Kemira No. 5	0.35	0.10	30	10.2	7.9
3	Kemira No. 2	0.29	0.16	57	10.2	7.9
4	Kemira No. 5	0.35	0.10	30	10.2	7.9
5	Kemira No. 15	0.34	0.17	51	8.6	8.0
5	Kemira No. 15	0.34	0.16	46	9.4	7.9
5	Kemira No. 15	0.37	-	-	9.0	7.7
6	Fly ash (Low)	0.39	0.16	43	10.8	8.1
6	Fly ash (Low)	0.34	0.17	49	8.7	7.9
6	Fly ash (Low)	0.30	0.16	52	8.2	8.1
7	Fly ash (High)	0.33	0.18	33	8.6	7.9
7	Fly ash (High)	0.36	0.17	47	9.7	8.1
7	Fly ash (High)	0.36	0.17	47	9.7	8.1
7	Fly ash (High)	0.32	0.16	50	9.5	8.0
8	Stalosan	0.35	0.16	43	9.3	8.0
8	Stalosan	0.31	0.16	49	7.9	8.2
8	Stalosan	0.35	0.16	52	8.9	8.1
9	Control	0.33	0.11	33	8.6	7.9
9	Control	0.35	0.15	42	8.0	8.0
9	Control	0.32	0.15	46	8.8	8.1

9.2 Appendix 2: Results from the Kjeldahl analyses of the slurry samples on the second measuring occasion.

Treatm. No.	Additive	Total-N [%]	Amm.-N (%)	Amm.-N / Total-N [%]	Total solids [%]	pH
1	Add A	0.33	0.15	46	9.0	7.9
1	Add A	0.34	0.13	40	8.6	7.9
1	Add A	0.36	0.16	43	10.7	8.0
2	Penac G	0.36	0.21	59	9.8	8.1
2	Penac G	0.39	0.15	39	13.1	8.0
2	Penac G	0.31	0.16	51	8.7	8.0
3	Kemira No. 2	0.33	0.15	45	10.9	7.9
3	Kemira No. 2	0.30	0.14	46	11.6	8.0
3	Kemira No. 2	0.32	0.15	47	10.4	8.1
4	Kemira No. 5	-	-	-	-	-
5	Kemira No. 15	0.33	0.15	45	8.8	8.0
5	Kemira No. 15	0.30	0.15	52	9.1	8.2
5	Kemira No. 15	0.37	0.15	42	9.1	8.1
6	Fly ash (Low)	0.33	0.16	50	8.7	8.0
6	Fly ash (Low)	0.30	0.16	54	9.1	8.0
6	Fly ash (Low)	0.31	0.15	49	9.1	8.2
7	Fly ash (High)	0.27	0.16	57	9.8	8.2
7	Fly ash (High)	0.31	0.16	50	10.0	8.0
7	Fly ash (High)	0.37	0.13	36	13.1	7.8
8	Stalosan	0.36	47	43	9.6	7.7
8	Stalosan	0.39	0.15	39	10.6	8.0
8	Stalosan	0.33	0.16	49	9.3	7.7
9	Control	0.30	0.16	53	8.4	8.2
9	Control	0.32	0.15	46	8.3	8.0
9	Control	0.30	0.16	51	8.5	8.1

Ammonia emissions contribute substantially to environmental pollution and cause severe acidification. In Sweden, 20-25 % of the total ammonia emission derives from manure in animal buildings. One technique to decrease ammonia emissions from animal buildings is to apply emission-reducing additives in the manure. However, the efficiences of many of the manure additives on the market have not been determined, and those additives that have been evaluated are difficult to compare due to different test methods and methods of evaluation.

The objectives of this study were to investigate the abilities of different manure additives in reducing ammonia emission, for how long they would be efficient, and to which cost the additives can be used.

The results show that high reductions (up to 50 %) in ammonia emissions are pos-sible to obtain with some of the additives, at least during the first week after the appli-cation of the additives. The reductions decrease over time, and they are hardly noticeable after six weeks. The costs to which these additives can be used are high in relation to the amount of nitrogen they save.