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ESTIMATION OF THE EFFECTIVENESS OF NBPT FOR LIMITING AMMONIA EMISSION FROM UREA BASED ON THE FIELD EXPERIMENTS

OCENA EFEKTYWNOŚCI NBPT W OGRANICZANIU EMISJI AMONIAKU Z MOCZNIKA NA PODSTAWIE WYNIKÓW DOŚWIADCZENIA POLOWEGO

Abstract: The effectiveness of the ammonia emission reduction from NBPT-stabilized urea was investigated in 2011 during a field experiment on a grassland plot fertilized with a one-time dose of 60 kg N/ha. The obtained reduction coefficient of ammonia emission equaled 73% and 39-51% relative to urea without the inhibitor and ammonium nitrate, respectively.

Keywords: N-(n-butyl) thiophosphoric triamde (NBPT), urea, ammonia emission, field experiments

Due to its harmful effect in troposphere, ammonia is considered the major anthropogenic pollutant of atmospheric air [1-3]. Ammonia emission, or more precisely its wet and dry deposition, contributes to soil acidification, the eutrophication of water bodies, and the production of suspended matter. It is also responsible for bad odor present in the vicinity of the numerous ammonia sources. The processes of gaseous ammonia production in agriculture have been rather well investigated however their quantitative estimation is not always simple. Animal production and the release of ammonia from the utilized natural fertilizer are among the most frequently listed emission sources of this particular nitrogen form into the environment, contributing ca. 70% of the total ammonia emission from agriculture. The remaining 30% of gaseous ammonia originate from other agricultural sources, mainly mineral nitrogen-based fertilizers [1, 4, 5]. According to Sommer et al [6], the loss of nitrogen via emission of gaseous ammonia can vary widely between 0 and 50% of the used dose of pure component, and it mainly depends on the type of fertilizer, not so much on cultivated plants and the method of fertilizer application. Additional factors which may play a role in the emission of ammonia from fertilizers are climatic conditions (temperature, wind speed and precipitation) and the physicochemical properties of soil, including calcium content, cation exchange capacity and pH. Ammonium bicarbonate

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(presently pulled out of the EU market), urea, ammonium nitrate and, to a lesser extent, ammonium sulphate are among synthetic solid nitrogen-based fertilizers that are commonly used in agriculture [7, 8] and have a high potential for releasing ammonia. In the case of urea, a relatively high loss of nitrogen in the form of ammonia should be assumed. Depending on the aforementioned factors, this loss may vary from 20 to 60%, with the highest values being determined for the surface application of fertilizer, *ie* application without mixing of soil and fertilizer, in grasslands. Loss of ammonia from ammonium nitrate is visibly lower, and generally ranges from 2 to 10%. According to the National Centre for Emissions Management [9], in 2009, the annual ammonia emission to air from mineral fertilizers in Poland reached 80.5 Gg N-NH_3. Ammonia polluting the air is not only an ecological problem, but also an economic issue because the excessive losses of ammonia limit the effectiveness of agricultural production and the farmer's profit. Urea is a leading product on the global nitrogen-based fertilizer market, however it has a major disadvantage. Urea undergoes hydrolysis to ammonia, a reaction catalyzed by the enzyme urease at temperatures above 5ºC, which practically means after each application of this fertilizer in the field. At least during the first couple days after the application, it is possible to slow down the ammonia release by mixing the fertilizer with urease inhibitors. Among many chemical compounds classified as nontoxic only very few fulfill the strict criteria of not being harmful to soil microorganisms as well as being easily biodegradable several days after their application [10]. N-(n-butyl) thiophosphoric triamide (NBPT) is a relatively well-studied substance which satisfies the above requirements. At present, the patent for NBPT production is held by Agrotain International and SKW Piesteritz. Agrotain International registered its product in many countries, including the EU, under the trade name Agrotain®, while the company Keytrade Polska Sp. z o.o. has exclusive rights to distribute NBPT in Central Europe. Recently, Keytrade Polska has also introduced granulated urea coated with 0.5% NBPT into the Polish domestic market; the fertilizer's trade name is moNolit46®. In 2011, the effectiveness of NBPT for limiting ammonia emission from urea under conditions typical for a Polish farm was tested during a field experiment in grasslands. It should be mentioned that properly documented publications on this subject are still lacking in the Polish scientific literature.

The aim of this study was to quantitatively estimate the emission of ammonia from moNolit46® which had been applied as a one-time dose of 60 kg N/ha to experimental plots in grassland areas located on three farms in Zulawy, Poland. The obtained values of ammonia emission were compared to the emission values from ammonium nitrate and urea applied at the same time in identical total nitrogen doses to the control plots.

Experimental

Measurements of ammonia emission

Ammonia emission from the applied mineral fertilizers was estimated based on direct measurements of the mass of gaseous ammonia emitted from the experimental plot. The measurements were performed by using micrometeorological method of passive dosimetry [11-13], originally elaborated by the Swedish Environmental Research Institute (Gothenburg, Sweden) and later modified by the author for the purpose of this study. The original method was used to evaluate the emission of ammonia from nonpoint agricultural sources, particularly grasslands treated with natural fertilizers. Thirty-two passive dosimeter tubes [14] coated with a thin layer of sorption agent, *ie* oxalic acid, were placed on the measuring masts (Fig. 1) distributed symmetrically along the sides of the experimental plot. The exposure time was 24 hours. The vertical flux density of ammonia was measured for four height intervals, starting from the ground level (emission source) and ending at about 2-2.5 m. Ammonia in the form of ammonium oxalate was extracted from the dosimeter tubes with 5 cm^3 of deionized water. The colorimetric analysis of extracts was performed with a continuous flow autoanalyzer FIA Compact.

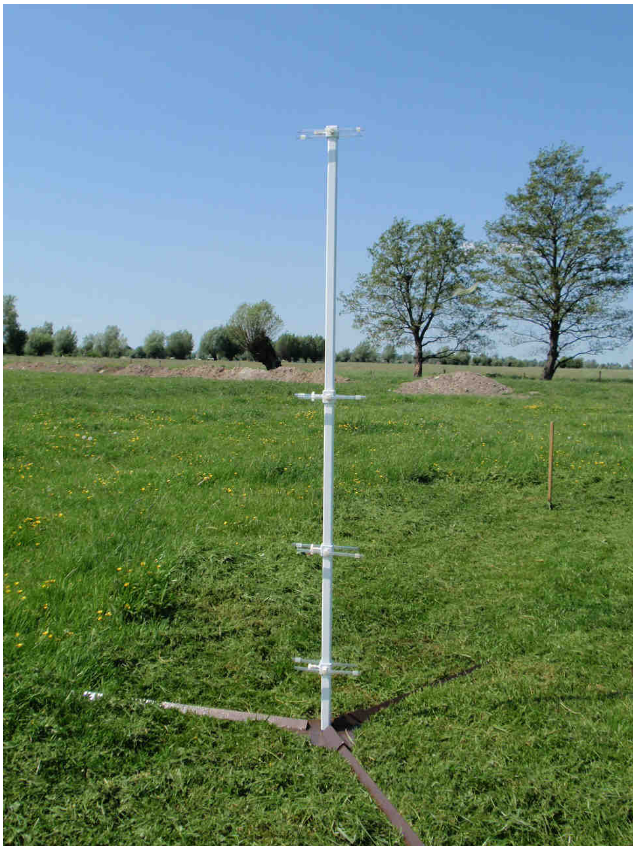

Fig. 1. The measuring mast ready for collecting data

Field experiments

In 2011, the field experiments were conducted in Zulawy in three farms coded as A, B and C (Fig. 2). All three family-operated dairy farms have been classified as large according to the EU criteria. They produce ca. 200 000 kg of milk per year, and sell the male calves for veal production. Two experimental plots, each 100 m^2 in size, were delineated in grasslands belonging to the farms. The experimental plots were located at least 200 m apart in order to minimize interactions between them. All plots were fertilized with the same total nitrogen dose of 60 kg N/ha after cutting and removing the grass. Each plot received only one type of fertilizer. In the case of farms A and C, moNolit46 and ammonium nitrate were used (Table 1), while moNolit46 and urea were applied on farm B. Field experiments were conducted from 30 May until 17 June 2011. A 4-day measuring cycle was used on the farms A and B, and a 5-day measuring cycle on farm C. Agrotechnical and meteorological observations were conducted to complement the measurements of ammonia emission. The influence of moNolit46 on the yield and quality of the produced biomass has not been assessed during field experimentation.

Fig. 2. Field measurement of ammonia emission on the experimental plot

Table 1

Characterization of soil and climatic conditions during field experiments

Farm code	Date on which measurements started	Fertilizer type	Soil pH in 1 M KCl	Max. air temperatue [°C]	Relative humidity [%]	Wind speed [m/s]	Comments
A	30 May 2011	moNolit46	5.54	26-35	52-75	0.8-3	No precipitation
		ammonium nitrate	5.22	28-33	44-75	0.8-3	Freshly cut grass
B	06 June 2011	moNolit46	5.01	25-30	52-79	0.3-2	Small rain on
		urea	4.73	25-30	51-75	0.3-2	day 4 (< 2 mm)
C	13 June 2011	moNolit46	6.60	22-28	44-92	0.4-2	Small rain on
		ammonium nitrate	5.34	22-27	52-89	0.4-2	day 3 (< 3 mm)

Results and discussion

The values of ammonia emission determined during field experiments (Table 2) indicate that the loss of gaseous ammonia from mineral fertilizers can vary widely. The values obtained under the described field conditions for different fertilizers ranged from 2.4 to 17.6 kg N/ha. The highest ammonia emission for the same total nitrogen dose of 60 kg N/ha was measured on farm A, *ie* 10.6 and 17.4 kg N/ha for moNolit46 and ammonium nitrate, respectively. Lower nitrogen loss in the case of moNolit46 was most likely due to the addition of NBPT which visibly inhibited the hydrolysis of urea and ammonia volatilization. Nevertheless, already four days after the application of fertilizers, 17.7 and 29% of nitrogen was released into the atmosphere from moNolit46 and ammonium nitrate, respectively. Ammonia emission from moNolit46 was lower by 39% compared to ammonium nitrate however economical and ecological losses were very visible, particularly in the case of ammonium nitrate. It should be mentioned that the weather conditions during field experimentation on farm A were rather extreme (see Table 1), *ie* the air temperature was periodically exceeding 35°C and there was no precipitation. Such conditions could stimulate ammonia volatilization. Zhang et al [15], Pagans et al [16], and Sommer et al [6] claim that temperature and wind speed can have a true effect on ammonia emission, particularly in the case of surface application of the fertilizer. According to the aforementioned authors, the specific grassland microclimate, in particular its high surface roughness and the restricted contact between soil and fertilizer due to the presence of vegetation can also result in a more dynamic ammonia volatilization. On farm B the values of ammonia emission from moNolit46 and urea were compared after the total nitrogen application of 60 kg N/ha to grassland for second growth after mowing. The 4-day ammonia emissions from moNolit46 and urea amounted to 2.4 and 9.6 kg N/ha, respectively. The maximum air temperature during the field experiment on farm B reached ca. 30ºC, and a small rainfall (< 2 mm) was noted on day 4. The total ammonia loss from moNolit46 relative to the total nitrogen dose was estimated at 4.3%, while for urea at 16.1%. The reduction of ammonia emission from moNolit46, which is NBPT-stabilized urea, in comparison to inhibitor-free urea was visibly higher (Table 3) and equaled *ca*. 73%, when expressed as nitrogen. The probability of obtaining such high effectiveness of NBPT for limiting ammonia emission from urea has been confirmed by the results of field experiments conducted by Cantarella et al [17]. The coefficient of emission reduction measured by these authors in soil covered with the remnants of vegetation and exposed to a low level precipitation reached 78%. Due to the fact that the values of ammonia emission from the first field experiment on farm A are questionable, it was decided to repeat the comparative measurements of ammonia emission from moNolit46 and ammonium nitrate in the next experiment on farm C. According to Trenkel [10], ammonium nitrate can be treated as "non-volatile standard" relative to urea which has a high potential for gaseous ammonia release. The field experiment on farm C was conducted in the second decade of 2011 by fertilizing the plots with moNolit46 and ammonium nitrate in a dose of 60 kg N/ha. The 5-day total ammonia emissions from moNolit46 and ammonium nitrate equaled 2.4 and 5.0 kg N/ha, respectively. The total ammonia loss from moNolit46 relative to the total nitrogen dose was estimated at 4.1%, while for ammonium nitrate at 8.3%. Therefore the reduction of ammonia loss from moNolit46 compared to "non-volatile" ammonium nitrate was *ca* 51%.

Table 2

Ammonia emission from nitrogen fertilizers applied to grassland

Farm code	Fertilizer type	Overall nitrogen dose [kg/ha]	Ammonia emission in consecutive days after the application of fertilizer [kg N/ha]						Total loss of ammonia nitrogen [%]
			1	2	3	4	5	Total	
A	moNolit46	60	4.14	4.58	1.91	0.00	-	10.6	17.7
	ammonium nitrate	60	7.83	5.42	2.64	1.51	-	17.4	29.0
B	moNolit46	60	0.38	1.87	0.30	0.00	-	2.6	4.3
	urea	60	5.10	4.40	0.14	0.00	-	9.6	16.1
C	moNolit46	60	0.51	1.76	0.57	0.11	0.00	2.4	4.1
	ammonium nitrate	60	1.08	2.51	0.82	0.54	0.00	5.0	8.3

Table 3

The effectiveness of NBPT in reducing ammonia emission

Farm code	Fertilizer	[% reduction]
A	moNolit46 - ammonium nitrate	39
B	moNolit46 - urea	73
C	moNolit46 - ammonium nitrate	53

Conclusions

Ammonia emission from agriculture, which is considered the major anthropogenic source of this gas, has been a long-standing problem due to economic reasons as well as increasing ecological threats on a global scale. The problem will have to be dealt with by undertaking innovative research followed by practical implementation of novel ideas mainly aimed at limiting ammonia volatilization. Due to technological and agronomic reasons, the leading role of urea in the global and domestic nitrogen-based fertilizer markets remains unchallenged. However urea has a main disadvantage, namely, it tends to release gaseous ammonia. Based on earlier studies conducted by ITP, Falenty (Poland), ammonia emission from fertilized grasslands can exceed 30% of pure nitrogen applied. Considering the basic concepts of Good Agricultural Practices and economic reasons, solid urea should not be recommended for fertilizing grasslands. However the owners of large production farms do not always respect these guidelines. At present [18], it is known that the use of urease as an inhibitor in, for example, moNolit46 can significantly limit the propensity of the fertilizer to hydrolyze for at least 4 to 5 days after surface application. Therefore the increased effectiveness of this nitrogen form used for mineral fertilization is highly probable, while ecological profit is unquestionable as documented by the results of field experiments from this study.

References

[1] Erisman J, Bleeker A, Hansen A, Vermeulen A. Agricultural air quality in Europe and the future parspectives. Atmos Environ. 2008;42:3209-3217. DOI: 10.1016/j.atmosenv.2007.04.004.

[2] Choudhury ATMA, Kennedy IR. Nitrogen fertilizer losses from rice soils and control of environmental pollution problems. Communications in Soil Science and Plant Analysis. 2005;36:1625-1639. DOI: 10.1081/CSS-200059104.
[3] Marcinkowski T. Emisja gazowych związków azotu z rolnictwa (The emission of gaseous nitrogen compounds from agriculture). Woda-Środowisko-Obszary Wiejskie. 2010;10(3):175-189.
[4] Marcinkowski T, Kierończyk M. Emisja amoniaku z wybranych nawozów naturalnych i mineralnych (Ammonia emissions from selected organic natural and mineral fertilizers). PAN. Zesz Prob Post Nauk Roln. 2006;512:411-419.
[5] Cameron KC, Di HJ, Moir JL. Nitrogen losses from the soil/plant system: a review. Ann Appl Biol. 2013;162:145-173. DOI: 1111/aab.12014.
[6] Sommer SG, Hutchings NJ. Ammonia emission from field applied manure and its reduction-invited paper. Eur J Agron. 2001;15:1-15.
[7] Misselbrook TH, Van der Weerden TJ, Pain BF, Jarvis SC, Chambers BJ, Smith KA, et al. Ammonia emission factors for UK agriculture. Atmos Environ. 2000;34:871-880.
[8] FAO, Global estimates of gaseous emissions of NH_3, NO and N_2O from agricultural land. 2001.
[9] GUS, Ochrona Środowiska. Warszawa 2010.
[10] Trenkel ME. Slow and controlleled release and stabilized fertilizers. Paris, France: International Fertilizer Industry Association (IFA); 2010.
[11] Kierończyk M, Marcinkowski T. Pomiar emisji amoniaku ze źródeł rolniczych metodą mikrometeorologicznej dozymetrii pasywnej (Aplication of micrometeorological method of passive dosimetry to monitoring ammonia emission from agricultural sources). Woda-Środowisko-Obszary Wiejskie. 2004;4(2):537-546.
[12] Ferm M, Marcinkowski T, Kierończyk M, Pietrzak S. Measurements of ammonia emissions from manure storing and spreading stages in Polish commercial farms. Atmos Environ. 2005;36:7106-7113. DOI: 10.1016/j.atmosenv.2005.08.014.
[13] Gericke D, Pacholski A, Kage H. Measurement of ammonia emissions in multi-plot field experiments. Biosystems Eng. 2011;108:164-173. DOI: 10.1016/j.biosystemseng.2010.11.009.
[14] Namieśnik J, Jamrógiewicz Z. Fizykochemiczne metody kontroli zanieczyszczenia środowiska. Warszawa: WNT; 1998.
[15] Zhang Y, Wu SY, Srinath K, Wang K, Queen A, Aneja VP, et al. Modeling agricultural air quality: Current status, major challenges, and outlook. Atmos Environ. 2008;42:3218-3237. DOI: 10.1016/j.atmsenv.2007.01.063.
[16] Pagans E, Barrena R, Font X, Sanchez A. Ammonia emissions from the composting of different organic wastes. Dependency on process temperature. Chemosphere. 2006;62:1534-1542. DOI: 10.1016/j.chemosphere.2005.06.044.
[17] Cantarella H, Trivelin PCO, Contin TLM, Dias FLF, Rossetto R, Marcelino R, et al. Ammonia volatilisation from urease inhibitor-treated urna applied to sudarcane trash blankets. Sci Agric. 2008;65,4:397-401. DOI: 10.1590/S0103-90162008000400011.
[18] Zaman M, Blennerhassett JD. Effects of the different rates of urease and nitrification inhibitors on gaseous emissions of ammonia and nitrous oxide, nitrate leaching and pasture production from urine patches in an intensive grazed pasture system. Agricult Ecosyst Environ. 2010;136:236-246. DOI: 10.1016/j.agee.2009.07.010.

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Abstrakt: W doświadczeniu polowym wykonanym późną wiosną w 2011 roku badano efektywność redukcji emisji amoniaku z mocznika stabilizowanego NBPT, który wykorzystywano do nawożenia użytków zielonych w jednorazowej dawce 60 kg N/ha. Uzyskany współczynnik redukcji emisji amoniaku w stosunku do mocznika bez inhibitora wynosił 73%, zaś w stosunku do saletry amonowej 39-51%.

Słowa kluczowe: NBPT, mocznik, emisja amoniaku, doświadczenie polowe