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DYNAMIC NITROGEN BALANCE IN THE EARTH'S PEDOSPHERE AND ATMOSPHERE

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ABSTRACT

This review paper looks at the dynamic balance between the pedosphere and the Earth's atmosphere regarding the intensity of the emission of nitrogen oxides and molecular nitrogen and their uptake by the biosphere. Maintaining this balance is important for minimizing the consequences of excessive N_2O emission (desertification, greenhouse effect), on the one hand, and encouraging nitrogen fixation processes, on the other hand, which protects the soil from degradation.

Keywords: nitrogen, nitrogen fixation, balance, balance, cycle.

INTRODUCTION

According to modern data, microorganisms play a leading role in circling all biogenic macro and microelements and the transformation and geochemical migration of many other chemical elements in the biosphere (Đukić et al., 2007).

The soil microbial community's participation in the global cycle of elements is well known only when it comes to carbon, while their role in the transformation of other biogenic elements, especially nitrogen, is still not well known. Therefore, this review paper aims to stimulate thinking and practical activities in that direction.

Bacteria are present in almost all ecosystems, both terrestrial and aquatic, and play crucial ecological roles. For example, bacteria mediate the mineralization of labile carbon (C). Moreover, anammox bacteria play a vital role in the nitrogen cycle, and rhizobia is involved in nitrogen fixation. Bacteria affect local and global biogeochemical cycles by absorbing organic carbon and nutrients, and therefore, the study of these microorganisms is key to understanding ecosystem dynamics (Meng et al., 2022).

Throughout the history of scientific research, nitrogen (N) has continuously emerged as the most important component in promoting increased productivity in plant development. Within the soil matrix, N manifests in various guises – as inorganic entities like ammonium and nitrate, and in organic incarnations such as amino acids (Pruthviraj et al., 2024).

Among the chemical elements, nitrogen is one of the most abundant elements on Earth, making up approximately 78.1% of the atmosphere. It is also an essential nutrient for life, and it can take many chemical forms in soil. The reactions making possible the transformations among these forms are mainly driven by soil microorganisms. Several nitrogen-containing compounds are also toxic. Soil microbial reactions involving nitrogen, therefore, have the potential to affect human and environmental health, sometimes spatially and temporally far from the microorganisms that originally performed the transformation. During the last decades, anthropogenic activities have also seriously impacted the global biogeochemical nitrogen cycle (Martínez-Espinosa et al., 2023).

Nitrogen (N) is an essential element in biological systems and one that often limits production in both aquatic and terrestrial systems. Due to its requirement in biological macromolecules, its acquisition and cycling have the potential to structure microbial communities, as well as to control productivity on the ecosystem scale. In addition, its versatile redox chemistry is the basis of complex biogeochemical transformations that control the inventory of fixed (biologically available) N in local environments, on a global scale, and over geological time. Although many of the pathways in the microbial nitrogen cycle were described more than a century ago, additional fundamental pathways have been discovered only recently. These findings imply that we still have much to learn about the microbial nitrogen cycle, the organisms responsible for it, and their interactions in natural and human environments. Progress in N-cycle research has been facilitated by recent rapid technological advances, especially in genomics and isotopic approaches (Ward and Jensen, 2014).

CHEMISTRY AND BIOGEOCHEMISTRY OF NITROGEN

Nitrogen is the primary macrobiogenic element. It belongs to the group of macroelements because its total forms in the soil are represented on average above 0.10%, and biogenic because it participates in a series of important physiological-biochemical processes in plants. In the soil, nitrogen mainly comes from proteins and other nitrogenous substances that are synthesized by plants and soil microorganisms. Rocks and minerals do not contain nitrogen, but they may contain NH_4^+ ions originating from precipitation or organic matter (Stojanova, 2018).

Nitrogen (N) belongs to the V subgroup of the periodic system of elements and has five electrons in its outer shell, due to which it has a clearly expressed tendency to fill that shell up to an octet. Valence states with the values -3, 0, +3, +5 are most suitable for nitrogen. In the ground state, nitrogen has an outer electron shell structure of $2s^2\,2p^3$ and is threevalent. Successive nitrogen ionization energies have the following values (eb): 14.53; 29.59; 47.43; 77.45; 97.86. The affinity of a nitrogen atom for one electron is +12 kCal/g-atom and for three – 500 kCal/g-atom.

The melting point of nitrogen is at -200˚C and the boiling point is at -195˚C.

In the composition of natural compounds on Earth, nitrogen is represented by two stable isotopes - ^{14}N and ^{15}N, whose participation is 99.635% and 0.365%, respectively. Radioactive isotopes (^{12}N, ^{13}N, ^{16}N, ^{17}N) can be obtained artificially, and are characterized by a short life span; one of them with the longest lifetime (^{13}N) has a half-life of 10.8 minutes, which makes it impossible to use highly sensitive radioisotope methods in the study of nitrogen metabolism in living cells and the specificity of its transformation in nature.

The total nitrogen content in the soil crust is estimated at 0.03%. Its largest part (about $4x10^{15}$ t) is in the Earth's atmosphere in the form of free (molecular) nitrogen (N_2), where it constitutes the main part (79%) of the air. Molecular nitrogen (N_2) is chemically very inert and under normal conditions practically does not react with metals or metalloids. Heating increases its chemical activity, above all concerning metals. With some of them, it binds, forming nitrides (for example Mg_3N_2). In the upper layers of the earth's atmosphere, the photochemical dissociation of the N_2 molecule is continuously taking place, as a result of which the N^+ ion is present in a small amount over 500 km.

Nitrogen traverses various classifications, each tethered to distinct criteria. Anchored in the quantum demanded by plants, it claims the designation of a macronutrient, necessitating a quantity of 1000 µg g−1 dry matter for optimal growth. This nutrient dynamic is reflected differently across soil and plant domains: nitrogen's nitrate form assumes a mobile disposition within the soil, while its ammonical form exhibits reduced mobility (Pruthviraj et al., 2024).

The N_2 molecule contains three bonds and is characterized by the nuclear distance d (NN)=1.095A, wave number = 2331 cm^{-1}, power constant k=22.4, and dissociation energy 226 kCal/mol. The breaking energy of the first of the three bonds in the N_2 molecule is 130 kCal/mol. 941 kJ/mol is required to break all three bonds. The solubility of N_2 in water is low – about 2 Vol%.

In the earth's crust, nitrogen creates three basic types of minerals that contain CN, NO_3^{-}, and NH_4^+. They are rare in nature, and sodium (Chilean) saltpeter ($NaNO_3$) and potassium (Indian) saltpeter (KNO_3) have limited industrial importance. Small amounts of nitrogen are found in coal (1.0-2.5%) and oil (0.2-1.7%).

In the biosphere of the Earth, bound nitrogen is concentrated mainly in the composition of soil organic matter (1.5 x 10^{11} t) and in the biomass of prokaryotes (1.3 x 10^{11} t), which is significantly more than in the biomass of plants (1 x 10^9 t) and animals (6.1 x 10^7 t) (Orlov and Bezuglova, 2000).

Nitrogen present in the air finds its conversion through diverse pathways. Blue-green algae facilitate the process through electrochemical fixation while nitrifying bacteria also play a role. This atmospheric nitrogen, once harnessed, contributes to the pool of nitrate nitrogen within the soil. The nitrate nitrogen, ensconced within the soil, embarks on its transformation journey. Denitrifying bacteria orchestrate the conversion of nitrate nitrogen back into nitrogen gas, releasing it into the atmosphere once more. Throughout the storage phase, nitrogen losses are a reality, often manifesting as ammonia volatilization, with the majority of losses from manure stacks occurring in this gaseous form. Environmental elements, such as ambient temperature, wind velocity, and solar radiation, wield their influence on the pace of loss from open storage setups. As manure makes its way into the soil, nitrogen losses continue to shape the narrative. The spectrum of these losses encompasses ammonia volatilization (ranging from 5% to 35%), denitrification (exceeding 10%), nitrogen leaching (ranging between 2% and 50%), immobilization, as well as soil erosion or runoff losses. The complicated connection between these changes and losses emphasizes how dynamic nitrogen is in the larger ecological framework (Figure 1) (Pruthviraj et al., 2024).

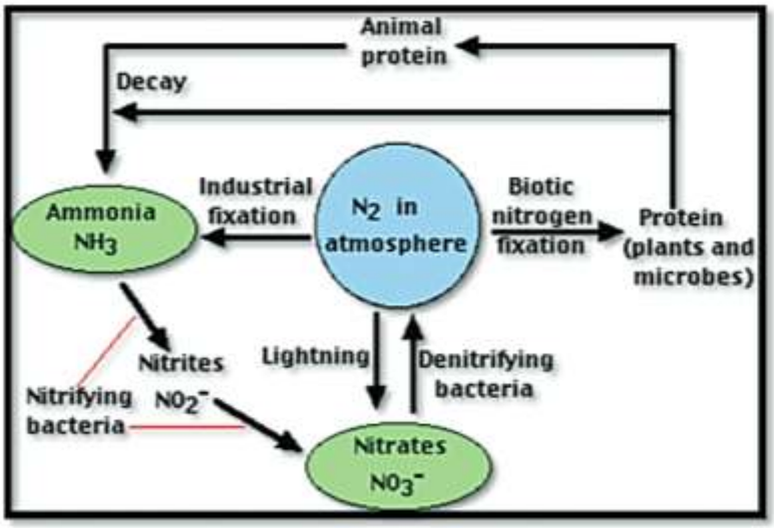

Figure 1. Nitrogen dynamics in the atmosphere (Sardar et al., 2023).

Considering that nitrogen transformations in soils are dynamic and highly dependent on the microbial biodiversity inhabiting those environments apart from climates, cropping systems, and management practices, it is important to obtain information from experiments in which all these parameters are considered to monitor nitrogen chemical transformations, not only in natural soils (not affected by anthropogenic activities) but also in soils for agricultural practices (Martínez-Espinosa et al., 2023).

PARTICIPATION OF MICROORGANISMS IN THE BIOGEOCHEMICAL CYCLE OF NITROGEN

Biogeochemical cycles are critical components of ecosystem dynamics and contribute to the degradation of refractory organic materials as well as the recycling of nutrients, toxic elements, carbon, nitrogen, sulfur, and phosphorus. Biogeochemical cycles can be either directly or indirectly altered by human activities. Direct effects include changes in the biological, chemical, and physical properties and processes of the environment. However, global warming and climate change may threaten the balance of biogeochemical cycles. Moreover, several studies have indicated that bacteria play an important role in biogeochemical cycles. For example, particle-associated bacteria seem to play a much more important role in biogeochemical cycles than free-living bacteria (Meng et al., 2022).
The biophilicity (average content of the element in living systems concerning its content in the earth's crust) of nitrogen is similar to the biophilicity of carbon. The index of biogenic enrichment of soil with nitrogen about the earth's crust is 1000, and that of plants concerning soil is 10000 (Kovda, 1985).
Summarizing the characteristics of the participation of microorganisms in the biogeochemical cycle of nitrogen, the following can be highlighted (Đukić et al., 2007):

- nitrogen cycling in nature is carried out by microorganisms, primarily prokaryotes;
- the high mobility of all natural nitrogen compounds and the high rate of metabolism are the main causes of the absence of its visible accumulations in nature (in the form of minerals and agronomic ores) and in the composition of reserve substances of living cells;

- nitrogen, the only one of all biophilic elements, is initially absent in the parent rocks and decomposes in the soil as a result of the activity of diazotrophic bacteria, which completes the formation of its most important property – fertility;
- only soils, due to their unique properties, can accumulate and retain nitrogen in the composition of humus, which is why they play the role of the main natural reservoir and source of accessible forms of nitrogen;
- to the greatest extent, nitrogen cycling is carried out in the soil, because (and as a consequence of that) in terms of total biomass, biological diversity, and productivity, land ecosystems exceed ocean ecosystems almost 1000 times;
- the biogeochemical cycle of nitrogen in the biosphere is closely connected with the biogeochemical cycle of carbon;
- the existing global soil degradation is manifested by disturbing the biogeochemical cycle of nitrogen – by changing the existing dynamic balance between its content in the soil and the atmosphere.

If nitrogen enters the biosphere during nitrogen fixation, it is lost during other processes of its biogeochemical cycle, primarily in the form of gases (Jemcev and Đukić, 2000; LaSarre et al., 2024). In the nitrogen cycle, two links (nitrification and denitrification) are responsible for the creation of gaseous compounds, as end products - nitrogen suboxide (N_2O) and molecular nitrogen (N_2).
Nitrogen suboxide (hemioxide, dinitrogen oxide, "happy gas") is one of the most important biogenic microgases of the Earth's atmosphere, which is responsible not only for the creation of the greenhouse effect but also for the breakdown of the planet's ozone layer (the so-called stratospheric outflow of N_2O occurs). Compared to other microgases of the greenhouse (CO_2 and CH_4), nitrogen suboxide is characterized by a significantly greater (approximately 150 times, than carbon dioxide, and 40 times, than methane) shielding ability, and significantly exceeds them in terms of residence time in the atmosphere (about 130 years), which predetermines the importance of studying the soil as its basic source in nature (Table 1).

Table 1. Some properties of the most important greenhouse gases (Bauwman, 1990)

Properties/gases	CO_2	CH_4	N_2O
Protective effect	1	39	150
Role of living beings, %	30	80	90
Residence time in the atmosphere, year	100	10	130

The total content of nitrous oxide in the atmosphere is estimated at 1500 Tr $N\text{-}NO_3^-$, and the concentration increases up to 320 ppb (Bowman, 1990). Annually, the concentration increases by 0.2-0.3%, and lately, the pace of this process has been increasing. Data on the content of nitrous oxide in frozen air bubbles in the glaciers of Antarctica and Greenland are usually used as a control initial concentration. According to those estimates, even 200 to 300 years ago it was at the level of 200-280 ppb, therefore, there is a shift in the dynamic balance of the content of nitrogen oxides in the atmosphere towards its constant increase, and the average annual intake of nitrogen oxides has increased by almost 50 %.
In addition to the formation of nitrogen suboxide in the biosphere, primarily in the soil, its absorption (reduction to N_2) is constantly taking place, and this poorly studied process can serve as another drain for N_2O (the so-called tropospheric drain).

Although the reduction of nitrous oxide can take place with the participation of four enzyme systems: Cu-dependent nitrous oxide reductase (rusticyanin), Mo-dependent nitrogenase, Ni–Fe-dependent dehydrogenase and Co-dependent synthase (Berks et al., 1995), in nature, this process is carried out, basically, with two groups of bacteria - denitrifiers and nitrogen fixers (Umarov, 1990; Cabello et al., 2004).
According to the results of research in the last two decades, there are significant differences between different types of soil in terms of the rate of formation and absorption of N_2O. Zonal soils are characterized by a balanced process of nitrogen suboxide formation and absorption, and the result is a relatively low emission of this gas. On the contrary, saline soils, as well as soils with a disturbed structure (arable eroded soils) are characterized by a low ability to absorb nitrogen-suboxide and therefore can have the property of its active "generator". These data indicate a special (possibly, leading) role of saline and eroded soils in the creation of nitrogen suboxide in global relations. Bearing in mind that more than 35% of land in the world is in a state of desertification and salinization, that it is subjected to aeolian and water erosion, and in the previous 50 years the speed of such degradation has increased by 30 times compared to the previous period (Jemcev and Đukić, 2000; Dobrovoljskij 2003; Đukić et al., 2018), the huge role of soil in changing the nitrogen-suboxide balance in the Earth's atmosphere is quite clear (Table 2).

Table 2. Area of degraded lands in the world (Dobrovoljskij, 2003)

The cause	Surface area	
	10^9 ha	%
Water erosion	1.09	55.6
Aeolian erosion	0.55	27.9
Chemical degradation (salination, pollution, etc.)	0.23	12.2

The nitrogen status of most terrestrial ecosystems has not yet been determined, because the extent of their participation in nitrogen transformation processes and its redistribution between the land and the atmosphere is unknown (Figure 2).

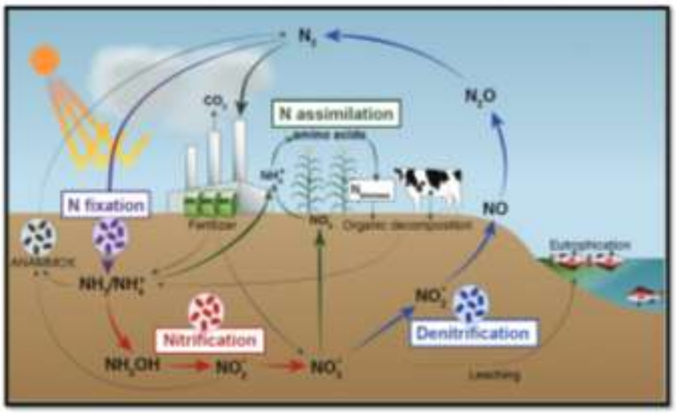

Figure 2. Nitrogen cycle (Martinz-Espinosa et al., 2023).

CONCLUSION

Looking at the dynamic balance of the earth's pedosphere and atmosphere, it can be concluded that the total nitrogen content in the earth's crust is about 0.03%, while the largest part of it is in the earth's atmosphere (about 4 x 10^{15}t) in the form of free (N_2) nitrogen, making up the main part (79%) air. Atmospheric nitrogen and its mineral forms (containing ions CN^-, NO_3^-, and NH_4^+) from the soil are concentrated in the composition of soil organic matter and the biomass of pro- and eukaryotes (some microorganisms, plants, and animals). Microorganisms play the greatest role in maintaining the dynamic balance of nitrogen in the earth's soil and atmosphere, including it in the biogeochemical cycle. Due to the disruption of that cycle, and thus the disruption of the dynamic balance between the nitrogen content in the soil and the atmosphere, global soil degradation occurs.

During the nitrogen fixation process, nitrogen reaches the biosphere, while during other processes (nitrification and denitrification) it is lost, conditionally, in the form of gases (N_2O) and molecular nitrogen (N_2). N_2 is responsible for the formation of the greenhouse effect and the depletion of the planet's ozone layer. It is significantly more aggressive than CO_2 and CH_4. The concentration of N_2O in the atmosphere is constantly increasing.

On the one hand, the process of creating N_2O is constantly taking place, and on the other hand, the process of its reduction to N_2, so this poorly studied process can serve as another drain of N_2O. Although N_2O reduction can be performed with the participation of four different enzyme systems, in nature this process is mainly performed by two groups of bacteria – nitrogen-fixing and denitrifying.

Different soils differ in the rate of formation and absorption of N_2O. While the ratio is balanced in zonal soils, it is not in saline and degraded soils.

The nitrogen status of most terrestrial ecosystems has not been determined, so the levels of their participation in nitrogen transformation processes and their redistribution between the land and the atmosphere are not known.

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