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# Nitrogen transformations from nitrogen fertilizers in soils of central and eastern Europe in changing climatic conditions

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## Abstract

Agriculture contributes to global warming mainly through the emission of methane and nitrous oxide. Nitrous oxide is particularly important, as it accounts for a significant share of total nitrogen emissions from arable land It is produced as a result of anaerobic microbiological changes of nitrogen introduced into the soil along with mineral fertilizers. Changes in weather patterns in response to climate change may significantly affect the efficiency of fertilizer nitrogen in agriculture, and, consequently, entail undesirable environmental effects. This issue is of particular importance in view of the dominant role that this fertilizer element plays in agriculture, and, on the other hand, due to the global environmental risk within the "nitrogen cycle". The analysis, carried out in this paper indicates, that transformations of nitrogen compounds in the soil, caused predominantly by the climate condition, result in nitrogen release from the agricultural production area. The dispersion in the form of molecular nitrogen ($N_2$) is mainly the result of denitrification processes. By this way over 50% of nitrogen lost from agriculture is dissipated from the agricultural land. From the agricultural point of view, denitrification is a process that limits the resources of available nitrogen, but from the environmental viewpoint, this process should be considered as a natural mechanism of environmental self-purification and water protection. Although it constitutes only about 25% of the total loss of this element the dilution of nitrogen from agricultural areas by leaching, is considered to be the most cumbersome for the water environment.

## 1. Introduction

The assessment of impact of weather conditions on the transformation of nitrogen compounds introduced as organic and mineral fertilizers has long been a subject of research, but changing weather conditions related to global warming imply a reassessment of this impact, especially in the context of environmental effects (Olesen et al., 2011). The aim of the study is to summarise the knowledge on the impact of moderate climate conditions on the nitrogen transformations in soil.

Over the last several decades the term 'climate change' has assumed a new meaning in the context of global warming and temperature rise on the Earth surface, while causes of climate change have been intensively studied on the global scale. The present state of knowledge on the causes of climate change has been specified by consecutive reports of the Intergovernmental Panel on Climate Change (IPCC). These reports as well as other accounts, such as that of the American National Academy of Sciences (NAS), as well as the report published by the G8 Group, state that most of temperature changes over the last 50 years shall be attributed to human activities. The temperature rise, observed in the years 1906–2005 near the Earth surface, was + 0.74 ±0.18°C (IPCC 2007), and the decade 1999–2008 being the warmest decade for the past hundred years (Wang et al., 2010). IPCC suggested that global mean air temperature may rise by up to +6°C by the end of the 21st century (Oni et al., 2017). The European Union has been undertaking climate protection activities globally since the 90-ties of the 20th century. The EU has played a key role in establishing the United National Framework Convention on Climate Change and the Kyoto Protocol. The Protocol sets the legally binding goals for the industrialized countries, aiming at the reduction of emission of greenhouse gases (GHG) and as effect in the beginning of 2007 EU has set an ambitious goal - to reduce the emission of GHG by at least 20% by 2020.

Agriculture is also responsible for emitting GHG to the atmosphere, albeit at a lower scale than the other sectors. This applies, in particular, to large-scale and industrial agriculture. It is estimated that this share does not exceed 10% of the emissions produced by the national economy (Sapek et al., 2002). A relatively small share of agriculture in the global GHG emission is due to the fact that agricultural land, covering more than half of the EU surface area, is a large coal stock. The $CO_2$ emission from soils is compensated by its absorption by plants, and, as a result, agriculture contributes to reducing its emission. Agriculture contributes to global warming mainly through the emission of methane and nitrous oxide. Particularly significant is the share of nitrous oxide, which accounts for as much as 50% of the total emission of GHG from agricultural land. The annual global $N_2O$ emissions from soils are comparable to the $N_2O$ emissions from fossil fuel combustion (Oertel et al., 2016), and in Poland almost 80% of the annual $N_2O$ emissions originate from agriculture, and its main source is the use of agricultural soils (Wiśniewski, 2019). It is produced as an outcome of microbial transformation of nitrogen introduced into the soil with mineral fertilizers. It is expected that, with regard to agriculture, the increasing probability of extreme weather events will result in a significant increase in the risk of failed harvest. Extreme weather events will primarily involve restrictions on the availability of water resources and floods. It is estimated, that yields harvested on more than 80% of agricultural land in Europe depend on the amount and distribution of precipitation. Water shortage in agriculture poses already a challenge in many parts of Europe, and this state is likely to worsen. Weather scenarios predict, that by 2070, there will be an increase in water deficient areas in Europe, from the current 19% to 35% (Iglesias and Garrote, 2015). It is known, that nitrogen cycle processes in terrestrial ecosystems are highly sensitive to temperature and soil moisture changes (Dirnbőck et al., 2017). Within this context, the relevance is increasing of the effect of climate changes, which result in significant fluctuations in soil moisture and temperature, on the transformation of soil nitrogen, particularly of the nitrogen introduced with natural and mineral fertilizers.

Changes in weather in response to climate change may significantly affect the efficiency of fertilizer nitrogen in agriculture, and, consequently, entail undesirable environmental effects. This issue is of particular importance in view of the dominant role that this fertilizer element plays in agriculture, and, on the other hand, due to the global environmental risk within the nitrogen cycle.

## 2. Conditions of nitrogen fertilizer transformation in the soil

The transformation of nitrogen compounds in the soil environment is influenced by multiple factors related to soil properties including pH and exchange capacity, its reaction as well as farming practices, which vary greatly, depending on the level of agricultural technology. In this context, studies on the effect of weather conditions on transformations of nitrogen fertilizers are difficult to make an unambiguous estimate, and, in particular, to make a quantitative evaluation.

### 2.1. Conditions related to the content of organic carbon.

As it is known, nitrogen is present in the soil surface layer mainly in the form of organic compounds. They represent more than 90% of the total soil nitrogen (Stevenson, 1982). Polish soils contain small amounts of nitrogen. The content of the total nitrogen in soils ranges from 0.02 to 0.35%. Chernozems, black earths and peat soils are more rich in nitrogen. However, most of the soils in Poland are sandy soils containing no more than 0.1% N. The transformation of soil nitrogen is quantitatively associated with the transformation of organic carbon. It depends on the same factors, which determine the processes of decomposition and synthesis of soil organic compounds, including soil humus. The content of soil organic matter and the associated nitrogen content, which is usually about 5% of its amount, is a function of contrasting processes of mineralization and humification of organic matter. These processes, as microbiological processes, are strongly affected by temperature and humidity of the soil environment. Organic carbon is the basic energy and building material for soil microorganisms (Bouwman et al., 2013, Laegreid et al., 1999)

The direction of mineralization processes is determined by the ratio of carbon to nitrogen in the organic fertilizer material. If, in the organic fertilizer material, this ratio is significantly bigger than in the microbial biomass (excessively wide: C:N > 40:1), immobilization processes dominate, whereas when it is narrower (< 20:1), then there prevail mineralization processes.

The significant effect of these transformations, dependent on the C:N ratio in the organic fertilizer material consists. In the first case, in the plant's disadvantage due to the decrease in the mineral nitrogen forms in the soil, and, in the second case, in the beneficial to plants rise in the soil mineral nitrogen. This decrease can significantly modify the effect of weather conditions on nitrogen transformation in the soil, as a result of multiple interactions of various intensity. Mineralization and immobilization processes are an essential part of the small nitrogen cycle within the soil-plant system. This circulation is closely related to the so-called large cycle, in which nitrogen present in the atmosphere takes part (Mariano et al. 2016).

### 2.2. Conditions associated with agrotechnical treatment

It should be emphasized that under conditions of cultivated soils, the transformation of nitrogenous organic compounds to mineral forms and their re-conversion to organic forms, depends not only on weather conditions, but also on agrotechnical factors related to cultivation (mechanical or no-till), fertilization technique (on-surface or in-depth application now increasingly in use), and on plant protection treatments (impact on the state of microorganisms), which significantly modify the supply of atmospheric air to the soil environment and the soil microbial activity. This makes it difficult to precisely assess the impact of weather conditions on nitrogen transformations. Separation of the above effect from that of the cultivation technology often encounters methodological problems, what leads to a considerable divergence of results obtained by various researchers.

The experiment which was carried out by Nivelle et al. (2016) in Northern France confirmed that agricultural practices have significant influence on content of C and N in soil. Combining no-till with winter cover crops (with a low or a high prevalance of legumes), irrespective of the presence of N fertilizers, resulted in the end of the experiment with increased of the total soil organic C and N contents above 20% over the course of 5 years.

### 2.3. Conditions associated with the heterogeneity of the soil environment

The soil environment is a very heterogeneous system. This is, to a large extent, due to its three-phase nature with varying proportions of individual phases and their differentiated spatial layout. This intricate system is additionally complicated by the heterogeneity of the soil solid phase itself, with all its layers and microspaces formed by its lumpy structure. Moreover, soil is an environment, in which various transformations of organic and mineral nitrogen compounds are directly related to the functioning of microorganisms, or to biochemical reactions controlled by enzymes secreted into the soil environment by living cells, or those entering after their death and degradation. This complexity of the soil environment favors the coexistence of a variety of biological processes that require extremely different conditions. As a result, nitrification and denitrification processes commonly occur in parallel (Stein and Klotz, 2016). The first occurs under conditions of good oxygenation, while the other requires anaerobic conditions. The scheme of the nitrogen cycle in the environment was presented in Fig. 1.

## 3. The effect of weather conditions on transformations of nitrogen supplied to soils as organic fertilizer materials

Organic fertilizer materials introduced into the soil environment are incorporated into the microbial transformation cycle, which develops a specific, weather-dependent balance of mineralization and immobilization processes. The driving force behind these processes is the energy released by the transformation of carbon compounds. The equilibrium formed under these conditions is strongly shifted towards the formation of organic compounds, mainly proteins and humus compounds, what is related to the formation of humus fractions resistant to mineralization. As a result, the mineral nitrogen forms in soils account for only 1 to 5% of the total soil nitrogen. The equilibrium of the above processes at this level is determined by the relative ratio of carbon and nitrogen contents in the organic material, which is due to the energy needs of soil microorganisms. The main factor responsible for maintaining the above balance is a good oxygenation of the soil environment. Theoretically, such conditions occur at low soil moisture. However, due to the microbiological character of the transformation of organic compounds, the peak mineralization occurs at the humidity optimum for the soil microorganisms. In practice, the differences in the mineral nitrogen content, and thus the differences in the rate of organic com-

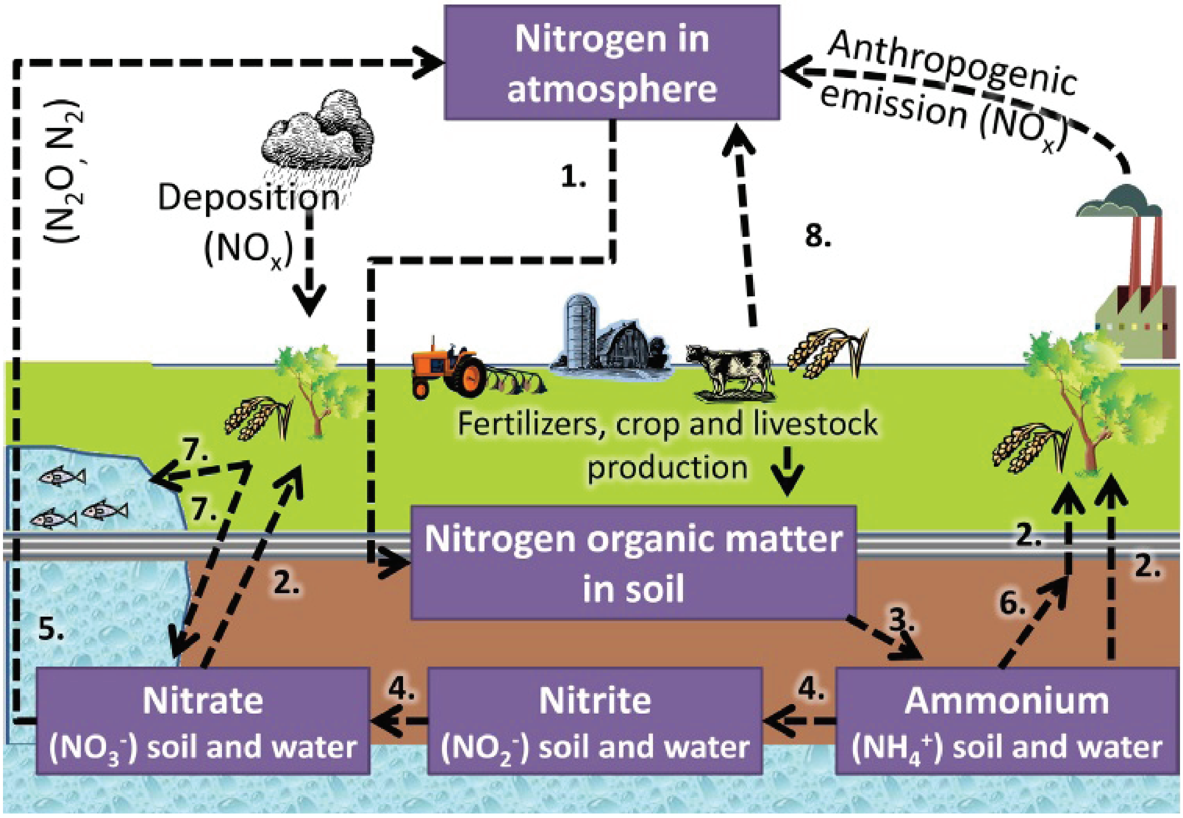

**Fig. 1.** The nitrogen cycle in the environment (after Bednarek et al., 2014). The nitrogen cycle: (1) uptake of nitrogen by plants from the atmosphere, (2) uptake of ammonium and nitrate by plants from soil and water, (3) ammonification, (4) nitrification, (5) denitrification, (6) nitrate immobilization by soil sorption, (7) nitrate leaching from the soil, (8) release of ammonia ($NH_3$), gaseous nitrogen and nitrous oxide to the atmosphere

pound mineralization, change only slightly in a relatively wide range of soil moisture levels. It is to be expected, that the lack of precipitation for a short time period, during the growing season, will have little impact on mineralization processes of organic fertilizers introduced into the soil. Low temperatures and excess water in the soil environment persisting for an extended period of time create an anaerobic milieu which reduces microbial activity in the soil environment. This limits the rate of mineralization and promotes the long-term accumulation of organic matter, thus contributing to the growth of soil organic nitrogen. This also applies to any fertilizer forms of organic matter entering the soil. Likewise, under conditions of high temperatures and soil drought microbial activity is reduced, what leads to reduction of $N_2O$ production (Inglett et al., 2005, Zhang et al., 2019).

High temperatures, while ensuring the optimum soil moisture, create conditions conducive to shifting the balance of microbial processes towards the organic matter mineralization, what results in the release of organic nitrogen and the formation of mineral nitrogen forms, such as ammonium forms, which, as a result of further changes, undergo oxidation processes to nitrates. The organic fertilizer material used in such conditions will be a good source of nitrogen for plants. The impact of soil temperature and moisture on the mineralization rate of soil nitrogen was recognized in the 1970s of the last century by Stanford et al. (1973, 1974). They showed that the mineralization of soil nitrogen follows the van Hoff's rule, that the temperature increase by 10°C increases the intensity of mineralization twice.

Weather factors are however, an important environmental pollution when applying organic fertilizer. In temperate climates, changes in the dynamics of temperature and humidity during the vegetation period have increasingly been observed. If, after the application of organic fertilization under a spring plant, the weather pattern during the initial vegetation period will be characterized by drought periods, whereas later in that period there will be a change in weather circumstances, consisting in an improvement in soil moisture conditions, undesirable environmental effects may be expected. Under these conditions, the main rate of mineralization will be significantly moved beyond the vegetation period, what will lead to the occurrence of mineral forms of nitrogen that cannot be used by the crop, and will be subject to the risk of leaching or release during autumn and winter and early spring (Erbas and Solakoglu, 2017; Rutting et al., 2018).

Meteorological factors, and, in particular, temperature and precipitation, have a significant effect on the rate of mineralization of soil nitrogen, which is one of the major causes of a high variability of mineral nitrogen forms in the soil during vegetation. This is an important obstacle when using chemical methods for determining the content of plant available nitrogen in the soil (Haohao et al. 2017; Luce et al., 2011). Contemporary systems of fertilization diagnoses take into account the effect of weather conditions on the mineral nitrogen content in soils. For diagnostic purposes, the content of mineral nitrogen in the soil is usually determined early in the spring, before the vegetation starts, when the soil microbial activity is still at its minimum, due to the low soil temperature (Arbacaukas et al., 2018; Villar et al., 2019).

The transformation of organic nitrogen compounds in the soil environment leads, ultimately, to the formation of ammonium, which is the basic form of nitrogen that can be taken up by plants. While mineralization leads to the oxidation of carbon bonds in organic compounds, the degree of nitrogen oxidation remains largely unchanged and is (-3) N. As a next stage ammonium salts or ammonia are formed, i.e. the nitrogen compounds which undergo further oxidation-reduction reactions. These changes are dangerous to the environmentally and lead to the formation of nitrates (oxidation) and subsequently nitrogen oxides (reduction), which are the main environmental risk factors due to fertilization. The nitrogen circle was presented in Fig 2.

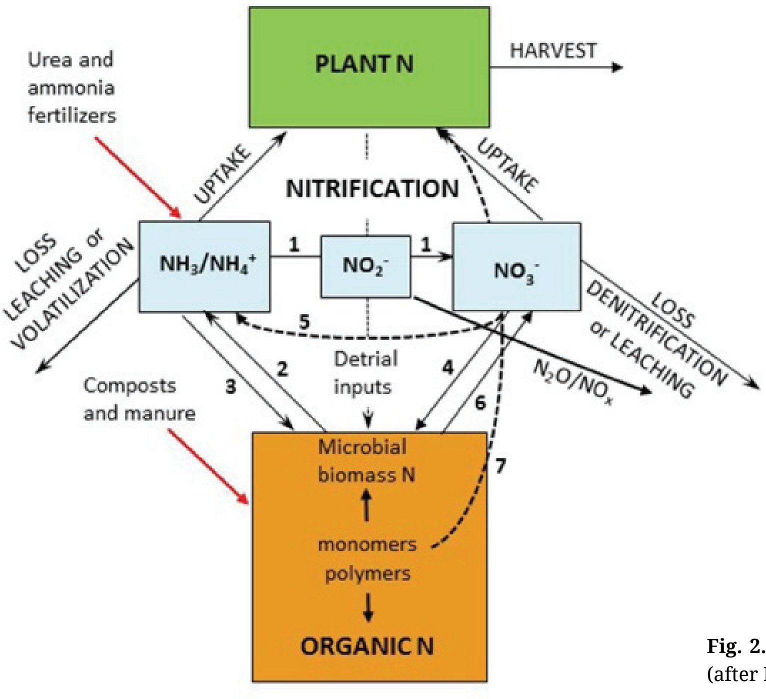

**Fig. 2.** The soil internal nitrogen circle (after Norton and Ouyang, 2019)

It should be emphasized, that while mineralization is a natural process necessary to maintain biological balance in the soil environment, providing plants with the necessary nitrogen source, further oxidation and reduction processes of ammonium ion constitute the main permanent risk of nitrogen losses from the soil environment as well as of its dissipation in the hydrosphere or return to the atmosphere in the form of nitrogen oxides or $N_2$. Weather factors, and mainly precipitation and its distribution during the vegetation season, contribute to nitrate leaching, posing an environmental risk associated with organic fertilization, of particular importance under conditions of light soils. Nitrates leaching may result in contamination of drinking water with nitrates, which may pose a significant risk for human health (Królak and Raczuk, 2018). For this reason, the relevant legislation in the European Union sets the allowable deadlines for the use of organic fertilizers, and determines the allowable dose of nitrogen that can be introduced on one occasion, in the form of organic fertilizers, onto the surface unit of farmland (Sosulski et al., 2017).

Organic fertilization contributes to an increase in $N_2O$ emission from the soil. This emission from the soil fertilized with manure for many years was greater than that from the soil fertilized with mineral fertilizers (Jäger et al., 2011; Salehi et al., 2017). This is due to the increase in the content of simple organic compounds that provide electron donors and energy substrate for denitrifying bacteria in the soil environment (Rivett et al., 2007). In addition, the increase in the soil organic matter content due to organic fertilization enhances the activity of denitrifying bacteria by increasing the consumption of $O_2$ in the mineralization process (Cannavo et al., 2004). Due to a relatively low content of organic carbon in the Polish soils, the conditions are generally unfavorable to denitrification, thus, periodic soil moisture rises, associated with precipitation incidents, constitute a key factor which supports denitrification and increases $N_2O$ emission (De Brogniez et al., 2015; Jager et al., 2011; Meng et al., 2005, Sosulski et al. 2017). In the literature, the opinion is widely adopted, that denitrification under conditions of organic fertilization is an important natural mechanism contributing effectively to the purification of nitrate loaded waters (Andersen et al., 2016; Fotyma and Fotyma, 2000; Greenan et al., 2006; Sosulski et al., 2017).

Another important factor, which may have significant influence on the N cycling, is the concentration of $O_3$ in the air.

It was demonstrated that elevated $O_3$ in soil is an important factor affecting microbial community structure and activity and may change N availability, which may lead to the increase N loss from soil (Simpson et al., 2014, Wu et al., 2016).

## 4. Effect of weather conditions on transformations of nitrogen from mineral fertilizers in soils

Nitrogen is introduced into the soil environment with nitrogen fertilizers in three forms; ammonium ion ($NH_4^+$), nitrate ($NO_3^-$) or amide ($-NH_2$). The first two forms are directly available to plants, while the amide form found in urea, to be assimilable, must be hydrolysed by the urease enzyme produced by soil microorganisms.

### 4.1. Amide form of nitrogen

Weather factors are decisive for the rate of urea hydrolysis. Low temperatures below 6°C in the spring, persisting for a long time, significantly delays its decomposition into ammonium form, which can persist in this conditions for up to two weeks. At the soil temperature of about 10°C, its hydrolysis usually does not take longer than one week. The urea hydrolysis process is conducive to environmental neutralization in soil microspaces, which results in the urea-forming ammonium ion being much more susceptible to volatilization in the form of ammonia than other nitrogenous mineral fertilizers. As a result, the spring weather patterns, characterized by a high temperature and good humidity, can significantly increase nitrogen losses in the form of ammonia from the cultivated field (Długosz and Piorowska-Długosz, 2016).

In modern mineral fertilization systems, deep application of mineral fertilizers is increasingly used. Under such conditions, the ammonium ion and ammonia resulting from urea hydrolysis are much more easily sorbed by the soil colloidal system compared to the surface application, which significantly reduces nitrogen losses as well as the related environmental effects (Mitchell et al., 1998).

### 4.2. Ammonium form of nitrogen

Ammonium ion in the soil environment is subject to nitrification, which is a typical biological oxidation process, carried out by autotrophic bacteria: *Nitrosomonas* and *Nitrobacter*, thus gaining the energy needed to bind and reduce carbon dioxide. This process is characterized by a low unit energy efficiency resulting in the need to oxidize large amounts of ammonium nitrogen. Nitrification intensity is strongly controlled by weather conditions., especially temperature (Gnida et al., 2016).

During the vegetation period with high temperatures, ammonium ions are converted to nitrates within a few days, what results, in the nutrient-rich soils, in plants feeding mainly on nitrate ions, irrespective of the form of nitrogen used for plant fertilization. This process takes place in two clearly discrete stages. In the first stage, ammonium ion is oxidized to nitrates (III), and to nitrates (V) in the second stage. Under normal weather conditions, nitrates (III) do not usually accumulate in soils. However, under conditions of excessive precipitation and the resulting limited oxygen supply to the soil, the atypically high levels of nitrates may accumulate under conditions of insufficient aeration. These circumstances may occur in waterlogged soils or under conditions of long-term precipitation, especially in heavier soils. Unusual excessive accumulation of nitrates (III) in the soil may lead to the formation of nitrosamines, the compounds which are undesirable in the soil (Laegreid et al., 1999, Rees et al., 2013).

Potential conditions for nitrite accumulation in the soil appear as a result of the excess nitrate content (e.g. as a consequence of excessive fertilization) when, due to the unfavorable weather conditions (e.g heavy rain) , that occur, even only periodically, are the conditions for nitrates reduction. Identification of the conditions where nitrosamines may form in wet soils and water is important, because of the risk they may pose to human and animal health (Gilli et al., 1984; Jensen, 1982).

### 4.3. Nitrate form of nitrogen

The nitrification process during the vegetation period increases the mobility of mineral nitrogen compounds through diffusion migration, and is considered as beneficial to plants, despite that it acidifies the soil environment. However, when this process occurs beyond the vegetation period, it is an important factor increasing the risk of nitrogen losses through leaching, especially under heavy precipitation conditions (Myrbeck and Stanberg, 2014; Sosulski and Mercik, 2011). The level of nitrates in tile drainage is also affected by mineralization-immobilization processes in the soil, which are tied to temperature and elevated carbon dioxide (Wang et al., 2015).

It is common knowledge, that nitrates move more easily with water infiltrating the soil profile than ammonium cation (Sapek et al., 2002). The amounts of eluates of both nitrates and ammonium are similar only in soils not fertilized with nitrogen. Nitrate leaching is associated with the vertical movement of water deep into the soil profile, triggered by atmospheric precipitation and is higher than that of ammonium cations. The results of studies showed that a significantly lower nitrate leaching is observed in dry years than in wet years (Mitchell et al., 1998; Szucs, 1991).

Although the nitrate leaching research takes a considerable space in the domestic and foreign literature, it is difficult to unequivocally estimate the amount of nitrogen dispersed by leaching. It is estimated, that in view of the changing climatic and soil conditions in Poland, the average amount of nitrogen lost through leaching ranges from a few to about 40 kg N per hectare per year (Mitchell et al., 1998; Sosulski et al., 2017; Sosulski et al., 2011). In extremely adverse weather conditions (high rainfall) , the loss can reach much higher values, of up to even 60-120 kg N $ha^{-1}$. In the model studies using red clay soils and $^{15}N$ isotopic techniques, it was demonstrated that, under heavy rainfalls, high nitrogen losses may occur with surface runoff, especially during the initial plant growth period, amounting even up to 18% of the nitrogen dose applied (Zheng et al., 2016). That is why, efforts are being made to reduce the intensity of this process, and to reduce the amount of nitrates in the soil environment, in view of the hazards for the ground- and surface waters. The efforts include, *inter alia*, the introduction of new nitrogen fertilizers containing nitrification inhibitors as well as biodegradable coating fertilizers to ensure the gradual release of nitrogen, adapted to the rate of plant uptake. Technologies for in-depth fertilization have also been developed, based on the new generation fertilizers that provide plant nutrition exclusively with ammonium nitrate (Oertel et al., 2016; Rosas et al., 2015; Spicher et al., 2016).

When referring to the accuracy of the assessment of weather condition effects on nitrogen losses through leaching, it should be emphasized that one of the main reasons hampering this accuracy is the high intensity of nitrate transformations in the natural environment, which occur not only directly within the soil profile, but also, indirectly, outside the profile. The main type of these transformations is the reduction of nitrates to nitrogen oxides and to molecular nitrogen that occurs in the so-called *transition zone* or ecoton. This is the natural environment, in which the nitrate flux moves between the agricultural space and the ground- and surface waters. It consists of, among others, unsaturated and saturated zones of soils, underground and surface drainage systems, mid-field water reservoirs, marshes, peatlands, woodlands, etc. Various studies emphasize the importance of the transition zone in self-cleaning of waters, moving from agricultural areas to the widely understood hydrosphere (Cors and Tychon, 2001; Dhondt et al., 2001). Denitrification is a decisive process for removal of excess nitrates from infiltrating waters (Sosulski et al., 2016).

### 4.4. Nitrogen in the form of $N_2O$

As was shown in many studies, nitrates dominate in the soil solutions sampled from soils remaining in good agriculture and having a well-regulated reaction (pH). Under anaerobic conditions, which periodically occur in topsoil after heavy precipitation incidents, nitrates are reduced to gaseous products such as nitrous oxide ($N_2O$), nitric oxide-2 (NO) and molecular nitrogen ($N_2$). Nitrate or nitrite reductase containing bacteria are mainly capable of carrying out this process. The intensity of this process, in addition to precipitation, is favored by the high organic matter content as well as neutral soil reaction (pH about 7). Denitrification occurs in all soils, and is a natural process that provides links between the soil nitrogen cycle and the global nitrogen store, which is the atmosphere (Signor and Cerri, 2013).

The analysis of soil conditions for the oxidation-reduction processes indicates that nitrification and denitrification are a sequence of closely interrelated transformations showing a layer-specific differentiation. Nitrification is predominant in the upper soil layer, although in the so-called micro-zones denitrification takes place, whereas in deeper layers, where nitrates migrate, denitrification dominates. The intensity of these processes is controlled by weather conditions that shape the temperature and aeration of the soil profile. The analysis of the zonation-model that describes the oxidation-reduction transformations in the soil profile, results in the conclusion that denitrification is a natural mechanism limiting nitrate leaching into groundwater (Jahangir et al., 2012). Based on a linear regression the model was created to describe the analyzed variables. As a result of Pearson's test and Shapiro-Wilk the variables which did not fulfill the tests assumptions were eliminated. In the resulting linear regression model, 63% of the variability of $N_2O$ emissions is explained by variability in use of nitrogen fertilizers. The nitrogen losses by leaching in this mechanism are replaced by nitrogen gas losses through volatilization in the form of nitrogen oxides and molecular nitrogen. From the environmental point of view, denitrification should be assessed as a positive process limiting the mineral nitrogen leaching from farmland, especially under conditions of increased atmospheric precipitation (Kolasa-Więcek, 2013; Sosulski et al., 2013).

Recent interest in the drivers of denitrification and nitrification processes in cultivated soils is due to the fact, that they release significant amounts of nitrous oxide, which is a major GHG, with direct global warming potential 298 times higher than that of carbon dioxide (Rosas et al., 2015). According to the

National Centre for Emission Balancing and Management, more than 85% of $N_2O$ emissions in Poland originate in agriculture, including around 70% from cultivated soils (KOBiZE, 2014). One of the main factors affecting the intensity of $N_2O$ formation, apart from the content of $N-NO_3$ in the soil and soil pH, is the soil temperature. Weather changes that increase the air temperature will thus significantly increase the emission of this gas from the soil. This process is further shaped by a whole series of other factors, such as soil moisture, its granulometric composition, fertilization level, which makes it difficult to determine the specific role of particular factors in the emission of nitrous oxide (Amha and Bohne, 2011; Firestone and Davidson, 1989).

A detailed analysis of the interdependence of factors controlling $N_2O$ emission indicates that the intensity of this process is determined by the interrelated weather conditions, which control the soil moisture- and nitrate contents (Dobbie et al., 2003; Vitale et al., 2017). Referring to the conditions prevailing in Poland, Goliński et al. (2000) demonstrated that the overall conditions of the Polish soils do not, generally, favor denitrification processes, in view of the dominance of light soils with low water content, easily overdrying in the absence of precipitation. Weather conditions that cause soil moisture to persist in the range of 60–90% of the capillary capacity, for a longer time period, encourage a higher intensity of the denitrification processes and associated $N_2O$ emissions (Smith et al., 1998). It is believed that in the excessively waterlogged soils, the major driver behind $N_2O$ emission is denitrification, while in the optimally wet soils (35–60% of the capillary capacity) the process is mainly governed by nitrification (Bateman and Baggs, 2005). Moreover, it was shown that the maximum $N_2O$ emission from the soil is most likely to be observed immediately after heavy rain moistening the overdried soil (Flessa et al., 1995). Such phenomena have been observed in recent weather anomalies, characterized by prolonged drought episodes terminated by the long-lasting heavy precipitation periods (Westra et al., 2013). $N_2O$ emissions from the soil occur not only during vegetation period, but also during the winter. Kaiser and Ruser (2000) have shown that as much as 50% of the gas emissions occur in winter, which is due to the alternating processes of freezing and de-freezing of the soil (Mogge et al., 1999).

## 5. Nitrogen in $NH_3$ form

An important issue in agriculture is the transformation of ammonium nitrogen leading to ammonia emission, which is one of the important elements of nitrogen dissipation from agricultural areas. Literature holds that the dominant source of ammonia emission in agriculture is animal production, accounting for 3/4 of its emission. Approximately 25% of the total ammonia emission from agriculture is released due to the transformation of fertilizers. According to Sapek et al. (2002), the ammonia emission from agricultural areas in 2000 amounted to about 300 Mtand showed a downward trend. Emissions of ammonia from cultivated fields under conditions of exclusive mineral fertilization, without natural fertilizers, vary between 2–6 kg $ha^{-1}$ a year (Sosulski and Łabętowicz, 2007). The scale of this emission is largely related to the soil reaction (pH) and the technique of fertilizer application. Soil liming and surface application of natural and mineral fertilizers favors this emission. The increasingly implemented techniques of in-depth application of slurry and mineral fertilizers greatly contribute to reducing this emission in agriculture (Misselbrook et al., 2019). A good example is the dynamic development of the RSM liquid fertilizer (ammonium nitrate + urea) technology in Poland. RSM is a coarce spraying technique or a filling technique. Using one of the techniques depends on the stage of development of the plant (Sztuder, 2007).

The weather conditions during the vegetation period significantly affect the processes of ammonia formation and its emission from the soil, via the influence on the activity of soil microorganisms, soil moisture and aeration. Under conditions of good soil moisture, ammonia resulting from the transformations of the organic and mineral fertilizers, is dissolved in soil solutions, in which as ammonium ion ($NH_3 + H_2O = NH_4OH$) is predominantly subject to processes of exchangeable sorption.

When there is no precipitation, especially after applying fertilizers, the major part of ammonia is volatilized in view of good soil aeration. The amount of ammonia emission from the area of agricultural production cannot be equated with the amount of nitrogen dispersed in this way from agriculture to the natural environment, because significant amounts of ammonia are returned to the soil with precipitation water. It is estimated, that the amount of atmospheric ammonia returning to the soil is approximately 3.9 N-NH kg $ha^{-1}$ per year( Sapek et al., 2002). Taking into account the area of agricultural land, it can be calculated, that the amount of nitrogen deposited solely by wet precipitation, in the scale of Poland, equals the amount of nitrogen that is released from the soil as a result of fertilization (Sosulski and Łabętowicz, 2007).

## 6. Conclusions

From the analysis of the effects of weather conditions on fertilizer changes, it can be inferred, that changes in soil temperature and moisture during vegetation period constitute major drivers controlling the mineralization of organic nitrogen fertilizer and the oxido-reductive transformations of mineral nitrogen. This is determined by the weather unpredictable dynamics and variability, increasing over the recent years. This may lead locally to a periodic disruption of the dynamic balance of fertilizer nitrogen transformations in the soil environment. Such a disruption of transformations processes causes their unfavorable orientation resulting in excessive nitrate leaching and excessive emission of ammonia and nitrous oxide. This requires that appropriate preventive measures will be taken on the part of science and agricultural practice, aiming at the development of new generations of fertilizers and the introduction of novel cultivation technologies, in particular, the in-depth application of fertilizers.

The above analysis indicates, that transformations of nitrogen compounds in the soil, caused predominantly by the climate system, result in nitrogen dispersion from the agricultural production area. The dispersion in the form of molecular nitrogen is mainly the result of denitrification processes. By this way over 50% of nitrogen lost from agriculture is dissipated from the agricultural land. From the agricultural point of view, denitrification is a process that limits the resources of available nitrogen, but from the environmental viewpoint, this process should be considered as a natural mechanism of environmental self-purification and water protection. Dilution of nitrogen from agricultural areas by leaching, although constituting only about 25% of the total loss of this element, is considered to be the most cumbersome for the environment.

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## Przemiany nawozów azotowych w warunkach klimatu umiarkowanego

### Słowa kluczowe

Zmiany klimatu
Azot
Nawozy
Rolnictwo
Gleba
Podtlenek azotu

### Streszczenie

Rolnictwo przyczynia się do globalnego ocieplenia głównie poprzez emisję metanu i podtlenku azotu. Szczególnie istotny jest udział podtlenku azotu, który stanowi aż 50% całkowitej emisji z gruntów rolnych. Jest on wytwarzany w wyniku przemiany mikrobiologicznej azotu wprowadzanego do gleby wraz z nawozami mineralnymi. Zmiany warunków pogodowych w odpowiedzi na zmiany klimatu mogą istotnie wpłynąć na efektywność wykorzystania azotu nawozowego w rolnictwie, a w konsekwencji pociągnąć za sobą niepożądane skutki środowiskowe. Kwestia ta ma szczególne znaczenie ze względu na dominującą rolę, jaką ten element nawozowy odgrywa w rolnictwie, a z drugiej strony ze względu na globalne ryzyko środowiskowe w ramach tzw. cyklu azotowego. Przeprowadzona w pracy analiza wskazuje, że spowodowane głównie warunkami klimatycznymi przemiany związków azotu w glebie powodują uwalnianie się azotu z obszaru produkcji rolnej. Dyspersja w postaci azotu molekularnego jest głównie wynikiem procesów denitryfikacji. W ten sposób ponad 50% azotu traconego z rolnictwa jest usuwane z gruntów rolnych. Z rolniczego punktu widzenia denitryfikacja jest procesem, który ogranicza zasoby dostępnego azotu, ale z punktu widzenia ochrony środowiska proces ten należy uznać za naturalny mechanizm samooczyszczania się środowiska i ochrony wód. Chociaż stanowi on jedynie około 25% całkowitej straty tego pierwiastka, to jednak rozcieńczanie azotu z obszarów rolniczych poprzez ługowanie jest uważane za najbardziej uciążliwe dla środowiska wodnego.