Nitrous oxide emissions from the soil under different fertilization systems on a long-term experiment

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ABSTRACT

The research aimed at the assessment of N₂O emission from agricultural soils subject to different fertilization conditions. It was carried out on a long-term experiment field in Skierniewice in Central Poland maintained with no alterations since 1923 under rye monoculture. The treatments included mineral (CaNPK), mineral-organic (CaNPK + M) and organic (Ca + M) fertilization. Measurements were conducted during the growing periods of 2012 and 2013. N₂O emissions from the soil were measured *in situ* by the means of infrared spectroscopy using a portable FTIR spectrometer Alpha. N2O fluxes over the measurement periods showed high variability with range 0.13-11.20 g N₂O-N/ha/day (median 2.87, mean 3.16) from mineral treated soil, 0.23-11.06 g N₂O-N/ha/day (median 3.64, mean 3.33) from mineral-organic treated soil and 0.25-12.28 g N2O-N/ha/day (median 3.14, mean 3.55) from organic treated soil. N2O fluxes from manure-treated soils were slightly higher than those from soils treated exclusively with mineral fertilizers. N2O fluxes were positively correlated with soil temperature, air temperature, and content of both, NO₃ and NH₄, in the soil (0-25 cm) and, to a lesser degree, negatively correlated with soil moisture. Based on the measured N2O flux and its relationship with environmental factors it can be concluded that both, nitrification and denitrification the are important sources of N2O in mineral soils of Central Poland, where the average soil water-filled pore space during the growing period range from 22–35%. Under the climate, soil and fertilization conditions in Central Poland, the N_2 O emission from cultivated soils during the growing period is approximately estimated as 0.64–0.73 kg N/ha.

Keywords: N₂O emission; rye monoculture; static experiment; organic-mineral fertilization

Nitrous oxide ($\rm N_2O$) emission from agricultural soils is well addressed in the international scientific literature, including assessment of the influence of various agricultural engineering factors (Bouwman et al. 1993, Kaiser and Ruser 2000, Ruíz-Valdiviezo et al. 2013), and the development of emission models of various complexity (Farquharson and Baldock 2008, Metivier et al. 2009). The soil moisture, temperature, content of both, $\rm NO_3^-$ -N and organic carbon, and fertilization are described as the most important factors determining $\rm N_2O$ flux from the soil (Tiedje et al. 1982, Mogge et al. 1999, Dobbie and Smith 2003). In Poland, Włodarczyk et al. (2004) studied the effect of denitrification on $\rm N_2O$ emission from the soil. It is estimated,

however, that only approximately 10% of arable soils in Poland have properties favoring intensive denitrification (Goliński et al. 2000). Bateman and Baggs (2005) demonstrated that nitrification could be a dominant source of $\rm N_2O$ in the soils with soil water-filled pore space below 60%. $\rm N_2O$ flux from the soil and its determinants have not been comprehensively evaluated in the climate, soil and fertilization conditions of Poland.

Long-term fertilization experiments are well established in evaluation of the impact of mineral and organic fertilization on the nitrogen compounds changes in the soil (Dendooven et al. 1996). This study quantifies soil $\rm N_2O$ emission from a long-term fertilization experiment with rye monocul-

ture in the climate and soil conditions of Central Poland and analyzes the relationship between the N_2O emission and environmental factors.

MATERIAL AND METHODS

The research was carried out on a long-term experiment field in Central Poland (Skierniewice) belonging to the Warsaw University of Life Sciences-SGGW, maintained with no alterations since 1923 under rye monoculture. The soil is Luvisols (FAO 2006) soil of the type of loamy sand with the following fractions in the 0-25 cm layer: sand (> 0.05 mm) -87%, silt (0.002-0.05 mm) -5%, clay (< 0.02 mm) -7%. The average annual temperature and precipitation are 8° C and 520 mm, respectively.

The mineral (CaNPK), mineral-organic (CaNPK+M) and organic (Ca + M) fertilization systems were studied. Each treatment had 5 replications with an experimental plot area of 36 m².

Mineral fertilizers were applied at the following rates: 90 kg N (ammonium nitrate), 26 kg P (triple superphosphate) and 91 kg K/ha (potassium chloride 50%) in both, mineral and mineral-organic fertilization systems. Manure was applied at the dose of 30 t/ha at 4-year intervals and at 20 t/ha yearly in the treatment subject to mineral-organic and organic fertilizing, respectively. Consequently, the annual doses of nitrogen applied in the mineralorganic and organic fertilization systems can be respectively approximated as 127.5 kg N/ha and 100 kg N/ha. Liming at 1.43 t Ca/ha was applied to all investigated treatments every fourth year. N₂O emission from the soil was measured in situ by means of the infrared spectroscopy using a portable FTIR spectrometer model Alpha (Brucker Optic GmbH, Ettlingen, Germany). The N₂O flux from the soil was calculated as an increase in the N_2O concentration in the chamber (\emptyset = 29.5 cm, h = 20 cm) after a 10 min exposure to the soil surface. The results were extrapolated to 24 h and 1 ha. Measurements were conducted in 2012 (30 measurements, 22 March to 22 October) and 2013 (28 measurements, 19 April to 23 October) in all replications. $\mathrm{N}_2\mathrm{O}$ emission was expressed in mg N/ha/day.

Ploughing layer soil sampling was conducted on all measurement dates in all replications. The $\mathrm{NH_4^+-N/NO_3^--N}$ content was measured using the Skalar San Plus analyzer (Breda, Netherlands), after fresh soil extraction in 0.01 mol/L $\mathrm{CaCl_2}$ with soil/extractant ratio of 1:10. The soil mois-

ture was assessed for each object as a decrease in the sample weigh after oven-drying in 105°C. Atmospheric and soil temperatures were measured by the Experimental field's meteorological station.

Statistical analyses were performed with the IBM SPSS Statistics 21.0. The Mann-Whitney test and Bonferroni correction for multiple comparisons were used (P < 0.05). The Pearson correlation coefficients were calculated at P < 0.05.

RESULTS

The highest content of organic carbon and total nitrogen was found in the soil treated annually with manure (10.6 g C/kg and 0.96 g N/kg), followed by the soil under mineral-organic (8.8 g C/kg and 0.88 g N/kg) and mineral fertilization systems (5.68 g C/kg and 0.56 g N/kg). Soil pH in 1 mol/L KCl of these objects ranges from 5.8 to 6.2, with the highest values in the treatments under organic fertilization system.

The average content of mineral nitrogen in the soil under mineral and mineral-organic fertilization systems was higher in 2012 than in 2013, whereas the mineral nitrogen content in the manure-treated soil was found similar in both years (Table 1).

The average soil mineral N content was higher under mineral-organic fertilization system than under the mineral or organic ones but the differences were not statistically significant. In 2012, the average NO₃-N soil content was higher (under mineral and organic fertilization systems) or similar (under mineral-organic fertilization) to the NH_4^+ -N soil content. In 2013, the content of NH_4^+ -N in the soil was higher than that of NO₃-N on all investigated treatments. The changes in the soil content of NO₃-N and NH₄-N during the study period are presented in Figure 1. Fluctuations in mineral N content in the soil treated exclusively with manure were lower than those in the soil under mineral-organic and mineral fertilization systems. The spring application of ammonium nitrate led to an immediate increase in the content of both mineral forms of nitrogen in the soil under mineral and mineral-organic fertilization systems to the highest levels observed during the investigation period. In 2012, the content of mineral N in the soil under the mineral-organic fertilization system continued to increase after ammonium nitrate spring fertilization till the third decade of May. After a peak of mineral N soil content subsequent

Table 1. Content of mineral N (NO $_3^-$ -N/NH $_4^+$ -N) in soil (mg N/kg) and N $_2$ O-N emission from soil (g N/ha/day)
in different fertilization systems

Fertilization		2012				2013			
		NO ₃ -N	NH ₄ ⁺ -N	N _{min}	N ₂ O-N	NO ₃ -N	NH ₄ ⁺ -N	N _{min}	N ₂ O-N
CaNPK	mean	5.04	3.85	8.89	3.00	3.42	3.76	7.18	3.32
	median	3.60	2.55	6.40	2.85	3.19	3.12	6.54	3.02
	min-max	0.07-15.66	0.03-18.84	0.39-30.11	0.13-11.20	0.75-10.67	0.89-12.64	2.00-21.89	0.14-10.65
CaNPK + M	mean	7.23	7.47	14.70	3.44	4.81	5.17	9.98	3.84
	1 median	5.07	3.41	8.90	3.13	4.13	4.21	8.37	3.53
	min-max	0.25-32.50	0.05-30.73	0.58-56.57	0.40 - 9.93	1.20-14.80	1.17 - 18.44	2.54-32.12	0.23-11.06
Ca + M	mean	5.78	2.88	8.66	3.69	3.86	4.62	8.48	3.40
	median	6.13	2.94	9.25	3.06	3.73	4.44	8.27	3.15
	min-max	0.39 - 13.4	0.12 - 8.42	1.33-18.33	0.33 - 12.28	1.30 - 8.01	0.89-10.07	4.00-14.39	0.25 - 9.04

CaNPK - mineral, CaNPK + M - mineral-organic, Ca + M - organic fertilization systems

to the application of ammonium nitrate (enhanced by manure mineralization in the CaNPK + M treatment) a decrease in the soil content of both mineral N forms was observed (until the third decade of June 2012 and mid-May 2013). Further changes in NO_3^- -N and NH_4^+ -N soil content were of lower amplitude. After a period of intensive N uptake by rye resulting in a notable decrease in NO_3^- -N/ NH_4^+ -N content in the soil, a gradual increase in the soil content of both mineral N forms was

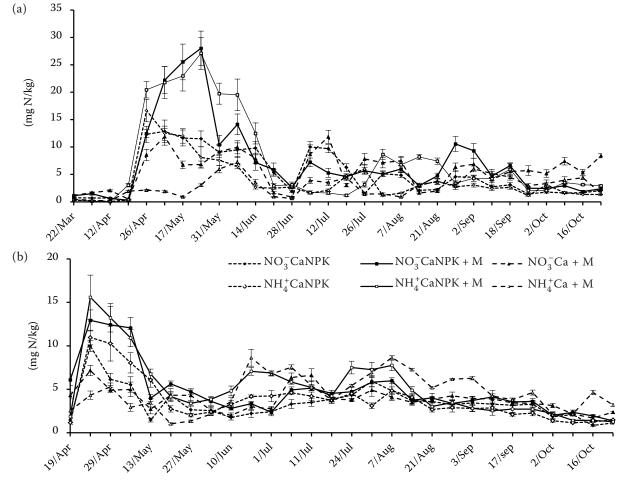


Figure 1. Soil content of NO_3^- -N and NH_4^+ -N under different fertilization systems in 2012 (a) and 2013 (b). CaNPK – mineral, CaNPK + M – mineral-organic, Ca + M – organic fertilization systems

80

40

20

0

summer flood.

(SWFPS)

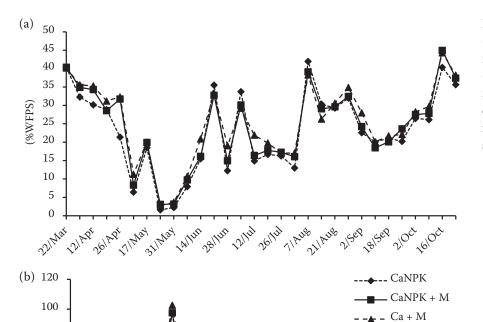


Figure 2. Moisture of soil (0–25 cm) under different fertilization systems in 2012 (a) and 2013 (b). CaNPK – mineral, CaNPK + M – mineral-organic, Ca + M – organic fertilization systems; WFPS – soil moisture

observed, most markedly in the manure-treated soil (CaNPK + M, Ca + M). In 2013, the increase in NH_4^+ -N soil content was distinctly higher than that of NO_3^- -N. The dominance of NH_4^+ over NO_3^- was probably caused by a permanent reduction in the nitrifying bacterial flora as a result of the

A decrease in the soil content of both forms of mineral N was noted from the beginning of September, probably as a result of decreased intensity of N compounds transformation and N uptake by germinated rye. An increase in the mineral N content observed in the end of the vegetation period in the soil treated exclusively with manure is explained by treatment application at that time.

The soil moisture observed across various fertilization systems was similar and varied over time as depicted in Figure 2. The average soil moisture in 2013 exceeded that in 2012 by approximately 36%. The air and soil temperatures are presented in Figure 3. In most instances, the average daily soil temperature values slightly exceeded the respective air temperature values.

N₂O flux over the measurement periods showed high variability with range 0.13–11.20 g N₂O-N/ ha/day (median 2.87, mean 3.16) from mineral treated soil, 0.23–11.06 g N₂O-N/ha/day (median 3.64, mean 3.33) from mineral-organic treated soil and 0.25-12.28 g N₂O-N/ha/day (median 3.14, mean 3.55) from organic treated soil. In both 2012 and 2013, the differences in N_2O emission from the soil under diverse fertilization systems were of no statistical significance (Table 1). Daily N₂O emission from the soil is depicted in Figure 4. Spring application of ammonia nitrate resulted in high N₂O emission from the soil. Simultaneously, increased N₂O emission was observed from the soil fertilized exclusively with manure regardless of lower mineral N content in the manure treated soil. During the flooding at the beginning of June 2013 no rapid increase in soil N₂O emission was noted. This phenomenon can be explained by the low mineral N content in the soil and low temperature (Figures 1 and 3). From the end of May to the end of the second decade of June 2012, N₂O emission from the soil treated exclusively with ma-

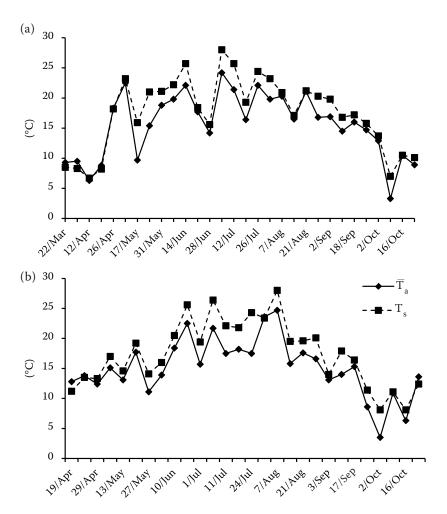


Figure 3. Atmospheric (T_a) and soil (T_s) temperatures in 2012 (a) and 2013 (b)

nure exceeded that from the soil subject to mineral fertilization only, as revealed in the majority of measurements. Similar situation was observed at the end of August/beginning of September 2012. In 2013, the dynamics of N₂O emission from the soil was found similar across different fertilizations systems. On some occasions in the second half of the vegetation period, N₂O emission from the soil under mineral and mineral-organic fertilization systems reached or even exceeded the N₂O emission from the soil during the spring nitrogen peak in the soil (Figure 4). This finding can be explained by high correlation between N₂O emission and the air and soil temperatures, the latter being higher in the second half of the growing period than in spring.

The N₂O fluxes from the soil were positively correlated with the soil and atmospheric temperatures (r = 0.77, P < 0.01 and r = 0.73, P < 0.01, respectively), the soil NO $_3^-$ content and soil NH $_4^+$ content (r = 0.61, P < 0.01 and r = 0.47, P < 0.01, respectively) (Table 2). The relationship between N₂O emission from the soil and the soil moisture was described by a

negative correlation coefficient, low in terms of the absolute value and significance.

DISCUSSION

Emission of N_2O from manure-treated soils (Ca + M, CaNPK + M) slightly exceeded the emission from the soil subject to pure mineral fertilization (CaNPK). The difference was determined by a unique interplay between the weather and soil factors. Kaiser and Ruser (2000) obtained similar results on a sandy loam soil. According to Cannavo et al. (2004), additional oxygen consumption in organic treated-soil promotes denitrification. In a study by Mogge et al. (1999), N₂O emission from cattle slurry-treated soil was 40% higher than that from the soil under mineral fertilization. As reported by Sánchez-Martín et al. (2008), N₂O emission is related to organic carbon content in the soil. The authors hypothesize that denitrification is an important source of N₂O in C-poor soil. This can be explained by the results of Tiedje et

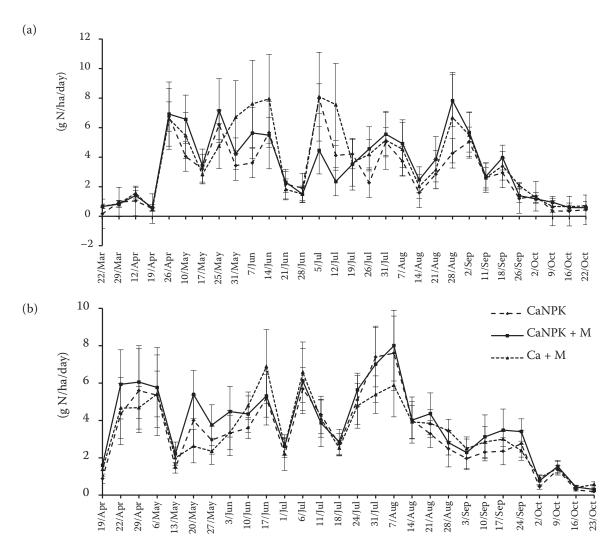


Figure 4. N_2O-N emission from soil under different fertilization systems in 2012 (a) and 2013 (b). CaNPK – mineral, CaNPK + M – mineral-organic, Ca + M – organic fertilization systems

al. (1982), who demonstrated that organic carbon is more important than oxygen in determining the denitrifying enzyme content in habitats. The availability of organic carbon does not only support the activity of denitrifiers per se, but also has an indirect effect of causing microsite anaerobiosis, due to increased respiratory demand for oxygen. Therefore increased availability of labile carbon would favor complete denitrification to N₂. The use of an organic fertilizer instead of an inorganic one could contribute to a reduction in N₂O emission. Organic fertilizers mitigated N₂O emission from Scottish grassland (Ball et al. 2004) as compared to mineral fertilizers. The use of organic fertilizer instead of an inorganic one could contribute to a reduction in N₂O emission. In our study, N₂O flux from the organic treatment was insignificantly higher than that from the mineral one, regardless of similar nitrogen doses applied under different fertilization systems. Organic carbon content in manure-treated soil (Ca + M) was nearly two-fold higher than in the soil under mineral fertilization system (CaNPK). Based on the research by Tiedje et al. (1982) it is suggested that the high content of organic carbon and total nitrogen in the soil treated exclusively with manure promotes the growth of bacteria whose metabolism results in $\rm N_2O$ production it the soil.

Several attempts were made to model N_2O emission and/or its causative processes in various agroecosystems (Zheng et al. 2008). According to Dobbie and Smith (2003) the key factors affecting N_2O emission from the agricultural soil included the soil moisture, temperature and NO_3^- -N content. In our study, N_2O emission from the soil was positively correlated with soil and air temperatures, N_2O flux being considerably higher in July than in March or October (Table 3). On the contrary, upon the climate conditions of Germany, high

Table 2. Correlation coefficients between N_2O-N emission form soil and mineral N content in soil, soil moisture (%WFPS), atmospheric temperature (T_a) and soil temperature (T_s)

Fertilization	NO ₃ -N	NH ₄ +N	%WFPS	T_a	T_s
CaNPK	0.66**	0.48**	-0.28*	0.73**	0.78**
CaNPK + M	0.59**	0.56**	-0.24^{*}	0.69**	0.72**
Ca + M	0.76**	0.46**	-0.33*	0.80**	0.82**
Mean	0.61**	0.47**	-0.25**	0.73**	0.77**

^{*}P < 0.05; **P < 0.01; CaNPK – mineral, CaNPK + M – mineral-organic, Ca + M – organic fertilization systems

 N_2O emission from the soil was observed even in February and October (Kaiser et al. 1998), and up to 50% of emission took place in the winter (Kaiser and Ruser 2000). This phenomenon is attributed to the lack of freezing/thawing cycles (Mogge et al. 1999).

In our study, N_2O emission from the soil was positively correlated with the soil NO₃-N and NH₄+N content. N₂O emission from the soil was better correlated with the soil content of NO₃-N (product of nitrification and precursor of denitrification) than with the soil content of NH₄⁺-N. The relatively high correlation between N₂O emission from the soil and NH₄⁺-N soil content suggests that the nitrification can be an important source of the soil N₂O in Poland. The N₂O flux from the soil could be more significantly correlated with the soil NH₄⁺-N content than with the soil NO₃⁻-N content, as shown by Fu et al. (2012). According to Liu et al. (2007), NH₄⁺-N enhances the N₂O emission from the soil only at lower soil moisture. The high emission of N₂O from both the soil with high mineral N content following spring fertilization and that with low mineral N content in the second half of the vegetation period (higher air/soil temperatures) suggests that N2O flux depends on the amount of mineral N as well as on the intensity of its transformation in the soil.

In our study, the relationship between N₂O emission from the soil and the soil moisture was described by a low negative correlation coefficient (r = -0.253, P = 0.01). In contrast to our results, Smith et al. (1998) demonstrated that the N₂O flux from the soil increased with soil moisture increasing over 60-90% water-filled pore space. In our study, comparably high soil moisture was evidenced only at the beginning of June 2013 and it was not accompanied by a rapid increase in N₂O emission from the soil. This finding is explained by very low soil NO₃-N content at that time, subsequent to an intensive nitrogen uptake by plants in the preceding period. Bateman and Baggs (2005) evidenced that all N₂O emitted at 70% WFPS was produced during denitrification, whereas nitrification was the main process producing N₂O at 35-60% WFPS. Given that the majority of measurements in our study revealed soil moisture below 50% WFPS, it can be concluded that nitrification was a key source of N₂O emission and that both, denitrification and nitrification are important sources of N₂O from light sandy soils of Central Poland.

The $\rm N_2O$ emission from cultivated light sandy soils of Central Poland during the growing period was estimated as 0.64 kg $\rm N_2O$ -N/ha in the mineral fertilization system and 0.72 kg $\rm N_2O$ -N/ha in the organic and mineral-organic fertilization systems.

Table 3. Average daily N_2O-N emission from soil (March–October) and total N_2O-N emission from soil during growing period in 2012 and 2013 in different fertilization systems

Period							Growing		
Treatment	III	IV	V	VI	VII	VIII	IX	X	period
(g N/ha/day)								(g N/ha)	
CaNPK	0.6	3.2	3.8	3.7	4.6	3.7	2.5	0.6	635.3
CaNPK + M	0.7	3.7	4.8	4.2	4.4	4.8	3.0	0.8	731.3
Ca + M	0.8	3.2	4.0	4.9	5.0	2,2	2.9	0.8	712.8
Mean	0.7	3.4	4.2	4.3	4.7	4.2	2.8	0.7	693.1

CaNPK - mineral, CaNPK + M - mineral-organic, Ca + M - organic fertilization systems

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