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The influence of mineral fertilization and legumes cultivation on the N_2O soil emissions

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ABSTRACT

The research aimed at the assessment of the influence of mineral nitrogen (CaNPK) fertilization and lupine cropping on the N_2O emissions from agricultural soil. Observations were collected from CaNPK and Ca fertilization systems (further referred to as NIL due to the absence of nitrogen (N) fertilizers) in two consecutive years (2012 and 2013) on a long-term (since 1923) field experiment in Skierniewice in Central Poland. N_2O emissions from the soil were measured *in situ* by the means of infrared spectroscopy using a portable FTIR spectrometer Alpha (Bruker). N_2O fluxes from soils treated under CaNPK and NIL treatments were similar. No significant influence of the current treatment or cropping on the N_2O emissions was noted in the CaNPK treated soil. N_2O emissions in 2012 (barley, ammonium nitrate application) and 2013 (lupine, no mineral nitrogen application) were similar (0.17–23.04 g N_2O-N/ha/day, median 4.29 and 0.09–19.46 g N_2O-N/ha/day, median 4.45, respectively). During the growing period of 2012 (barley, ammonium nitrate application), the N_2O-N emissions from the CaNPK treated soil (uncorrected for NIL) represented 1.02% of the applied N dose. In the growing period of 2013 (lupine, no mineral nitrogen application), the yield-scaled N_2O-N emissions from CaNPK and NIL treatments equaled respectively to 4.4 g and 5.4 g N_2O-N per 1 kg of nitrogen accumulated by lupine.

Keywords: greenhouse gas emissions; nitrification; nutient cycling; long-term experiment

It is generally acknowledged that the nitrogen (N)-fertilization leads to an increase in N_2O emissions from agricultural soils (Hofstra and Bouwman 2005). The magnitude of this effect depends upon the fertilizer and the soil conditions. Bouwman (1996) showed higher average fertilizer-induced N_2O emissions from ammonium nitrate and urea treatments than from ammonium salts. Vermoesen et al. (1996) demonstrated that N_2O emissions from nitrate treatment exceeded those from ammonium fertilization uniquely in acidic soil, where denitrification is the dominant process. At higher pH (7.0–8.1 pH) values, where nitrification is dominant, the N_2O production was higher from ammonium. Compared with the addition of nitrate, application of ammonium enhanced the N_2O emissions from soils with the effect on N_2O fluxes evident uniquely under lower moisture conditions (Liu et al. 2007). Bateman and Baggs (2005) evidenced that all N_2O emitted at 70% water-filled pore space (WFPS) was produced during denitrification, whereas nitrification was the main process producing N_2O at 35–60% WFPS. Bouwman (1996) found a simple linear relationship between the total annual N_2O-N emissions from the soil and N applied independently of the type of fertilizer; later several authors confirmed a linear relationship between N application and N_2O-N emissions (McSwiney and Robertson 2005, Kim and Dale 2008). N_2O-N emissions from agricultural fields were found to vary between 0.8% and 1.8% of N applied (Flessa et al. 1995, Kaiser and Heinemeyer 1996). Kaiser et al. (1998) and Rudaz et al. (1999) reported a greater range of N_2O-N losses (0.05–5.2%). Jungkunst et al. (2006) reported a considerable variability in annual N_2O-N

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emissions from soils expressed as fractions of N input (0.18–15.54% of N applied) uncorrected for background annual N_2O emissions from arable soils spread across Germany. In contrast, in a large literature survey, Bouwman et al. (2002) reported a principally stable N_2O emissions of approximately 1 kg N_2O-N/ha at application rates of 25–150 kg N/ha. At application rates over 200 kg N/ha, significant increases in N_2O emissions were observed. Van Groeningen et al. (2010) obtained similar results in their meta-analysis with essentially stable total emissions of N_2O-N between 1 and 2 kg N_2O-N up to an application rate of 187 kg N/ha. An increase in fertilizer rates above 200 kg N/ha induced significant increases in N_2O-N emissions.

Cultivation of nitrogen-fixing leguminous plants leads to a direct (from agricultural fields) and indirect (e.g. from ground and surface waters as a result of denitrification of N leached from soils) N_2O emissions from agricultural soils (Eichner 1990, Bouwman 1996). Velthof et al. (1998) proposed that the N_2O emissions from soils under legumes should be lower than those from soils under N-fertilization. According to Bouwman (1996) and Beuchamp (1997), high N_2O emissions under legumes (0.07–4.8 kg N_2O-N/ha/year for alfalfa, soybeans and clover) may result from an input of symbiotic fixed N into the soil.

The mineral-organic treatment is the most common fertilization system in Poland (www.stat.gov.pl). In this system, mineral fertilizers, as the main source of nutrients, are applied in the background of manure. Recently, a gradual increase in the legume acreage has been observed in Poland, probably resulting from the governmental agricultural policy.

It is of interest to determine the effect of application of mineral fertilizers and cultivation of legumes as a source of biologically fixed nitrogen on the N_2O emissions from the soil in the climate, soil and agricultural conditions of Central Poland and to analyse the relationship between environmental factors and the N_2O emission.

MATERIAL AND METHODS

The research was carried out in a long-term field experiment in Central Poland (Skierniewice) belonging to the Warsaw University of Life Sciences-SGGW, maintained with no alterations since 1923 with an experimental plot area of 36 m^2 (51°96'60''N, 20°16'63''E). Plants were cultivated in rotation: potatoes (30 t manure/ha), spring barley, yellow lupine, winter wheat, and rye in an experiment conducted in 5 replications. The investigation was conducted in 2012 (barley) and 2013 (lupine) under mineral (CaNPK) and NIL fertilization (Ca). Liming at 1.43 t Ca/ha as calcium carbonate was applied to both investigated treatments (CaNPK and NIL) before barley cultivation. Other mineral fertilizers were applied as a part of the CaNPK treatment as follows: in 2012 – 90 kg N (ammonium nitrate), 26 kg P (triple superphosphate) and 91 kg K/ha (potassium chloride 50%) and in 2013 (phosphorus and potassium at the same rates but no nitrogen). The treatments' names are consistent with other publications from the long-term experiment in Skierniewice.

The soil was Luvisols (FAO 2006) loamy sand with the following fractions in the 0–25 cm layer: > 0.05 mm 87%; 0.002–0.05 mm 5%; < 0.002 mm 7%. The average annual temperature and precipitation were 8°C and 520 mm, respectively. The impact of long-term fertilization and plant cultivation on the chemical soil properties and yields studied in the long-term field experiment in Skierniewice was reported elsewhere (Mercik and Stępień 2005, Sosulski et al. 2011).

N_2O emissions from the soil were measured *in situ* with 0.3 ng N_2O-N/m^3 sensitivity by means of the infrared spectroscopy using a portable FTIR spectrometer model Alpha (Bruker, Ettlingen, Germany). N_2O flux from the soil was calculated as an increase in the N_2O concentration in the chamber (ø = 29.5 cm, h = 20 cm) after a single 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-MAR to 22-OCT) and 2013 (27 measurements, 19-APR to 23-OCT) in all replications. N_2O emissions were expressed in mg N/ha/day and N/ha/growing period.

Soil sampling (at 0–25 cm depth) was conducted on all measurement dates in both treatments. The NH_4^+-N/NO_3^--N content was measured using segmented flow analyzer model San Plus Analyzer (Skalar Analytical BV, Breda, the Netherlands), after fresh soil extraction in 0.01 mol/L $CaCl_2$ with soil/extractant ratio of 1:10. The soil moisture was assessed as a decrease in the sample

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weigh after oven-drying in 105°C and expressed as a proportion of pore space filled with water (% WFPS), as determined by water content and total porosity. Atmospheric and soil temperatures (at the depth of 5, 10 and 20 cm) were measured by the Experimental Field's Meteorological Station (51°96'53''N, 20°16'02''E). The content of organic carbon (TOC) in the soil was measured in soil samples with the Thermo Electron-C analyzer model TOC-500 (Shimaidzu, Kyoto, Japan) at a single occasion (after harvesting) in 2012 and 2013. The soil total nitrogen (TN) content and the N content in lupine (grain and straw) were measured in samples collected after harvest in 2012 and 2013 with the Vapodest model (Gerhardt, Bonn, Germany) VAP 30 analyzer. Yields of barley and lupine were measured on all replications under both treatments.

Statistical analyses were performed with the SPSS software 21.0 (IBM, Chicago, USA). Mann-Whitney U test and Bonferroni correction for multiple comparisons were applied (at $P < 0.05$). Pearson correlation coefficients were calculated at $P < 0.05$.

RESULTS

Soil conditions. The soil content of both organic carbon and total nitrogen was significantly higher under CaNPK (7.35 g C/kg ±0.15 SD (standard deviation) and 0.71 g N/kg ±0.02 SD) than under NIL (6.14 g C/kg ±0.17 SD and 0.59 g N/kg +0.02 SD). Soil pH (1 mol/L KCl) was similar in these treatments (pH 6.6 and 6.5, respectively). In both years of investigation the median soil NO_3^--N and NH_4^+-N content was higher under CaNPK than under NIL with the exception of NO_3^--N soil content in 2013, which was similar under both treatments (Table 1). The median NO_3^--N and NH_4^+-N content in the CaNPK-treated soil was insignificantly higher in 2012 (N application, barley) than in 2013 (no N application, lupine). Under NIL fertilization, the soil content of NO_3^--N was higher than that of NH_4^+-N in 2013 (lupine), while in 2012 (barley) the differences in soil content of NO_3^--N and NH_4^+-N soil were negligible. No differences between NO_3^--N and NH_4^+-N soil content were observed under CaNPK.

Important differences in the temporal patterns of soil NO_3^--N and NH_4^+-N content were observed as depicted in Figure 1. The essential difference between the patterns in CaNPK-treated soil consisted in an increase in the content of both mineral nitrogen forms in the spring 2012 (N application, barley) following an ammonium nitrate application, whereas in 2013 (no N application, lupine), a gradual increase was observed until the first decade of August. The increase in the content of both mineral nitrogen forms in the spring 2012 subsequent to ammonium application delineated the difference between CaNPK and NIL. In 2013 (cultivation of lupine, no application of nitrogen in CaNPK), no distinct differences in the temporal patterns of soil NO_3^--N and NH_4^+-N content were observed between CaNPK and NIL treatments.

In both years, a drop in the soil NO_3^--N content observed at the end of the growing period followed numerous fluctuations in the soil content of both mineral N forms in summer.

The soil moisture, daily air and soil temperature were similar across various treatments and

Table 1. Content of NO_3^--N and NH_4^+-N in soil (mg N/kg) and N_2O-N emissions from soil (g N/ha/day) (n = 150 for 2012, n = 135 for 2013)

Fertilization		2012			2013		
		NO_3^-	NH_4^+	N_2O	NO_3^-	NH_4^+	N_2O
Ca	median	5.23	5.11	2.75	5.52	3.64	3.12
	mean	5.40	5.28	3.58	5.40	4.01	3.78
	min–max	0.83–12.00	0.02–13.77	0.08–18.07	1.23–11.41	0.99–10.30	0.03–17.06
CaNPK	median	6.00	6.09	2.89	5.69	5.84	3.48
	mean	8.21	7.91	4.29	5.70	5.80	4.45
	min–max	1.52–23.13	0.21–26.88	0.17–23.04	1.43–12.00	0.09–13.36	0.09–19.46

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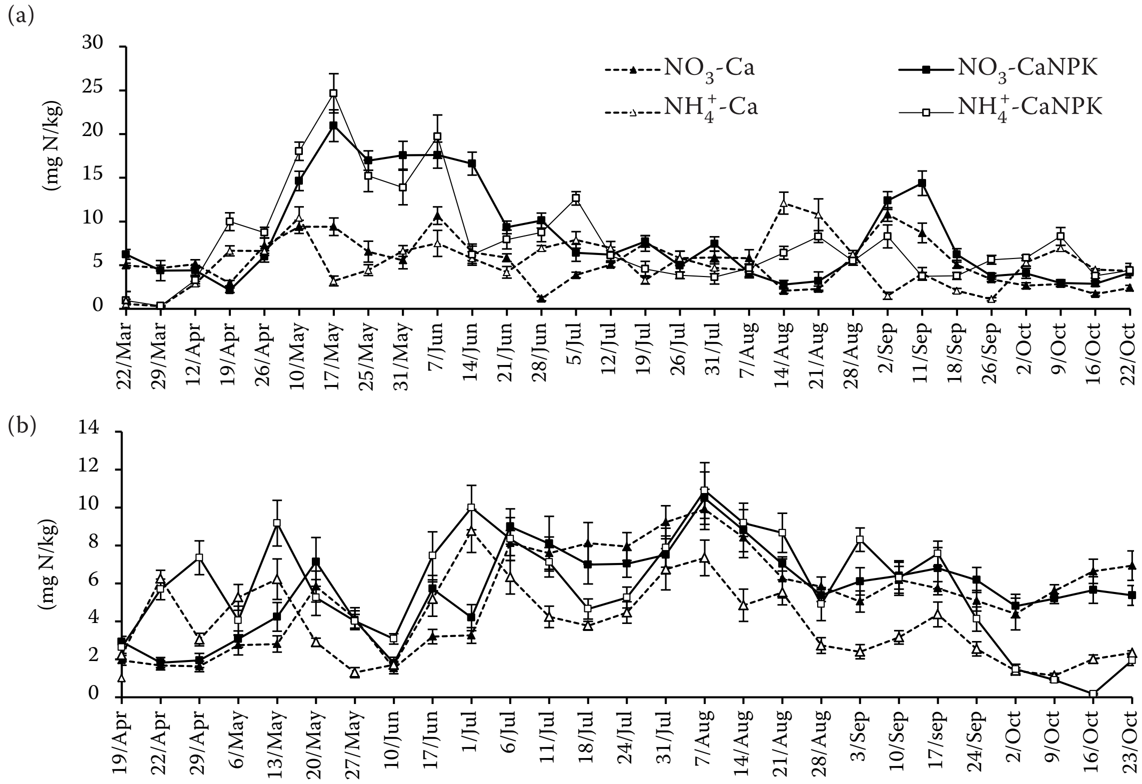

Figure 1. NO_3^--N and NH_4^+-N soil content under NIL (Ca) and mineral (CaNPK) treatments in (a) 2012 and (b) 2013

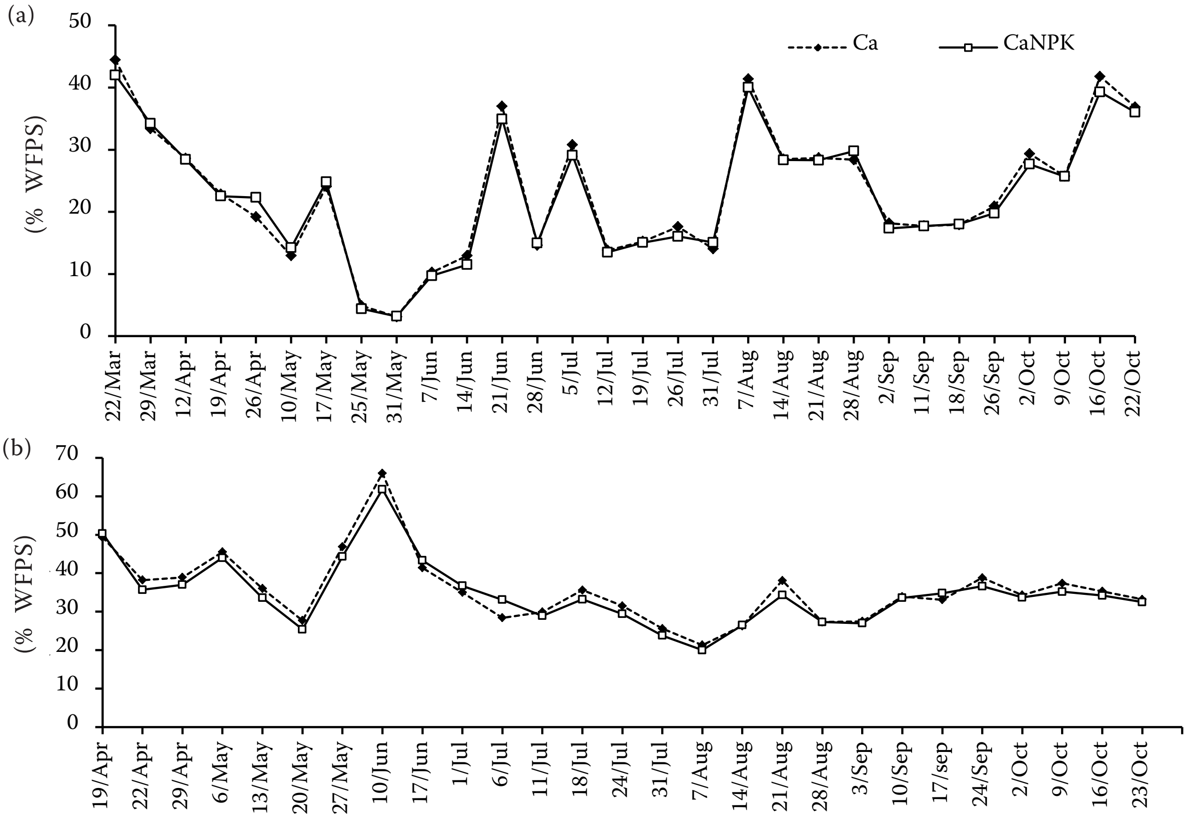

Figure 2. Soil moisture (0–25 cm) under NIL (Ca) and mineral (CaNPK) treatments in (a) 2012 and (b) 2013. WFPS – water-filled pore space

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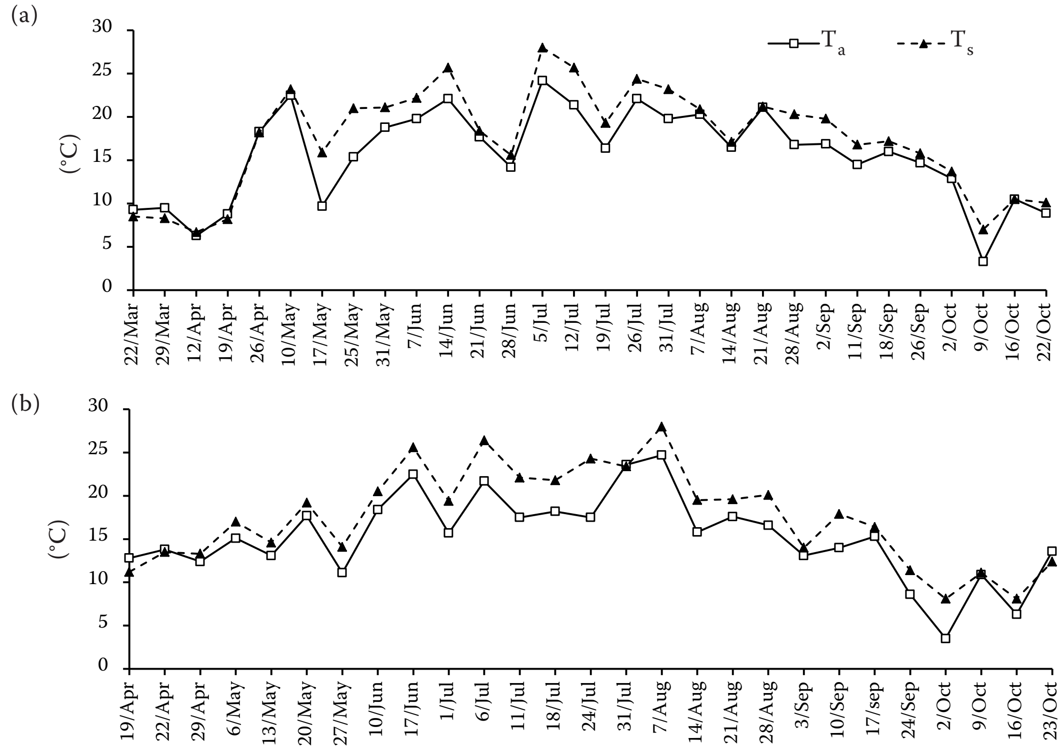

Figure 3. Atmosferic (T_a) and soil (T_s) temperature at 5 cm depth in (a) 2012 and (b) 2013

varied over time as depicted in Figures 2 and 3. The average soil moisture in 2013 exceeded that of 2012 by approximately 53%.

N_2O emissions. The N_2O fluxes were slightly higher from the soil under mineral than under NIL NPK-fertilization (Table 1). The N_2O flux over the measurement period showed high variability within a range of 0.03–18.07 g N_2O-N/ha/day from NIL and 0.09–23.04 g N_2O-N/ha/day from CaNPK-treated soil. Under CaNPK, N_2O fluxes were insignificantly higher in 2013 (no N application, lupine) than in 2012 (N application, barley). The patterns of N_2O emissions from the soil were found similar across the examined treatments (Figure 4) especially in 2013, when nitrogen was not applied to the soil under CaNPK. In 2012, the application of ammonium nitrate to the CaNPK-treated soil resulted in an increase in N_2O emissions over those from NIL exclusively in May/June and July/August. Under both treatments, an increase in N_2O emissions was observed from the early spring till the first/second decade of June followed by a decrease that lasted until the beginning of July. This pattern was consistent over both years of experiment; however in 2012 the subsequent peak occurred in the first decade of July, whereas in 2013, it was noted in the first decade of August. A subsequent decrease in N_2O fluxes was observed in both years towards the end of the growing period. N_2O emissions from the soil calculated for the growing period on the CaNPK were higher than on the NIL treatment (0.92 vs. 0.77 kg N_2O-N/ha in 2012 (barley) and 0.84 vs. 0.71 kg N_2O-N/ha in 2013 (lupine)).

The N_2O fluxes from the soil were positively correlated with the soil and atmospheric temperatures ($r = 0.83$, $P < 0.01$ and $r = 0.77$, $P < 0.01$, respectively) and both the soil NH_4^+ and NO_3^- content ($r = 0.45$, $P < 0.01$ and $r = 0.38$, $P < 0.01$, respectively) (Table 2). The relationship between N_2O emissions from the soil and soil moisture was described by a negative correlation coefficient ($r = –0.25$, $P = 0.01$), low in terms of the absolute value and significance.

Plant yields and N accumulation by legumes. As expected, the average barley grain yield obtained in the long-term experiment was higher under mineral fertilization (CaNPK) than under NIL treatment (3.59 vs. 2.56 t/ha). The lupine grain and straw yield was higher under mineral fertilization (1.56 t/ha ±0.16 SD) and (8.45 t/ha ±0.90 SD, respectively) than under NIL treatment (1.17 t/ha

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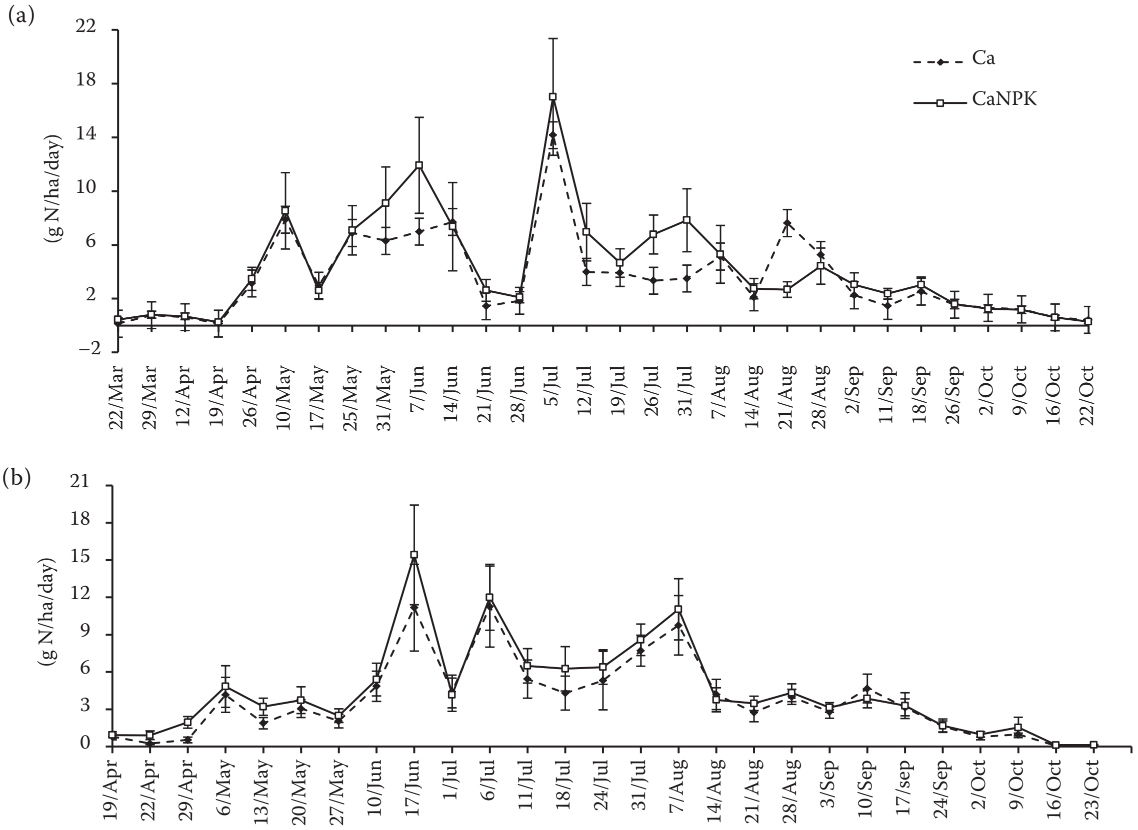

Figure 4. N_2O-N soil emissions under NIL (Ca) and mineral (CaNPK) treatments in (a) 2012 and (b) 2013

±0.16 SD and 5.55 t/ha ±1.42 SD, respectively). Consequently, the N-accumulation by lupine was higher under mineral fertilization (192.26 kg N/ha ±14.66 SD) by approximately 46.5% than under NIL treatment (131 kg N/ha ±20.89 SD).

DISCUSSION

Several studies have indicated that N-fertilization leads to increased N_2O emissions from the soil (Bouwman 1996, Hofstra and Bouwman 2005). Our results show, however, similar N_2O fluxes from CaNPK and NIL-treated soils and correspond with those of Kaiser and Ruser (2000) and Meng et al. (2005). The latter found no significant relationship between the soil N_2O emissions and N-fertilization rate in long-term experiments in Germany. Insignificant differences in N_2O-N emissions from the soil under CaNPK and NIL treatments resulted from multifactorial impacts (soil properties influenced by long-term and recent fertilization, soil mineral N-content, soil conditions including moisture and temperature and yields). The long-term CaNPK treatment had no significant impact on the N_2O-N soil emissions.

Table 2. Correlation coefficients between N_2O-N soil emissions and mineral nitrogen (N) content in soil, water-filled pore space (% WFPS), atmospheric (T_a) and soil (T_s) temperature at 5 cm depth

Fertilization	NO_3^--N	NH_4^+-N	WFPS	T_a	T_s
Ca	0.33**	0.47**	–0.24**	0.78**	0.84**
CaNPK	0.39**	0.44**	–0.27*	0.78**	0.84**
Mean	0.38**	0.45**	–0.25**	0.77**	0.83**

*$P < 0.05$; **$P < 0.01$

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It, however, led to an increase in the average barley yield by 40.2% as compared to the NIL treatment.

Van Groeningen et al. (2010) showed stable annual emissions of 1–2 kg N_2O-N/ha from the soil treated with up to 187 kg N/ha. During the growing period, the NIL-uncorrected N_2O-N emissions from the CaNPK-treated soil under barley reached 1.02% of N dose (0.92 kg N/ha) and remained in the range reported by Flessa et al. (1995) and Kaiser et al. (1998).

The TOC and TN soil content was impacted by long-term manuring (under potatoes) and legumes cultivation in both studied treatments and in CaNPK by the application of NPK. In spite of the differences in the nitrogen supply and the soil TOC or TN content, the N_2O-N emissions from the soil were similar on both (CaNPK and NIL) treatments. Our earlier research (Sosulski et al. 2014) showed no significant influence of TOC and TN soil content under long-term rye monoculture and diverse fertilization systems (mineral, mineral organic and organic) on the N_2O-N emissions from the soil. While the TOC soil content from barley and CaNPK in the current research was lower than that from rye-monoculture and comparable (mineral-organic) fertilization reported in our earlier publication (Sosulski et al. 2014) (7.35 g C/kg vs. 8.80 g C/kg), the N_2O-N emissions from the soil under barley were higher by 26.5% than the N_2O-N emissions from the soil under rye monoculture (0.92 and 0.73 kg N_2O-N/ha, respectively). An effect of crop residues in the soil on the N_2O-N soil emissions provides a plausible explanation for this observation, as the crop residues differ between the long-term crop rotation with legumes and long-term cereal monoculture. On the other hand, the N_2O-N emissions from the soil under barley and CaNPK in the current research (0.92 kg N_2O-N/ha) were higher by 45.2% than the N_2O-N emissions from the soil under rye-monoculture (0.64 kg N_2O-N/ha) with notably lower (5.68 g C/kg) TOC content, which resulted from an exclusive use of mineral fertilization since 1923, as reported in our earlier publication (Sosulski et al. 2014).

In our current research, the soil N_2O-N fluxes in 2013 (no N-application, lupine) were insignificantly higher than in 2012 (N-application, barley). The data are consistent with the previous observations of increased N_2O-N emissions from the soil under nitrogen-fixing plants (Eichner 1990, Bouwman 1996). Different weather conditions in the two years of study could have had an impact on the N_2O-N emissions from the soil. To control for the potential influence of weather conditions a reference was made to the contemporaneous emissions from rye monoculture under analogous treatment (Sosulski et al. 2014). No notable differences in regard to N_2O-N emissions were observed in 2013 between the studied soil under lupine and rye-monoculture described elsewhere (3.48 vs. 3.53 g N_2O-N/ha per day, respectively). This finding is in contradiction to the assessment by Velthof et al. (1998) regarding lower N_2O emissions from soils under legumes than from N-fertilized soils. The annual N_2O-N emissions under legumes were reported to range between 0.07 and 4.8 kg per ha (Bouwman 1996, Beuchamp 1997). In our study, N_2O-N emissions from the soil under lupine during the growing period did not exceed 0.84 kg N_2O-N/ha. The yield-scaled N_2O-N emissions ranged from 4.4–5.4 g N_2O-N per 1 kg of nitrogen accumulated by lupine. We found the N_2O fluxes to be positively correlated with the soil and air temperatures and both NH_4^+-N and NO_3^--N soil content. Smith et al. (1998) noted a linear relationship between the soil temperature and N_2O soil emissions. Fu et al. (2012) found that the N_2O soils emissions were better correlated with NH_4^+-N than with the NO_3^--N soil content. The NH_4^+-N soil content impacts the N_2O emissions from soil only at the lower moisture conditions (Liu et al. 2007) where nitrification is dominant (Vermoesen et al. 1996).

In our study, the relationship between N_2O emissions from the soil and the soil moisture was described by a low negative correlation coefficient ($r = -0.25$, $P = 0.01$). In contrast, Smith et al. (1998) demonstrated that the N_2O flux from the soil increases with soil moisture over 60–90% WFPS. We evidenced comparably high soil moisture (and low soil mineral N content) only at the beginning of June 2013 and it was accompanied by a decrease in N_2O emission from the soil. Based on the findings by Ruser et al. (2006) this phenomenon could be explained by a switch to N_2 emissions.

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