Jan Barwicki[1)], Kinga Borek[2)]
[1)] Agency for Restructuring and Modernisation of Agriculture (ARMA), 33 Poleczki Street, 02-822 Warsaw, Poland
[2)] Institute of Technology and Life Sciences in Falenty, Department of Rural Technical Infrastructure Systems, Branch in Warsaw, 32 Rakowiecka Street, 02-532 Warsaw, Poland

NOWE TECHNOLOGIE UTYLIZACJI ZMNIEJSZAJĄCE SZKODLIWĄ AKTYWNOŚĆ GNOJOWICY NA FARMACH I PODCZAS APLIKACJI NA POLU

UTILIZATION OF NEW TECHNOLOGY TO REDUCE HARMFUL ACTIVITY OF SLURRY ON FARM AND IN THE FIELD APPLICATION

Summary

Dairy and beef cattle farms have high concentration of slurry what creates ammonia emission problems. The article presents some proposals for development of new technology in this area. Using slurry acidification technology in the barn, in the storage or in the field we can avoid many environmental problems concerning ammonia emission. Besides that we can save on overall fertilizers usage on the farm. Ammonia emissions is a major problem associated with animal slurry management, and solutions to overcome this problem are developed worldwide by farmers and scientists. An obvious way to minimize ammonia emissions from slurry is to decrease slurry pH by addition of acids or other substances acting in similar way. This solution has been used commonly in Denmark, and its efficiency with regard to the minimization of NH_3 emissions has been documented in some studies. Acidification reduced NH_3 emission from stored slurry to less than 10% of the emission from untreated slurry, and the NH_3 emission from applied slurry on the field was reduced by 67%.

Key words: new technology, slurry acidification technology, ammonia emission, environment protection

INTRODUCTION

Discussing the problem of slurry influence on country side environment, it is important to provide some analysis of animal production, what has substantial influence on manure presence in close distance to houses and flats. In Figure 1 it is presented number of different animals, which are grown on farms in different countries of EU.

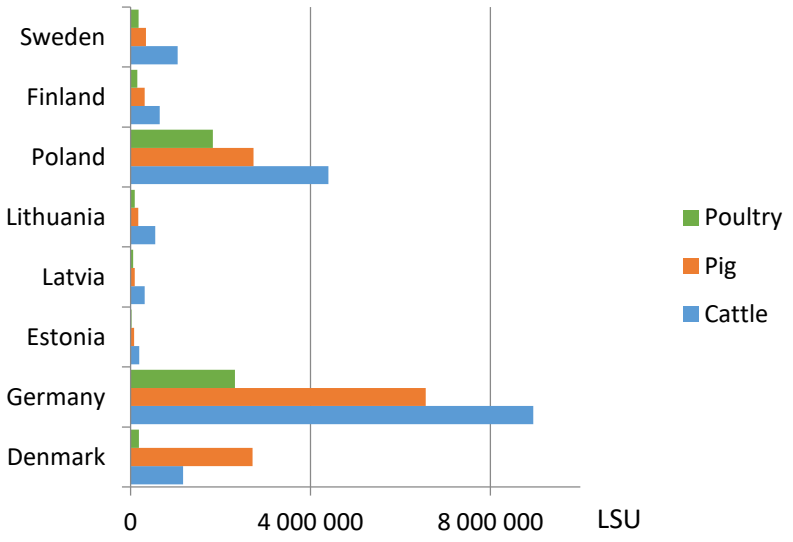


Fig. 1. Population of cattle, pig and poultry in different countries in LSU* [own study]
*The reference unit used for the calculation of livestock units (=1 LSU) - is the grazing equivalent of one adult dairy cow producing 3 000 kg of milk annually, without additional concentrated foodstuffs.

The international interest for slurry acidification is big and the current draft BREF (Reference Document for Best Available Techniques) has recognised slurry acidification, which will become a compulsory to BAT in all EU member states. There are three main technologies, namely in-house, tank and in-field acidification. Their effects in reducing ammonia emissions from stables, stores and fields are substantial, and in the range of 40 to 64% according official [4, 5, 9, 10, 13], among other the VERA technology verification programme set up in cooperation between Danish, German and Dutch environmental authorities.

Slurry acidification can be explain as equilibrium between the water bound ammonium (NH_4+) and the volatile ammonia (NH_3) is moved towards ammonium by adding acid to the slurry. Normally, concentrated sulfuric acid is used, and the costs of the acid in many cases outweighed by savings on purchase of S fertiliser. The nitrogen that is captured via avoided ammonia evaporation is turned into savings on purchase of N fertiliser, or in higher crop yields [2, 3]. Slurry acidification also has a considerable climate effect by increasing the carbon sequestration in soil. Reducing the loss of nitrogen from agriculture is key to reducing eutrophication of the Baltic Sea. Most of the airborne eutrophication to the Baltic Sea comes from ammonia emissions, and in the BSR almost all ammonia emissions are from livestock manure. Annual deposition of ammonia nitrogen to the Baltic Sea has been increasing during recent years and was greater in 2012 than in 1995. While emissions are decreasing slightly in some countries, HELCOM Baltic Sea Action Plan calls for a reduction of 118,000 tonnes of nitrogen annually to the Baltic Sea, and the Revised Gothenburg Protocol (2012) calls for ambitious reductions in ammonia emissions from all BSR countries. Slurry acidification also affects solid/liquid slurry separation efficiency positively; DM is higher, N lower and P higher in the solid fraction. A combined treatment should efficiently prevent gaseous emissions, increase fertilizer value of slurry and reduce transport and energy costs [15, 16, 21].

Acidification of animal slurry has proved to be an efficient solution to minimize NH_3 emissions in-house, during storage, and after soil application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions.

Acidification of slurry is one method to reduce ammonia emissions. Mainly implemented in Denmark, SAT use sulfuric acid to decrease the pH in in-house, in storage or in field system. Organic acids could be a good alternative to sulfuric acid to develop SATs for organic farming. Successive acidifications of slurry could be a solution to keep a stable pH and avoid ammonia emissions during all the period of storage.

Slurry acidification is used mainly in Denmark where 20% of all animal slurry was acidified in 2016 (Karen Peters, Danish Ministry of Environment and Food, personal communication, September 28, 2016). Slurry can be acidified at different stages of the manure handling chain: in-house, in-storage and in-field. In Sweden, legislation forbids keeping slurry in the animal house and requires frequent removal, and therefore in-house slurry acidification is not very relevant for implementation. Consequently, acidification in-storage or in-field is more suitable to control ammonia emissions in Sweden. In Denmark the in-storage technique has been developed to acidify in the storage tank or lagoon under heavy mixing just prior to spreading.

Titration is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified titrand (slurry in our study). Since volume measurements play a key role in titration, it is also known as volumetric analysis. A

reagent, called the titrant (acid in our study) is prepared as a standard solution. The titration permits determined from a known concentration of acid the volume needed to decrease the pH at 6.4, 6.0 or 5.5. Problems using sulfuric acid for acidification include possible toxic gas emissions like hydrogen sulphide. Moreover, sulfuric acid is not allowed in organic farming. Alternative acids have been tested to replace sulfuric acid for slurry acidification in order to improve slurry management [7, 8, 9]. The acid strength, the time before pH increase, the capacity to reduce ammonia emissions and the price were arguments when choose between organic acids. The use of an organic acid to replace sulfuric acid for slurry acidification could be an opportunity for organic farms to benefit from this technology.

DESCRIPTION OF ACIDIFICATION PROCESSES AND DEVELOPMENT OF NEW ENVIRONMENTAL SOLUTIONS

Just to explain, why ammonia evaporation doesn't exists, it can be explained by drawing the following equilibrium in slurry between ammonium salt and ammonia gas

$$NH_4^+ + OH \leftrightarrow NH_3 + H_2O$$

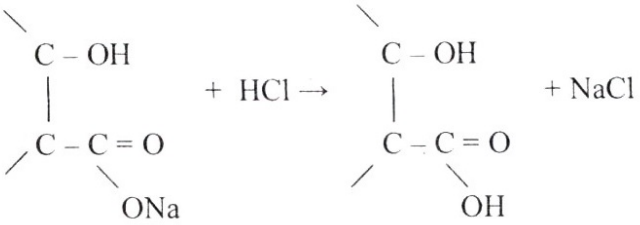
At pH=6,4 all mineralized N is found as ammonium, and no evaporation takes place [2].

In Denmark, the slurry should after lowering the pH <6 be spread within 24 hours according to rules. As the spreading season last for longer times, this could mean a period of several weeks per year. Economical calculations are needed to compare which solution is most profitable for individual farms. When hiring the service of acidification, the technology will be available also for smaller farms. Also, if surplus storage volume is needed because of foaming when adding acid, may make the alternative non-profitable compared to the other two alternatives [1].

Soil buffer properties will be called the ability of the soil to resist, within certain limits, sudden changes in the soil reaction caused by the inflow of hydrogen or hydroxide ions or changes caused by other factors. In contrast to aqueous solutions in the soil, there are some mechanisms that slow down the acidification and alkalization processes. Buffer properties depend on many factors, in particular on the size of the sorption complex, type of exchangeable cathodes, which is saturated. If there are no hydrogen ions able to be exchanged in the sorption complex, then each subsequent addition of the base will no longer be neutralized and hydroxyl ions will be present in the soil solution (for example, NaOH, KOH). In conclusion, it can be stated that the more hydrogen ions in a given soil, the higher the soil has the buffer properties relative to the bases. Soil humus plays an important role as a buffer, which is a mixture of weak organic acids and their salts with strong bases [14, 17, 18, 19, 20]. Such a system relieves acidification as follows:

a) $CH_3CH_2CH_2COONa + HCl \rightarrow CH_3CH_2CH_2COOH + NaCl$

b)



In both cases, a weak organic acid is formed instead of the acid strongly acidifying HCl. Regardless of this, caries in a specific way sorbents Al^{3+} ions with high toxicity to plants. Organic soils can therefore have low pH values, yet plants grow on them without disturbance. Another buffer system in the soil are carbonate and phosphate compounds:

- carbonate buffer - $H_2CO_3 + CaCO_3 \rightarrow Ca(HCO_3)_2$,
- phosphate buffer - $H_3PO_4 + Ca3(PO_4)_2 \rightarrow 3\ CaHPO_4$.

Adding acid to the soil (H_2CO_3 i H_3PO_4) they are neutralized by $CaCO_3$ or $Ca_3(PO_4)_2$.

Fig. 2. In storage acidification process in ITP Experimental Farm in Biebrza [Source: ITP, author: J. Barwicki]

Fig. 3. In storage acidification system TF-12 developed by Danish Co. ORUM [Source: ITP, author: J. Barwicki]

Fig. 4. Slurry mixing and acidification using ORUM system
[Source: ITP, author: J. Barwicki]

RESULTS AND DISCUSSION

Slurry acidification technology gives many advantages from the point of view soil fertilization and also the limiting of ammonia emission. Of course it requires provide safety procedures to avoid direct contact of farm workers with harmful activity of the acid. But heaving good acidification technology, which doesn't allow to have direct contact either in the storage area or in the field with the acid, this job is rather safe while fulfilling the procedures.

Fig. 5. In line reading of pH value of slurry during acidification of slurry in ITP Biebrza farm [Source: ITP, author: J. Barwicki]

Acidification reduces NH_3 emission from pig houses by 70% compared with the standard housing treatment. Little loss was observed from stored slurry, and the NH_3 emission from applied slurry was reduced by 67%. In consequence, a 43% (S.E. 27%) increase in mineral fertilizer equivalent (MFE) was measured in field studies.

Acidification of animal slurry has proved to be an efficient solution to minimize NH^3 emissions in-house, during storage, and after soil application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions.

Development of many groups of soil microorganisms, such as nitrifying bacteria, symbiotic and free-living bacteria assimilating nitrogen from the air is limited (which reduces the availability of nitrogen compounds for plants). In addition, in the acidic soils, the activity of many other groups of soil microorganisms, involved in the mineralization and humidification processes of organic matter, is reduced. Under acidic soil conditions, these processes are significantly slowed down, mainly due to fungi that tolerate low soil pH well. Amount of organic matter in the soil is reduced due to increased solubility and leaching into the soil profile of folic acids. Soil acidification also promotes the formation of salts of holmic acids with aluminium and iron, which easily leach into deeper soil profile layers [6].

Furthermore, acidification impacts positively on other slurry treatments such as solid liquid separation or composting; upon the use of a non-sulphur containing additive, it may also impact positively on biogas production. Nevertheless, acidification of slurry might induce higher losses by leaching, due to solubilisation of mineral elements [11, 12].

Table 1a. Results of chemical analysis of soil on ITP farm [Source: own study]

	Plot	Date	pH	Total N [%]	P [mg/kg]	K [mg/kg]	SO_4 [mg/kg]	Ca [mg/kg]	Mg [mg/kg]	Mn [mg/kg]	Zn [mg/kg]
Before using bovine slurry	I	2017-05-10	6.4	0.2-0.25	0.3-0.4	0.45-0.48	2	2100	55	30	2.1
Before using acidified bovine slurry	II	2017-05-10	6.5	0.3-0.4	0.2-0.3	0.4-0.45	2	2000	52	34	2.3
Before using bovine slurry	III	2017-06-10	6.4	0.25-0.3	0.3-0.4	0.45-0.48	1,5	1800	53	35	2.3
Before using acidified bovine slurry	IV	2017-06-10	6.5	0.3-0.4	0.2-0.3	0.4-0.45	1,3	1900	58	35	2.3

Table 1b. Results of chemical analysis of soil on ITP farm [Source: own study]

	Plot	Date	Humus [%]	Soil org. matter	Soil org. C [%]	Diss. organic carbon	Depth [cm]	B [mg/kg]	Cu [mg/kg]
Before using bovine slurry	I	2017-05-10		1.6	n.a.	-	0-30	-	0.5
Before using acidified bovine slurry	II	2017-05-10		1.9	n.a.	-	0-30	-	0.2
Before using bovine slurry	III	2017-06-10		2	n.a.	-	0-30	-	0.3
Before using acidified bovine slurry	IV	2017-06-10		1.4	n.a.	-	0-30	-	0.4

Alternatives to concentrated acids already exist but more research is still needed to improve both their technical and economic aspects. Moreover, the lack of specific equipment for the acidification of solid manures and the separated solid fraction narrows the possible fields of application of the treatment.

pH level of 5.5-6.4 is not very acidic, and no more acidic than rain water, which has a normal pH range from 4.5 to 8.5.

Table 2 Results of chemical analysis of slurry prepared for application on ITP fields [Source: own study]

The way of implementation	Dry matter content	Total N [kg/m^3]	NH_4-N [kg/m^3]	P [kg/m^3]	K [kg/m^3]	S [%]	pH on field surface	Ca [kg/m^3]	C in dry matter [%]
Cattle slurry	6,5	3,6	1,8	0,9	2,7	0,2	7,2	0,8	40
Acidified cattle slurry	6,7	3,6	1,9	0,9	2,9	3	5,86	0,85	34
Cattle slurry	7,2	3,4	2,0	0,9	2,7	0,3	5,7	0,7	41
Acidified cattle slurry	7,5	3,6	1,8	0,9	2,6	3	5,9	0,63	36

Corrosion of concrete in stables due to use of slurry acidification has never been an issue in Denmark, as it isn't for an outdoor concrete construction like this exposed to rain.

Acidification of animal slurry has proved to be an efficient solution to minimize NH_3 emissions in-house, during storage, and after soil application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions.

It is needed more information to have clear evidence that this technology does not induce any pollution swapping. Since slurry acidification is running successfully in Denmark, it is realistic that the technology can be applied in many other countries. However, such dissemination of acidification depends mainly on the country's legislation that will be altered only with a solid scientific basis.

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Jan Barwicki, Kinga Borek

Streszczenie

Bydło mleczne i mięsne utrzymywane w budynkach inwentarskich wyposażonych w podłogi szczelinowe powoduje wysoką koncentrację gnojowicy i jest przyczyną emisji dużej ilości amoniaku. W artykule przedstawiono wybrane propozycje dla rozwoju nowoczesnych technologii w tej dziedzinie. Wykorzystanie technologii systemu zakwaszenia gnojowicy w budynkach inwentarskich, zbiornikach lub bezpośrednio na polu pozwala na zmniejszenie emisji amoniaku, co wpływa pozytywnie na ochronę środowiska. Ponadto, możemy zaoszczędzić na ilości nawozów stosowanych w gospodarstwie. Rozwiązaniem tego problemu zajmują się naukowcy, farmerzy na całym świecie. Oczywistym sposobem minimalizacji emisji amoniaku jest zmniejszenie pH gnojowicy poprzez dodawanie kwasów lub innych substancji, działających w podobny sposób. Takie rozwiązania stosowane są w Danii, a jego skuteczność minimalizacji emisji NH_3 zostało udokumentowane w pracach naukowych. Zakwaszenie zmniejsza emisje NH_3 przechowywanej gnojowicy do 10% w porównaniu z gnojowicą bez zakwaszenia, a emisja NH_3 w polu była mniejsza o 63%.

Słowa kluczowe: nowe technologie, zakwaszenie gnojowicy, emisja amoniaku, ochrona środowiska