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Soil Physical Properties and Nitrous Oxide Emission from Agricultural Soils

Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik and Eugene V. Balashov

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1. Introduction

1.1. N₂O in agriculture and microbial processes of nitrification and denitrification

 N_2O is an important greenhouse gas as it contributes to global warming and the depletion of the stratospheric ozone layer (Bouwman, 1990; Crutzen, 1979; Houghton et al., 1990). At the present time the atmospheric concentration of N_2O is rising linearly at a rate of 0.3% per year (IPCC, 2007). Its current concentration in the atmosphere is equal to 319 ppbv (IPCC, 2007). A warming potential of 1 kg of N_2O is 310 times greater than 1 kg of CO_2 over a 100-year period (IPCC, 2007).

It is now widely accepted that agriculture is the main source of anthropogenic N_2O . The agriculture contributes to 60% of the global N_2O emissions (OECD. 2000). Agricultural soils are recognized as the major source of atmospheric N_2O , globally contributing 1.7-4.8 Tg N yr⁻¹ (IPCC, 2007; Mosier, 1998).

N₂O is formed in two microbiological processes – nitrification and denitrification (Bremner, 1997; Firestone and Davidson, 1989) (Figure 1).





Figure 1. Production of N₂O in soils during (a) nitrification and (b) denitrification processes. (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov)



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The contribution of these processes to N_2O emission will vary with climate, soil management and properties (Granli, Bockman, 1994; Skiba, Smith, 2000). During nitrification N_2O is formed as a by-product in the reactions of oxidation of NH_3 to NH_2OH and NH_2OH to NO_2^- under strictly aerobic conditions. These two reactions are catalysed by such enzymes as ammonia monooxigenase and hydroxylamine oxidoreductase (McCarty, 1999; Wood, 1986). The reaction of NO_3^- production from NO_2^- is catalysed by nitrite oxidoreductase (Bock et al., 1986).

In contrast to nitrification, N_2O is an obligatory intermediate product of denitrification. Denitrification is a stepwise reduction of NO_3^- to N_2 by facultative anaerobic microorganisms. Enzymes catalysing these above-mentioned four reactions are nitrate reductase, nitrite reductase, nitric oxide reductase and nitrous oxide reductase (Hochstein, Tomlinson, 1988).

Despite denitrification is considered as a strictly anaerobic process, it is now accepted that N_2O can be produced during nitrifier denitrification (as a pathway of nitrification) under aerobic conditions. During a first part of nitrifier denitrification an oxidation of NH_3 to NO_2^{-1} (nitrification) occurred, whereas a reduction of NO_2^{-1} to N_2O and N_2 is a second part of the microbial process (Poth, Focht, 1985; Ritchie, Nicholas, 1972).

The rates of these processes and of N₂O production are controlled by several soil factors: soil water-filled pore space (WFPS), oxygen availability, pH, mineral nitrogen (NO₃⁻, NH₄⁺), available soil organic carbon (SOC), and temperature (Dobbie et al., 1999; Dobbie, Smith, 2003; Khalil et al., 2004., Wlodarczyk et al., 2003). Nitrification is the main process of N₂O emission at 35-60% WFPS. Denitrification becomes more important at soil water contents greater than 60% WFPS due to a decreased oxygen supply (Dobbie, Smith, 2003; Drury et al., 2003).

N₂O flux from agricultural soils depends on a complex interaction between climatic factors, soil properties and soil management. Management practices such as tillage systems and fertilizer applications can significantly affect the production and consumption of N₂O because of alteration in soil physical, chemical, and biochemical properties. The only way to reduce N₂O emissions from agricultural soils is to affect the soil properties through: 1. application of appropriate soil tillage system, 2. improving efficiency of N fertilizers with better placement, timing and rates of required N for growing relevant crops with high N uptake efficiency (Chatskikh, Olesen, 2007).

1.2. Role of soil tillage and soil physical properties in N₂O emission from soils

Tillage systems change soil structural, air, and water status (Beare et al., 1994; Green et al., 2007; Simansky et al., 2008). Nevertheless, continuous use of conventional moulboard ploughing in traditional farming systems can lead to degradation of soil structure and to losses in soil organic matter through erosion and oxidation (Lal, 2004; Lopez-Garrido et al., 2011; Norton et al., 2006; Reicosky, 2002). H. Riley et al. (2008) showed that a 15-year conventional ploughing of loamy soil caused a significant increase in bulk density from 1.29 to 1.43 Mg m⁻³ and a significant decrease in total porosity from 49.1 to 44.8%. E. Balashov and N. Buchkina (2011) showed that a 75-year use of conventional mouldboard ploughing re-

sulted in a significant decline in a concentration of SOC (from 43.1 to 30.2 g C kg⁻¹ soil) as well as in an amount of water-stable aggregates (from 90.1 to 70.2%) and clay content (from 30.5 to 26.9%), compared to the fallow land in a clayey loam Haplic Chernozem.

There is a trend for the adoption of no-tillage and reduced tillage around the world, because these systems have been shown to improve soil organic matter status, structural state and water regime (Green et al., 2007; Simansky et al., 2008; Angers et al., 1997; Fernandez et al., 2010; Nyakatawa et al., 2000; Six et al., 2002; West, Post, 2002). V. Simansky (2008) reported that reduced tillage to a depth of 10-12 cm, compared to conventional tillage to the depth of 22-25 cm, led to a significant increase in the average amount of water-stable macro-aggregates of Orthic Luvisol. Long-term studies also suggested that the reduced tillage resulted in an essential change in soil structure that increased soil porosity and decreased bulk density (Zhang et al., 2007).

The conversion from mouldboard ploughing to no-tillage can result in a reduced N_2O emission (Almaraz et al., 2009) as well as in an increased N_2O emission from soils (Lemke et al., 1999). This unfavorable increase in N_2O emission can be caused by higher WFPS and bulk density of soils recently converted to no-tillage system (Liu et al., 2007).

Direct measurements of N_2O flux from soils with different tillage systems have shown that their effects on the greenhouse gas emission are governed by climatic conditions. According to the results reported in (Six et al., 2002), a conversion of conventional tillage to no-tillage resulted to an increase in soil organic matter level in temperate and tropical soils in a wide range of agroecosystems. In the temperate soils an increase in N_2O emissions and CH_4 uptake was observed under no-tillage compared with conventional tillage. In general, light-textured, well-aerated soils under drier climate conditions do not produce more N_2O when under no-tillage or reduced tillage system compared to conventional tillage. However, poorly aerated soils in wet climate can produce more N_2O when conventional tillage is converted for no-tillage or reduced tillage system (Chatskikh, Olesen, 2007; Ball et al., 1999; Choudhary et al., 2002).

Changes in the total porosity and the amount of water-stable aggregates may result in a formation of favorable conditions for denitrification as it can take place in soils with high availability of organic matter and low availability of oxygen. Oxygen is regarded as a key determinant of denitrification rates, while the importance of available SOC and NO_3^- (or other nitrogen oxides) will vary in the ecosystems (Robertson, Groffman, 2007). A proportion of the total gaseous products of denitrification that is actually emitted to the atmosphere as N_2O depends on the soil aggregation and water content (Smith et al., 2003). A destruction of soil aggregates by tillage can lead to an increase in availability of SOC for soil denitrifying microorganisms (Gregorich et al., 1989; Petersen et al., 2008).

Despite positive effects of no-tillage and reduced tillage systems on soil aggregation and porosity, denitrification can occur even in the soil aggregates under soil aerobic conditions (Smith, 1980). K. Khalil (2004) reported that significant denitrification rates (i.e. greater than 0.2 mg N kg⁻¹) from 2-3-mm aggregates were observed in the 0 and 0.35 kPa O₂ pressure treatments, whereas nitrification (both NH_4^+ and NO_2^- oxidation rates) was reduced by a fac-

tor of 4–10 when O_2 concentration decreased from 20.4 to 0.35 kPa. According to the results reported by Uchida et al. (2008), the highest N₂O-N fluxes of 9920 µg m⁻² h⁻¹ occurred in the 0–1.0 mm aggregates, while the respective values in the 1.0–2,0; 2.0–4.0 and 4.0–5.6 mm aggregates were 3985, 2135 and 2750 µg m⁻² h⁻¹.

An absence of tillage can lead to soil compaction and, as a result, to a reduced air-filled porosity and availability of oxygen (Rasmussen, 1999). At high soil water content, the effects of increasing soil bulk density may contribute to a formation of anaerobic conditions (Douglas, Crawford, 1998). R. Ruser et al. (1998) reported that an increase in bulk density of fine silty soil only by 20% led to increasing N₂O emission. According to the results reported by M. Beare et al. (2009), there was a strong exponential increase in N₂O production above 0.60 cm³ wFPS of a compacted fine loamy soil where denitrification was a dominant pathway of N₂O production.

Therefore, tillage systems can have contradictory effects on soil physical status and on N_2O emissions from soils. If it is necessary to obtain valid information on N_2O emissions from soils differing in soil physical status and tillage systems the site-specific measurements need to be carried out in various agroecosystems with different agricultural uses.

1.3. Role of increasing nitrogen rates in N₂O emission from soils

Application of mineral N-fertilizers into agricultural soils usually results in increasing N_2O emissions (Smith et al., 2003; Jones et al., 2007; MacKenzie et al., 1998; Rizhiya et al., 2011). However, there is contradictory information on linearity between applied N rates and N_2O emissions from soils. According to results reported by Gregorich et al. (2005), N_2O emission from agricultural soils increased linearly with the applied amount of mineral N fertilizer. At N rates not exceeding or equal to those required for maximum yields, N rates tended to create a linear response in N_2O emissions, with approximately 1% of applied mineral N lost as N_2O (Bouwman, 1996; Halvorson et al., 2008).

However, there are threshold N rates, which can exceed the crop and ecosystem uptake capacity (Grant et al., 2006). At N rates exceeding crop requirements, N₂O emissions are more variable and often rise exponentially with increasing N fertilization (Hobet et al., 2011; Snyder et al., 2009). C.P. McSwiney and G.P. Robertson (2005) reported on nonlinear increase between N₂O emission and N rates. N₂O emission was moderately low (20 g N₂O-N ha⁻¹ day⁻¹) at N rate of 101 kg N ha⁻¹, but at N rate above 134 kg N ha⁻¹, N₂O emissions sharply increased to about 450 g N ha⁻¹ day⁻¹. The greatest percentage of fertilizer N lost as N₂O (7%) occurred at the N rate of 134 kg N ha⁻¹. The authors also (1) found that the proportion of applied N lost as N₂O decreased to 2–4% (as emission factor) with N rates exceeding 134 kg N ha⁻¹ and (2) stated that this threshold of N₂O response to N fertilization could be reduced with no or little yield penalty by reducing N fertilizer inputs to levels that just satisfy crop needs.

According to J.W. Van Groenigen et al. (2010), agricultural management practices to reduce N_2O emissions should focus on optimizing fertilizer-N use efficiency under median rates of

N input, rather than on minimizing N application rates. The authors proposed to assess the N_2O emissions as a function of crop N uptake and crop yield.

1.4. Role of crop roots in N₂O emission from soils

Living roots of crops can play an integral role in soil N₂O production by providing their labile organic exudates and mineral N to microbial community involved into nitrification and denitrification. J.A. Bird (2011) reported that living roots of *Avena barbata* increased the turnover and loss of belowground ¹³C compared with unplanted soils. The rhizosphere of *Avena barbata* shifted the microbial community composition, resulting in greater abundances of gram-negative markers and lower abundances of gram- positive, actinobacteria and cyclopropyl PLFA markers compared to unplanted soil. According to the results of Khalid et al. in (Khalid et al., 2007), the presence of grass species significantly increased the size of a number of dissolved nutrient pools in comparison to the unplanted soil (e.g. dissolved organic carbon, total phenolics in solution) but had a little affect on other pools (e.g. free amino acids).

The plant roots change such soil physical properties as air porosity, pore distribution, penetrometer resistance, permeability and bulk density (Williams, Weil, 2004; Mitchel et al., 1995; Balashov, Bazzoffi, 2003). Balashov and Bazzoffi (2003) showed that the resilience capacity of wheat root system at the boot stage was sufficient for the formation and stabilization of water-stable aggregates in a sandy loam Typic Udorthents and a clayey loam Vertic Xerorthent compacted with ground contact pressures of 51 and 103 kPa. After the compaction with ground contact pressure of 154 kPa, the root system was unable to maintain the waterstable aggregation of soils even at its initial level. Therefore, roots of plants can improve soil physical status of compacted soils and can reduce a risk of formation of favorable conditions for denitrification, which are observed at WFPS exceeding 60%.

A rather high attention has been given to the dynamics of N_2O profile concentration and its subsequent diffusion to the soil surface. The concentrations and fluxes of N_2O are dependent on WFPS, mineral N content, microbial activity, temperature, and macro-porosity in the soil profiles (Burton, Beauchamp, 1994; Clough et al., 2005; Jacinthe, Lal, 2004; Kusa et al., 2010; Li et al., 2002; Muller et al., 2004; Phillips et al., 2012; Van Groenigen et al., 2005; Velthof et al., 1996; Yoh et al., 1997).

J.W. Van Groenigen et al. (2005) found that maximum N_2O concentrations were observed at depths of 48 and 90 cm at WFPS > 70% in a sandy soil. The authors reported that during the summer the maximum N_2O fluxes from the soil surface were coinciding with high subsoil N_2O concentrations suggesting that denitrification in the subsoil was a main determinant of N_2O formation. In winter with low air and soil temperatures as well as with low soil microbial activity high N_2O concentrations in the subsoil did not lead to corresponding high fluxes of N_2O from the soil surface.

K. Kusa et al. (2010) showed that the contribution ratios of the N_2O produced in the top soil (0–0.3 m depth) to the total N_2O emitted from the soil to the atmosphere in the treatments with the Gray Lowland soil and the Andosol were 0.86 and 1.00, respectively, indicating that

the N₂O emitted from the soils to the atmosphere was mainly produced in the top soil. Variations in the profile N₂O concentrations between two soils were caused by those in the soil structure, in particular, because of the presence of macro-pores and cracks in the soil structure, which resulted in different production and movement of N₂O in the soils. The higher N₂O production in the subsoil of the Gray Lowland soil could have been activated by NO₃⁻ leaching through macro-pores and cracks, and subsequently the N₂O produced in the subsoil could have been rapidly emitted to the atmosphere through the macro-pores and cracks.

The aim of this study was to quantify direct N_2O emissions from a light-textured arable soil under several crops grown on ridges, in North-Western Russia, that was typical of the region, during four growing seasons, with special attention to soil physical properties.

2. Materials and methods

The measurements of N₂O emission were conducted at the Menkovo Experimental Station of the Agrophysical Research Institute in the St. Petersburg region of Russia (59°34'N, 30°08'E) in 2004–2007. Average annual rainfall in the area for the previous 10 years was 1,109 mm, with 50–60% falling during the growing season (May–September). Average annual air temperature was +4.5°C, and average air temperature in the growing season was +13.6°C. The studied soil was the most typical soil of the area: a sandy loam Spodosol containing 7–8% clay, 17–23 g C kg⁻¹ soil, and with bulk density ranging from 0.95 to 1.5 g cm⁻³. Three 0.5-ha fields containing this soil were used to conduct the experiment. The first of them received 160 t ha⁻¹ (656 kg of total N ha⁻¹ or 219 kg of available N ha⁻¹), the second – 80 t ha⁻¹ (328 kg of total N ha⁻¹ or 108 kg of available N ha⁻¹) of farmyard manure (FYM) in spring of 2003 and early summer of 2004, and the third received no FYM.

Part of the field with no FYM was allocated for potato (*Solanum tuberosum* L.) in 2004 and 2005. Part of the field with the highest application of FYM was allocated for potato in 2005. All the three fields were used to grow cabbage (*Brassica oleracea capitat* L.) in 2006 and carrot (*Daucus carota* L.) in 2007. By 2005 the SOC content in the soils of the plots receiving 160 t ha⁻¹ of FYM, 80 t ha⁻¹ of FYM and no FYM at the beginning of the experimental studies was equal to 21, 19 and 17 g C kg⁻¹ soil, respectively.

In 2004-2005 large single plots were used for the experiment while smaller but randomized replicate plots were used in 2006 and 2007. The use of single plots earlier in the experiment was a necessary consequence of the cropping arrangements adopted by the manager of the experimental station. The experimental study described here was therefore the only available way in which to conduct this project. Mineral N fertilizer (ammonium nitrate, AN) was applied to the soil at different rates (Table 1). The mineral N was applied (broadcast) to the soil in granular form mechanically: before the furrows and ridges were formed (1st application) and the second and third time (for potato crop only) the fertilizer was applied to furrows. The depth of mouldboard ploughing for all the plots was 22–24 cm. Most of the plots were ploughed in spring between 13 and 20 May. Crops were planted within a day or two after mouldboard ploughing and harvested at the end of August/early September.

The closed chamber technique was used to measure direct N_2O fluxes from the soil. Gas samples were collected two-three times a week (between noon and 2 pm) throughout the growing seasons (May-September) of 2004–2007. Chambers were made of inverted cylindrical plastic buckets, 18.9 cm in diameter and 11 cm high, and put into the field every time before gas samples were collected (Figure 2). Eight replicate chambers were used at all the plots — four in the furrows and four on the ridges.

Year	Сгор	SOC,	Ammonium nitrate fertilizer application					
		g C kg ⁻¹ soil	1 st	Date	2 nd	Date	3 rd	Date
2004	Potato	17	72	14/05	48	17/07	0	
2005	Potato	17	72	13/05	38	10/06	10	27/07
		21	72	13/05	38	10/06	10	27/07
2006	Cabbage	17	0		0		0	
		17	70	15/05	0		0	
		19	0		0		0	
		19	90	15/05	0		0	
		22	0		0		0	
		22	110	15/05	0		0	
2007	Carrot	17	40	20/05	0		0	
		17	110	20/05	0		0	
		19	40	20/05	0	D)(E	0	
		19	120	20/05	0		0	
		23	60	20/05	0		0	
		23	130	20/05	0	_	0	

Table 1. Crops grown and rates of mineral fertilizers used during the growing seasons of 2003-2007 (Natalya P.Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov).



Figure 2. Chamber placement on the ridges and in the furrows of the potato (*Solanum tuberosum* L.), cabbage (*Brassica oleracea capitat* L.) and carrot (*Daucus carota* L.) plots. (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov)

Chambers were pressed into the soil to a depth about 2 cm and the soil outside the chambers was compacted against the chamber walls to make them gas-tight. A three-way tap on the top of each chamber was closed only after the chamber was fixed into the topsoil, to avoid extra air pressure inside the chamber. After 60 min gas samples were collected via the three-way tap. Similar sampling at the end of the closure period has been employed elsewhere (Ball et al., 2007; Hergoualc'h, 2008).

Gas samples were taken with a 60-ml syringe; 50 ml were flushed through a 10 ml vial that had been previously flushed with air, then the remaining 10 ml were forced into the vial to over-pressurise it. 3-ml subsamples from the vials were analysed for N₂O in a Carlo Erba 4130 gas chromatograph (GC) fitted with an electron capture detector. The GC was calibrated with standard gas mixtures. The detection limit for the sampling/analytical system was 0.05 ppm. Daily fluxes were calculated using the arithmetic mean of the four replicate chambers. Cumulative N₂O fluxes for different months as well as for whole growing seasons of 2004–2007 were calculated by plotting daily fluxes through time, interpolating linearly between them, and integrating the area under the curve. Cumulative standard errors were also determined by the same way (Dobbie, Smith, 2003; Buchkina et al., 2010).

The climatic factors most likely to affect the amount of N₂O produced in the soil were monitored during the experiment. Data on daily rainfall and air temperatures (maximum, minimum, and average) were collected from the Institute's meteorological station, situated c. 100 m from the experimental plots. Soil temperature at a 10-cm depth was measured with a digital thermometer on each sampling occasion. Soil bulk density and water content were measured (in three replicates) 1–2 times a month by standard methods (Rastvorova, 1988; Soil Survey, 1996) and the results were used to calculate water-filled pore space (WFPS). Soil samples for mineral nitrogen (NH_4^+ and NO_3^-), were also collected 1–2 times a month from the 0–10 cm layer. At least 10 subsamples were collected from each plot and combined. The composite samples were dried at room temperature and then amounts of NH_4^+ and NO_3^- were measured in water extractions using ion-selective electrodes in three replicates (Bankin et al., 2005). SOC content was measured by a wet combustion method using potassium dichromate ($K_2Cr_2O_7$) solution in sulfuric acid (Soil Survey, 1996).

All the measurements of the soil properties were done in three replicates. Means and standard deviations were calculated for each parameter within each treatment. Significance of differences between treatments was estimated by analysis of variance (one-way ANOVA) at p≤0.05. Relationships between the soil parameters were assessed with a linear regression analysis using computer statistical package.

3. Results and discussion

3.1. Weather conditions

The amount of precipitation and its distribution over the growing season (1 May–30 September) varied between the studied years significantly (Figure 3). The wettest growing season was 2004 and the driest 2006, with 845 and 456 mm of rain falling, respectively, compared to 575 mm in 2005, and 555 mm in 2007. During the growing season there were 75 days with rain in 2004, 55 in 2005, 41 in 2006 and 52 in 2007. Almost 75% of the rain fell on days when precipitation was greater than 10 mm: there were 25 such occasions in 2004, 15 in 2005, 13 in 2006 and 20 in 2007. The longest dry spells were observed in 2006: 27 days in late April-May, 15 days in July and 11 days in August. Even the wettest growing seasons of 2004 had a 10-day dry spell in May. The growing seasons of 2005 and 2007 had their longest dry spells in July (9 and 11 days, respectively) and in August-September (12 and 16 days, respectively). Amount of rainfall exceeded 100 mm in June, July, August and September of 2004, in May, June, and July of 2005, in May of 2006, in May and July of 2007.



Figure 3. Monthly rainfall during the growing seasons of 2004-2007. (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov)

Average air temperature for the studied growing seasons was more stable than the precipitation. July and August were always the warmest months, (16–20°C). In May, June and September the average was always between 10 and 15°C. The warmest growing season overall was 2006, averaging 15°C, compared to 14.4°C in 2005 and 2007, and to 13.9°C in 2004. In the growing season of 2005 the minimum air temperature never fell below zero but in all the other growing season it did: to -0.5°C at the end of May of 2004 and to -2.1°C in early May of 2006 and 2007. Maximum air temperatures were 27.2°C in 2004, 29.2°C in 2005, 33.8°C in 2006 and 31.4°C in 2007.

3.2. Soil properties

Soil bulk density varied during the growing seasons of 2004-2007 from 0.9 to 1.4 g cm⁻³ being the highest in potato furrows during the wettest growing season of 2004 and the lowest on cabbage ridges during the driest growing season of 2006 (Figure 4). The differences in soil bulk density between ridges and furrows were higher in the wetter growing seasons of 2004, 2005 and 2007 than in dryer growing season of 2006. That must be a result of soil compaction in the furrows during crop management operations. It was shown that the studied soils were much more easily compacted when wet than when they were relatively dry. In wetter growing seasons the differences in soil bulk density between ridges and furrows were greater in spring and early summer time when the ridges were formed for crop planting and mechanical cultivation of soil was regularly done (as a weed control operation). It also coincided with higher monthly rainfalls at the beginning of the wetter growing seasons. Later in the season the differences in soil bulk density between ridges and furrows were smaller. During the driest growing season of the four – 2006 – the difference in soil bulk density between ridges and furrows was less pronounced and did not change much during the season. The difference in soil bulk density between soils with the low (19 g C kg⁻¹ soil) and high (22 g C kg⁻¹ soil) SOC content was also often significant with more fertile soils having lower bulk density than the less fertile soils. Still, the differences in bulk density between soil ridges and furrows were almost always more significant than the differences in that for ridges (or furrows) between soils with different SOC content. The significantly higher bulk density of soil furrows, compared to that of soil ridges, could result in a formation of soil physical conditions more favorable for microbial process of denitrification in the studied soil (Beare et al., 2009).

The soil water content during the four studied growing seasons changed from 8 to 36% (of weight) and was higher than 20% for most of the wettest growing season of 2004, varied from 8 and 36% and from 8 and 31% during the growing seasons of 2005 and 2007, respectively, and never exceeded 24% during the driest growing season of 2006 (Figure 5). The differences in soil water content between ridges and furrows were greater in wetter growing seasons of 2004, 2005 and 2007 than in the driest of the four growing seasons of 2006. A combination of greater water content and higher bulk density in the soil of furrows as compared to the soil of ridges could lead to decreasing oxygen availability and to increasing N₂O fluxes as the intermediate of accelerated process of denitrification under such soil physical conditions (Drury et al., 2003; Beare et al., 2009).

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Figure 4. Soil bulk density (BD) in furrows and on ridges at the plots with potato (2004, 2005), cabbage (2006) and carrot (2007) at different soil organic matter (SOC) content (17, 19 and 21 g C kg⁻¹ soil). (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov)



Figure 5. Soil water content (W) in furrows and on ridges at the plots with potato (2004, 2005), cabbage (2006) and carrot (2007) at different soil organic matter (SOC) content (17, 19 and 21 g C kg⁻¹ soil) (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov).

The relationship between soil water content (average for a month) and monthly precipitation is shown on Figure 6 and 7. A linear correlation (p < 0.05) between the two parameters was higher for the soil with the lower SOC content than for the soil with the higher SOC (especially for furrows). The water-holding capacity of the studied soils was not very high as they were light- textured and should mainly depend on rainfall and SOC content. The higher SOC of a light-textured soil the more water it would be able to hold and would be less dependent upon rainfall if the dry spells were not very long.



Figure 6. Relationships between monthly precipitation and average (for a month) soil water content (W, % of weight) for (a) soil ridges and (b) soil furrows with the highest (22 g C kg⁻¹ soil) soil organic carbon content during the growing seasons of 2004-2007 (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov)

During the studied growing seasons the soil WFPS varied widely within and between years (Figure 8). In general, the soils of all plots were wetter in 2004 than in 2005, 2006, and 2007 with WFPS for most of the growing seasons varying from 35 to 70%, compared to 15–50% in 2005, 15–40% in 2006, and to 20–45% in 2007. In 2004, in contrast to all the other studied seasons, maximum values of WFPS were observed in June and July (40–85%). During the wettest part of the growing season soil in furrows was 20–40% wetter than soil on ridges (60– 85% versus to 40-45%, respectively). In May and August of 2004 the soil WFPS was lower than in the middle of the summer, changing from 20 to 40% and from 38 to 58%, respectively. The difference in soil water content between ridges and furrows during the drier part of the season was 10–20%. In 2005, the lowest values of soil WFPS were observed at the end of July, August and September, when WFPS on potato ridges went down to 10–22%, being the lowest of the year. During this dry spell the soil WFPS in potato furrows varied between 19 and 38%. The highest values of soil WFPS for the whole growing season of 2005 were observed in May and June but even then they were varying between 38 and 62%, and the difference between furrows and ridges was 11-13%. In 2006, the driest growing season of all, soil WFPS was very low in July (15-20%). The highest values of soil WFPS, but still quite low compared to the highest values of the other growing seasons, were observed in May and September (33-43%). The difference in soil WFPS between furrows and ridges during the growing season of 2006 was never higher than 8%. In 2007, the lowest values of the soil WFPS were found at the end of May-early June and at the end of June - early August (15-25%). Early May and August of 2007 were wetter but the highest values of the soil WFPS were not exceeding 53%. The difference in soil WFPS on ridges and furrows in 2007 was 7-10% during dry spells and 10-15% during wetter spells of the season. As was indicated above, nitrification is the main process of N_2O emission at 35-60% WFPS, but denitrification is more important at soil water content greater than 60% WFPS due to a decreased oxygen supply (Drury et al., 2003; Dobbie, Smith, 2003). Therefore, the observed soil moisture conditions were often more favorable for nitrification rather than denitrification during the growing seasons of 2004-2007.



Figure 7. Relationships between monthly precipitation and average (for a month) soil water content (W, % of weight) for (a) soil ridges and (b) soil furrows with the lowest (19 g C kg⁻¹ soil) soil organic carbon content during the growing seasons of 2004-2007 (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov).



Figure 8. Soil water-filled pore space (WFPS) for furrows and ridges for potato (2004 and 2005), cabbage (2006) and carrot (2007) at different soil organic matter (SOC) content (17, 19 and 21 g C kg⁻¹ soil) (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov).

The linear correlation between monthly rainfall and soil WFPS (average for a month) was strong for soil furrows as well as for soil ridges only during the driest growing season of 2006 (R²=0.80-0.88, p<0.05). For the growing season of 2007 this relationship was strong only for soil ridges (R²=0.92-0.94, p < 0.05) but not for furrows (R² = 0.65-0.81, p = 0.1-0.19) while in 2004 it was strong for soil furrows (R²=0.95, p < 0.01) but not for ridges (R²=0.57, p = 0.14). The relationship between monthly rainfall and soil WFPS (average for a month) for all 5 growing seasons is shown on the Figure 9. In average, the soil WFPS in furrows is more sensitive to monthly rainfall (R²=0.64, p < 0,001) than that on ridges (R²=0.37, p < 0,001). Our results corresponded with the data reported by L. Meng et al. (2005) where the strong correlations between WFPS and precipitation were also observed.

According to T. Granli and O.C. Bockman (1994) optimum soil temperatures for N₂O emissions vary between 25-40°C. During the growing seasons soil temperatures at 10 cm depth varied between 3 and 26°C, and were highest (15–26°C) always at the end of July and in early August. Average soil temperature was almost 1°C lower during the growing season of 2004 (14.3°C) and 2007 (14.4°C) than of 2003 (15.1°C), 2005 (15.2°C) and 2006 (15.0°C). Over the 4 years, higher soil temperatures were always found in those plots where soil was more exposed to the sun. The soil temperature was often higher in the ridges than in the furrows.

The experimental soil was very low with mineral N content when N-fertilizers were not used and contained 2–9 mg N kg⁻¹ soil at the beginning of all studied growing seasons. Soil mineral N concentrations always increased after N-fertilizer was applied to the soil to 20-100 mg N kg⁻¹ soil but were never high for longer than 3 weeks and were always back to below 10 mg N kg⁻¹ soil at the end of the growing seasons.



Figure 9. Relationships between monthly rainfall and soil water filled pore space (WFPS, average for a month) for (a) soil ridges and (b) soil furrows during the growing seasons of 2004-2007 (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov).

K. Dobbie and K.A. Smith (2003) reported that high N_2O emission could be even observed at WFPS (65%), soil temperature (4.5°C) and NO_3 -N content (5 mg kg⁻¹ soil). The results of our studies showed that these threshold limits had been observed or exceeded during the growing seasons of 2004-2007.

3.3. N₂O emissions

3.3.1. Daily fluxes

During the growing seasons 0f 2004-2007 daily N₂O fluxes varied highly between plots differed in fertilization, soil physical conditions and crops. Agricultural soils without any fertilization can produce N₂O during the growing season because of mineralization of soil organic matter and N rich plant residues. In our study the daily N₂O fluxes for the four studied growing seasons were never higher than 10 g N₂O–N ha⁻¹ on the unfertilized plots (both in furrows and on ridges). Conversely, daily N₂O fluxes from the soil could be very low even on fertilized soils (especially on ridges), indicating that other parameters, for example, soil mineral N content, temperature, soil WFPS and oxygen availability were main determinants controlling production of N₂O as the by-product of nitrification (Khalil et al., 2004; Meng et al., 2005; Conen et al., 2000).

Our data corresponded with the results published by H. Flessa and P. Dorsch (1995) and also by B. Ball et al. (2002) who found that application of N-fertilizers by itself did not always enhance N_2O emission and that weather conditions at the time of fertilizer application influenced N_2O emissions substantially. Nevertheless, C. Henault et al. (1998) reported that N_2O emissions were higher 20 g N ha⁻¹ day⁻¹ from soils with low water content as a result of domination of nitrification.

Possible differences in N₂O emissions from soils with different crop types depend on the management practices and climatic conditions. Tillage, sowing and other cultivations for agricultural plants can disturb soil aggregates, increase soil organic matter mineralization and deteriorate soil physical status and, as a result, can lead to an increased N₂O emissions (Elder, Lal, 2008; Ruser et al., 1998; Beare et al., 2009; Six et al., 1998). Crops can (1) demonstrate different rates of soil water uptake, (2) prevent the accumulated soil water against evaporation under different weather conditions, and (3) remove more N from the soil that will result in different availability of mineral N for nitrifying and denitrifying microorganisms.

During the growing seasons of 2004-2007 daily N_2O fluxes from the soil with crops grown on ridges (potato, carrot, cabbage) were often higher than those from the soil with cereals, grasses, grass-clover mixture and grass with oats (the latter crops grown in the same experiment are not being discussed in this paper but were described earlier in our paper - Buchkina et al., 2010).

For the latter crops daily N_2O fluxes were never exceeding 20 g N_2O -N ha⁻¹ while for the crops grown on ridges N_2O fluxes from the soil of furrows could be as high as 115 g N_2O -N ha⁻¹ day⁻¹ (Figure 10). Higher N_2O emissions from ridges can be explained by a greater mineralisation of soil organic matter that resulted to an increased N_2O emission from a bare soil subjected to a higher warming (Maljanen et al., 2002). According to the results reported by M. Maljanen et al. (2002), higher N_2O fluxes were observed from soils kept bare by tillage or cutting presumably from lack of competition for nitrate (NO_3^-) between microbes and plants.

Daily N_2O fluxes during the growing seasons of 2004-2007 were never affected by WFPS if no N had been applied with the mineral fertilizers as the original soil was very low in available N. However, in the N-fertilized plots the greatest N_2O fluxes were found when WFPS exceeded 40% (Figure 11) and that happened more often in the soil of furrows with the higher soil bulk density rather than in the soil of ridges with the lower soil bulk density. The highest N₂O emission in the cultivated soils generally are observed at 70–90% WFPS due to denitrification which rapidly increased when WFPS exceeded 60%, whereas at 30–70% WFPS nitrification was the main source of N₂O (Granli, Bockman, 1994; Smith et al., 2003; Maljanen et al., 2002).

It was shown for field experiments in Scotland (Dobbie et al., 1999; Conen et al., 2000) that high N₂O fluxes actually occurred more often when WFPS was higher than 60%. In our experiment the soil WFPS quite rarely exceeded 60% (the longest period for the four growing seasons was about 20 days in 2004 and only for potato furrows) as the rainfall of the area was less than it was in Scotland and also the soil of the experimental plot was light-textured with relatively easy drainage down the soil profile. The work of E.A. Davidson (1991) suggests that denitrification played its role in N₂O emissions from our soil only occasionally, when there were anaerobic conditions in some parts of the soil, while the main source of N₂O emission most of the time was nitrification. The same results were reported in our earlier work (Buchkina et al., 2010) for other crops (cereals, grasses, and grass-legume mixtures) at our experimental station.

Soils in the ridges and furrows could differ in bulk density, air and total porosity, available SOC, mineral N and oxygen availability. For instance, the average bulk density of the soil on ridges and in furrows was equal to 0.9 and 1.4 g cm⁻³, respectively. Therefore, the soil furrows could show more favorable conditions for denitrification before and after a rainfall. Our results corresponded with the data of Beare et al. (2009) who showed that most (88%) of the total N₂O production from compacted soil occurred after soil rewetting, at a time when there was ample NO₃⁻-N and dissolved organic carbon available and the air-filled porosity was low (0.22 cm³ cm⁻³), rather than during the drying phase when compacted soil was accumulating NO₃⁻N and air-filled porosity was high (0.62 cm³ cm⁻³). P. Merino et al. (2012) also reported that the interaction of WFPS and soil NO₃⁻ content was statistically significant (p < 0.001), indicating that the response of N₂O emission from a loamy clay soil to changes in NO₃⁻ content was very dependent on WFPS.



Figure 10. Daily N₂O fluxes from the soil under (a) cereals, grasses, grass-legume mixtures, grass-cereal mixtures during the growing seasons of 2003-2005 (Buchkina et al., 2010) and (b) crops grown on ridges (potato, cabbage, carrot) during the growing seasons of 2004-2007 (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov).



Figure 11. Soil water-filled pore space (WFPS) and daily N₂O fluxes (both from furrows and ridges) from the soil with potato (2004, 2005), cabbage (2006) and carrot (2007): (a) unfertilized plots, (b) fertilized plots (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov).

3.3.2. Cumulative fluxes and emission factors

Cumulative N₂O fluxes for the growing seasons of 2004-2007 from the studied soil for different crops varied from 0.34 ± 0.09 to 1.83 ± 0.45 kg N₂O-N ha⁻¹ (Table 2). Within the same growing season N₂O cumulative fluxes were higher from the soils of furrows than from the soils of ridges (especially, on the plots where mineral nitrogen was applied with fertilizers) but the difference was not significant when all the four growing seasons were taken into account: the cumulative N₂O fluxes from soils in furrows varied from 0.37 ± 0.10 to 1.83 ± 0.45 kg N₂O-N ha⁻¹ while from soils on ridges – from 0.36 ± 0.011 to 1.25 ± 0.29 kg N₂O-N ha⁻¹.

The lowest cumulative N_2O fluxes for both positions were measured for the growing season of 2006 – the driest of the four. During this growing season cumulative N_2O fluxes from soils of furrows were often even lower than those from soils of ridges in wetter growing seasons (Table 2, Figure 12). During the dry growing season of 2006 cumulative N_2O fluxes were not affected by N-fertilizer rates on the soils having SOC content of 17 and 19 g C kg⁻¹. On the plot containing 23 g C kg⁻¹ only the soil in furrows emitted more N_2O for this growing season the compacted soil in the furrows demonstrated greater soil water content than the uncompacted soil on the ridges. Hence, the first one had a higher amount of smaller pores than the latter one with a higher amount of larger pores. Therefore, during this growing season the compacted furrow soil with smaller pores could (1) hold more water, (2) have more favorable conditions for nitrification and denitrification, and (3) response in the higher values of N_2O emissions to the mineral N fertilization than the uncompacted ridge soil.

The cumulative N_2O fluxes from the soils showed the higher values during the wetter growing season of 2007 compared to the driest growing season of 2006 when there was no relationship between fertilizer rates and cumulative N_2O fluxes. In 2007, an increase in a rate on mineral N-fertilizer from 40 kg N ha⁻¹ to 110 kg N ha⁻¹ did not result in an increase of cumulative N_2O fluxes from the soil on ridges under carrot (Table 2). Only the rates of 120 and 130 kg N ha⁻¹ caused a significant increase of cumulative N_2O fluxes from this soil. Thus, the relationship of the cumulative N_2O fluxes with the mineral N rates was nonlinear for soil on ridges for the growing season of 2007. The cumulative N_2O fluxes from the soil in furrows under carrot were significantly higher than those from the ridges, and demonstrated a non-linear and unstable increase with increasing N rates from 40 kg N ha⁻¹ to 130 kg N ha⁻¹. However, the highest cumulative N_2O fluxes from the soil both on ridges and in furrows for the growing season of 2007 were observed at the N rate of 130 kg N ha⁻¹.

Year	Crop	Crop yield, kg ha ⁻¹	SOC, g kg ⁻¹ soil	N applied, kg N ha ⁻¹	Position	Cumulative N ₂ O flux, kg N ₂ O-N ha ⁻¹	Emission factor
2004	Potato	17000	17	120	Ridges	1.13±0.39	0.94
					Furrows	1.51±0.69	1.26
2005	Potato	18000	17	120	Ridges	0.60±0.21	0.50
					Furrows	0.91±0.35	0.76
	Potato	21000	21	120	Ridges	1.25±0.29	1.04
					Furrows	1.83±0.45	1.52
2006	Cabbage	41400	17	0	Ridges	0.37±0.08	-
					Furrows	0.45±0.11	-
	Cabbage	59900	17	70	Ridges	0.36±0.05	0.51
					Furrows	0.42±0.08	0.60
	Cabbage	45040	19	0	Ridges	0.43±0.06	-
					Furrows	0.53±0.07	-
	Cabbage	75900	19	90	Ridges	0.45±0.07	0.50
					Furrows	0.56±0.08	0.62
	Cabbage	81100	22	0	Ridges	0.34±0.09	-
					Furrows	0.37±0.10	-
	Cabbage	103320	22	110	Ridges	0.36±0.11	0.33
					Furrows	0.60±0.12	0.54
2007	Carrot	54830	17	40	Ridges	0.62±0.02	1.55
					Furrows	0.65±0.07	1.63
	Carrot	61220	17	110	Ridges	0.64±0.03	0.58
					Furrows	0.93±0.07	0.85
	Carrot	68110	19	40	Ridges	0.71±0.01	1.78
					Furrows	0.92±0.10	2.3
	Carrot	70170	19	120	Ridges	0.74±0.01	0.62
					Furrows	0.99±0.11	0.83
	Carrot	74570	23	60	Ridges	0.65±0.03	1.08
					Furrows	1.09±0.05	1.82
	Carrot	70040	23	130	Ridges	0.80±0.04	0.62
					Furrows	1.45±0.14	1.12

Table 2. Crops, amounts of mineral N-fertiliser applied, cumulative N₂O fluxes and emission factors.

According to several authors, there is the threshold of N rates which can exceed the N requirements of crops (Granli, Bockman, 1994) and if the N rates exceed crop requirements, N₂O emissions can become more variable and increase exponentially with increasing N fertilization (Hoben et al., 2011; Snyder et al., 2009). Our data supported the results received by these authors. In our opinion, the N rates of 120 and 130 kg N ha⁻¹ exceeded the threshold of N requirements of carrot during the growing season of 2007. Moreover, there was only a weak correlation (r=0.16) between the yields of carrot and the mineral N-fertilizer rates for the growing season of 2007.



Figure 12. Differences in cumulative N₂O fluxes between soil in ridges and on furrows (F) in relatively dry (2006) and wet (2007) growing seasons at different N-fertilizer rates (0, 60, 70, 130 kg N ha⁻¹) (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov)

It was recommended by J.W. Van Groenigen et al. (2010) that to obtain more valid information on N₂O emissions from agricultural soils it is better to assess N₂O emissions as a function of crop yield. According to our results, the ratios of N₂O cumulative fluxes (average for furrows and ridges) to carrot yields were equal to $1.16*10^{-5}$, $1.17*10^{-5}$, $1.27*10^{-5}$, $1.20*10^{-5}$ and $1.61*10^{-5}$ kg N₂O-N ha⁻¹ kg⁻¹ yield at the N-fertilizer rates of 40, 60, 110, 120 and 130 kg N ha⁻¹, respectively. These results also demonstrated that the N rate of 130 kg ha⁻¹ exceeded the N requirements of carrot during the growing season of 2007.

When all the data for all the growing seasons were taken into account we observed that the significant positive correlation between amount of N applied into the soil with mineral fertilizers and cumulative N_2O flux for a growing season was higher in the soils of furrows (r=0.66, p =0.01) than in the soil of ridges (r=0.56, p=0.01) (Figure 13). The soil of furrows contained the same amount of mineral N and carbon as the soil of ridges but often had higher water content, bulk density and WFPS and, as a result, demonstrated more favorable soil physical conditions for microbial process of denitrification.

The emission factor of 1% is recommended by (IPCC, 2006) for evaluating the efficiency of direct N_2O emissions from agricultural soils. The emission factor (calculated for 5 months' cumulative fluxes) for the different crops varied during the four growing seasons from 0.33 to 2.30%. The emission factors were expectedly higher in wetter growing seasons of 2004, 2005 and 2007 (0.50-2.30%) than in drier growing season of 2006 (0.50-0.62%) The emission

factors were often higher than 1% for the soil of both furrows and ridges only in wetter growing seasons of 2004, 2005 and 2007 but not in dry growing season of 2006.



Figure 13. Relationship between the rates of mineral nitrogen fertilizer and cumulative N₂O flux from a sandy loam Spodosol in furrows (black dots and line) and on ridges (empty dots and dotted line) for the growing seasons of 2004-2007 (Natalya P. Buchkina, Elena Y. Rizhiya, Sergey V. Pavlik, Eugene V. Balashov)

4. Conclusions

Cumulative N_2O fluxes from a sandy loam Spodosol for the growing seasons of 2004–2007 varied between 0.34±0.09 and 1.83±0.45 kg N_2O -N ha⁻¹ for different crops studied in this experiment. Seasonal N_2O cumulative fluxes were higher from the soils of furrows than from those of ridges (especially on the plots where mineral nitrogen was applied with fertilizers) only in wetter growing seasons of 2004, 2005 and 2007. This difference was not significant for the drier growing season of 2006 or when all the four growing seasons were taken into consideration as climatic conditions affected the relationship and made it much weaker.

The N application contributed to a higher N_2O emission from soil in furrows, where the soil was more compacted with higher water-filled pore space, than from soil on ridges but only in wetter growing seasons. During the dry growing season of 2006 there was no significant difference between N_2O emissions from soils on ridges and in furrows. There was a nonlinear N_2O response to increasing N fertilizer rates from the soil on ridges and in furrows for carrot during the wet growing season of 2007. The mineral N-fertilizer rate of 130 kg N ha⁻¹ could exceed the N requirements of carrot during the growing season of 2007.

Soil water-filled pore space affected N_2O emission from the soil only if mineral N-fertilizer was applied into the soil. Plots receiving no extra N never emitted much N_2O whatever the soil water-filled pore space.

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