N_2O emission from mineral soils – Reviews

T. WŁODARCZYK, J. GLIŃSKI, U. KOTOWSKA

Institute of Agrophysics, Polish Academy of Sciences, Lublin, Poland

ABSTRACT: Increasing deposition of N-compounds cause environmental problems such as leaching of nitrate or enhanced emission of N_2O. Most N_2O is formed from dissimilatory reduction of nitrate in oxygen deficient environment, although it can also be produced from chemolitotrophic and heterotrophic nitrification and assimilatory reduction of nitrate in aerobic conditions. N_2O production is affected by many physical and biochemical factors, such as: the nature and amount of organic matter available as energy sources to the denitrifiers and heterotrophic nitrifiers, the aeration/moisture status of the soil, the soil nitrate concentration, soil pH, and the soil texture. These factors interact in a complicated manner with microorganisms on a microscale level in the soil, creating the large spatial and temporal variability in denitrification and and influenced on N_2O/N ratio. The N_2O emission increased linearly with NO_3^- reduction and curvilinearly with organic matter content, dehydrogenase activity and pH value and decreased curvilinearly with oxygen content.

Keywords: assimilatory and dissimilatory reduction of nitrate; nitrification and environmental conditions

Increasing deposition of N-compounds cause environmental problems such as leaching of nitrate or enhanced emission of N_2O, which adversely affects the chemistry of the atmosphere and contributes to global warming described by a number of authors (BRUMME, BEESE 1992; WILLIAMS et al. 1992).

Ambient concentration of N_2O has increased slowly from 288 ppb in 1750 until 1950 (before the industrial revolution) and then more rapidly to a current atmospheric 306 ppb described by DUXBERY et al. (1993). In general, most N_2O is formed from denitrification in oxygen deficient environment, although it can also be produced from chemolitotrophic nitrification in aerobic conditions described by a number of authors (MARTIKAINEN, DE BOER 1993; RICE, ROGERS 1993).

N_2O production is affected by many physical and biochemical factors, such as nitrate and O_2 concentration, organic matter content, temperature, soil pH and soil moisture content described by a number of authors (HORN et al. 1994; YU et al. 2001).

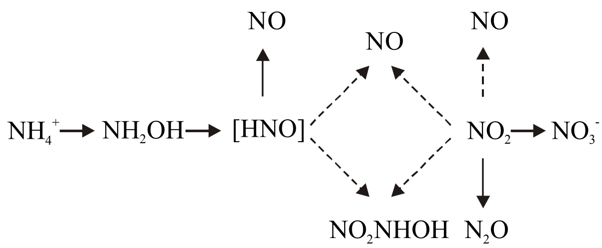
PROCESSES OF NITROUS OXIDE PRODUCTION

1.1. Nitrification

Although nitrification is understood to be an aerobic process there is strong evidence that it can also occur under anaerobic conditions. Nitrifying bacteria have been shown to produce NO and N_2O.

According to GROFFMAN (1991) two processes are responsible for N_2O formation from nitrification:

1. Ammonium oxidisers can use NO_2^- as an alternative electron acceptor when O_2 is limiting and produce N_2O. This process is called nitrifier denitrification.



2. Intermediates between NH_4^+ and NO_2^-, or NO_2^- itself, can chemically decompose to N_2O, especially under acidic conditions (a type of chemodenitrification).

The first type of reaction could be a process within nitrifiers to reduce accumulated nitrite levels which otherwise could cause intracellular toxicity described by BREMNER and BLACKMER (1981).

Nitrification is often considered to be the dominant source of N_2O in "aerobic" soils described by BREMNER and BLACKMER (1978).

Heterotrophic nitrification can occur in the presence of organisms, which oxidise ammonium in the presence of oxygen and an organic substrate and may simultaneously convert nitrite to gaseous products via denitrification. Therefore, heterotrophic nitrification might be linked to the nitrifier-denitrification described by a number of authors (ROBERTSON, KUENEN 1990, 1991).

1.2. Assimilatory reduction of nitrate

Nitrate constituates a real sink that sustains by assimilatory reduction to ammonia the life of plants and many microorganisms. In nitrate assimilation, the first step is the reduction to nitrite, which is accomplished by the enzyme nitrate reductase. Subsequently, the nitrite is reduced to hydroxylamine by the enzyme nitrite reductase to finally be reduced to ammonia described by PAYNE (1973). Some of studied nitrate reductases show the existence of an active form and an inactive form depends on the oxidoreduction conditions of the environment. In *Rhizobium japonicum,* for instance, the assimilatory enzyme is induced in aerobiosis and in the presence of nitrate; meanwhile in anaerobiosis, a dissimilatory nitrate reductase is induced described by DANIEL and GRAY (1976).

The net reaction is shown in following equation:

$$NO_3^- \rightarrow NO_2^- \rightarrow [H_2N_2O_2] \rightarrow [NH_2OH] \rightarrow NH_3$$
$$\downarrow$$
$$N_2O$$

where N_2O rather than N_2 may be produced as a by-product from the indicated intermediate (hyponitrite).

1.3. Dissimilatory reduction of nitrate

Dissimilatory reduction is the process through which some microorganisms use the energy generated by the electron transport from organic or inorganic source to nitrate or to a more reduced nitrogen oxide. This metabolic reduction uses cytochroms mostly as electron donors and occurs with a liberation of dinitrogen as the final product. However, some bacteria lack N_2O reductase, and so produce this gas as a terminal product, or lack nitrate reductase, yielding nitrite as an end product described by INGRAHAM (1981).

Non-denitrifying fungi and bacteria can produce N_2O during the **process of dissimilatory reduction of NO_3^- to NH_4^+.** This pathway, which is regulated by oxygen and unaffected by ammonium, can be a contributing source of N_2O from systems which suffer prolonged anaerobic periods (e.g. in sediments and rice paddy fields) described by a number of authors (MOSIER et al. 1983; TIEDJE 1988). The reaction shown is essentially the same as that which occurs during assimilatory NO_3^- reduction and involves the same precursor of N_2O, again probably hyponitrite described by a number of authors (FRENEY et al. 1979; MOSIER et al. 1983).

When the dissimilative reduction produces the gaseous dinitrogen or nitrous oxide compounds, the process is termed **denitrification**.

Biological denitrification is the last step in the N-cycle, where N is returned to the atmospheric pool of N_2. It is an anaerobic process. Biological denitrification is a respiratory process in which N-oxides (electron acceptors) are enzymatically reduced under anaerobic conditions to nitrous oxide and dinitrogen for ATP production by organisms that normally use O_2 for respiration. The process of denitrification (including rhizobial denitrification) can be presented as follows:

NO(+II)
⁞⁞

nitrate reductase — nitrite reductase — nitric oxide reductase — nitrous oxide reductase

$$NO_3(+V) \rightarrow NO_2(+III) \rightarrow [X] \longrightarrow N_2O(+I) \rightarrow N_2(0)$$

ENVIRONMENTAL FACTORS CONTROLLING DENITRIFICATION RATES

The primary factors that have been shown to control denitrification processes in the field are: (a) the nature and amount of organic matter available as energy sources to the denitrifiers, (b) the aeration/moisture status of the soil, (c) the soil nitrate concentration, (d) soil pH, (e) soil temperature and (f) the soil texture.

2.1. Organic matter availability

Denitrification is a respiratory process, which requires an easily oxidisable organic substrate. The presence of readily metabolised organic matter and the availability of water-soluble organic matter are closely correlated with the rate of biological denitrification and hence the potential production of N_2O from soil. There is observed very high correlation between N_2O emission and organic matter content described by WŁODARCZYK (2000) presented in Fig. 1.

Under field conditions the presence of crop residues increases denitrification especially under conditions of high soil moisture and adequate nitrate described by AULAKH et al. (1991).

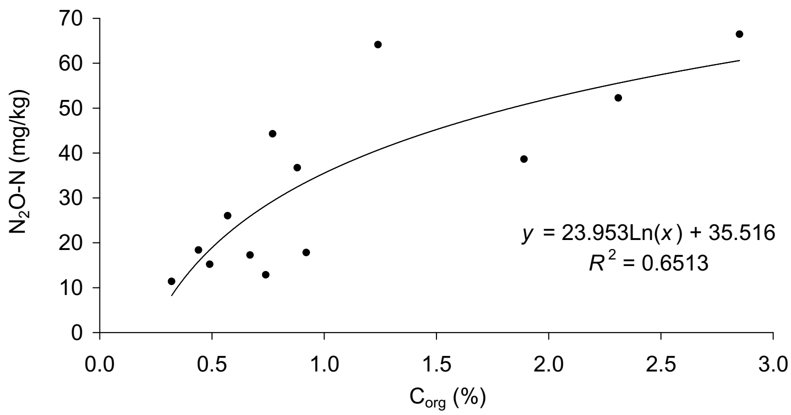


Fig. 1. Content of N_2O-N in the headspace as a function of organic matter content in Cambidols under flooding conditions – model experiment in closed vessels (WŁODARCZYK 2000)

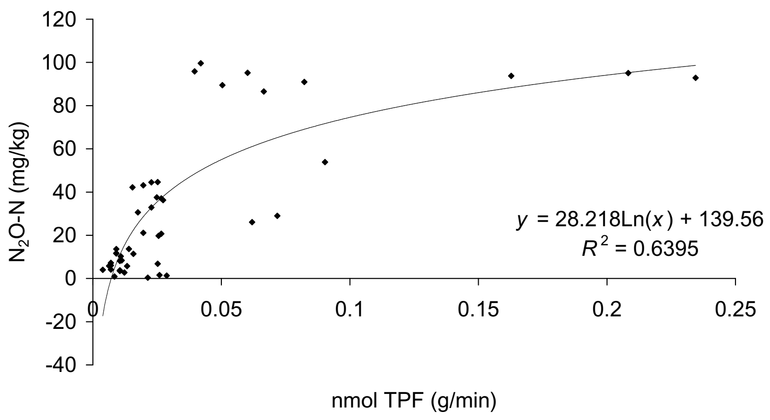


Fig. 2. Content of N_2O-N in the headspace as a function of soil dehydrogenase activity in Cambidols under flooding conditions – model experiment in closed vessels (WŁODARCZYK et al. 2001)

Organic soils generally show a high potential for denitrification and hence nitrous oxide production. Comparisons of organic to mineral soils confirmed higher N_2O fluxes from developed peat soils amended with synthetic urine compared to mineral soils treated in the same way described by CLOUGH (1994).

Dehydrogenases conduct a broad range of oxidative activities that are responsible for degradation, i.e., dehydrogenation, of organic matter. The amount of nitrous oxide formed due to denitrification showed high positive correlation with dehydrogenase activity described by WŁODARCZYK et al. (2001) presented in Fig. 2.

2.2. The aeration status of the soil

The oxygen status in soil, which is inversely proportional to the amount of moisture held there, appears in many studies to be one of the key factors influencing nitrous oxide production described by MCKENNEY et al. (2001). As the free oxygen in soil is depleted, a number of predictable changes in microbial activity occur. When the soil oxygen tension has been reduced to less than 1 percent (v/v), the microbial population appears to shift from being predominantly aerobic to anaerobic.

The inverse relationship between the rate of denitrification and O_2 concentration has been demonstrated in many studies described by a number of authors (BETLACH, TIEDJE 1981; BURTON, BEAUCHAMP 1985; WŁODARCZYK 2000). Fig. 3 presented N_2O emission as a function of O_2 content for the day of maximum emission described by WŁODARCZYK (2000).

Many studies showed that the reduction of N_2O to N_2 is more prone to inhibition by O_2 than reduction of NO_3^- to N_2O, thus the N_2O/N_2 ratio decreases with decreasing O_2 concentration. Thus, the presence of O_2 reduces the activity and delays the synthesis of nitrous oxide reductase relative to nitrate reductase and nitrite reductase, so that the N_2O/N_2 ratio increases with increasing O_2 concentration described by a number of authors (ERICH, BEKERIE 1984; TIEDJE 1988; BONIN et al. 1989; MASSCHELEYN et al. 1993).

2.3. Redox potential

Changes in soil redox potential are related to changes in oxygen levels. The occurrence of a variety of microbial processes is related to specific redox potential. The highest N_2O emission from Eutric Cambisol was observed at 200 mV described by WŁODARCZYK (2000) and presented in Fig. 4.

MASSCHELEYN et al. (1993) reported on N_2O emission from rice paddy soils at various redox potentials, ranging from +500 to –250 mV. Two maxima for N_2O evolution were found, at +400 mV when nitrification

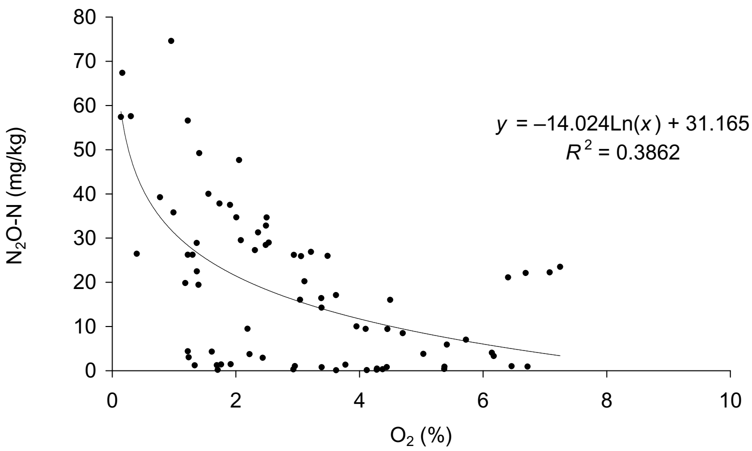


Fig. 3. Content of N_2O-N in the headspace as a function of O_2 content for the day of maximum emission in Cambidols under flooding conditions – model experiment in closed vessels (WŁODARCZYK 2000)

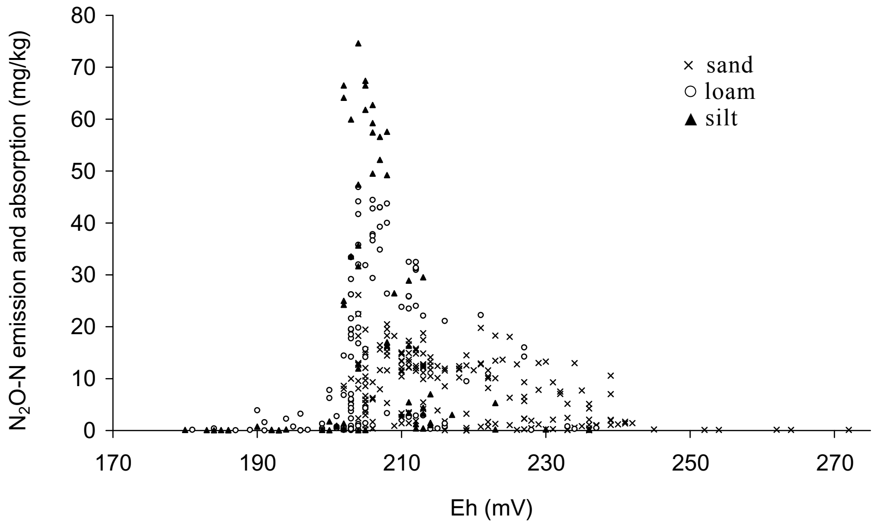


Fig. 4. Content of N_2O-N in the headspace as a function of Eh value for in Cambidols under flooding conditions – model experiment in closed vessels (WŁODARCZYK 2000)

was the source, and at 0 mV when N_2O was produced by denitrification.

KRALOVA et al. (1992) got similiar results in a study on denitrification in a soil suspension amended with NO_3^-. The maximum amount of N_2O was evolved at a redox value of 0 mV, while denitrification rates and N_2 emission continued to increase with lower redox levels.

2.4. The soil nitrate concentration

Because denitrification is an enzymatically catalysed process, the reaction rate of the process is anticipated to follow some form of Michaelis-Menten kinetics. That is, the rate of nitrate reduction to dinitrogen and nitrous oxide should increase until a saturating concentration is

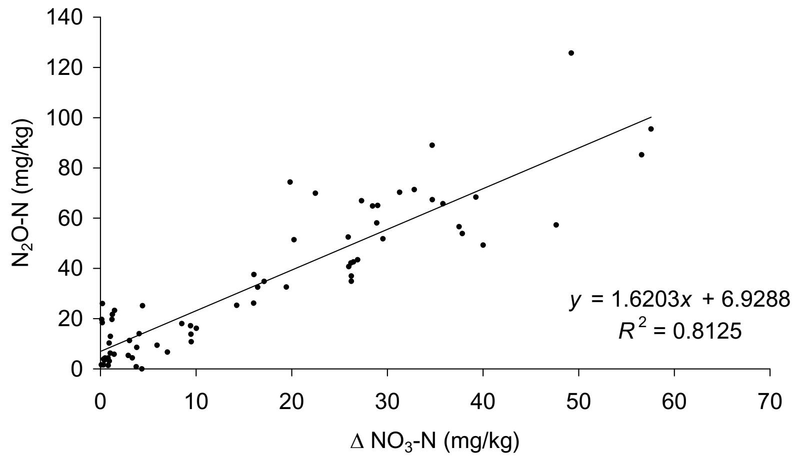


Fig. 5. Content of N_2O-N in the headspace as a function of NO_3^- reduction (Δ NO_3) in Cambidols under flooding conditions – model experiment in closed vessels (WŁODARCZYK 2000)

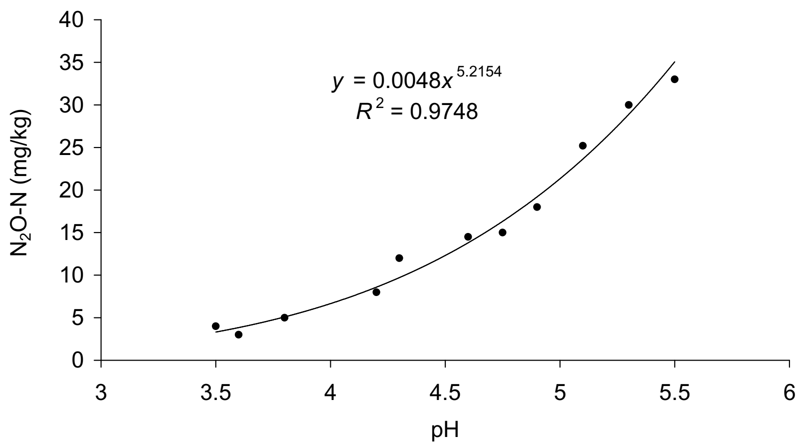


Fig. 6. Content of N_2O-N in the headspace as a function of pH for the day of maximum emission in Cambidols under flooding conditions – model experiment in closed vessels (WŁODARCZYK 2000)

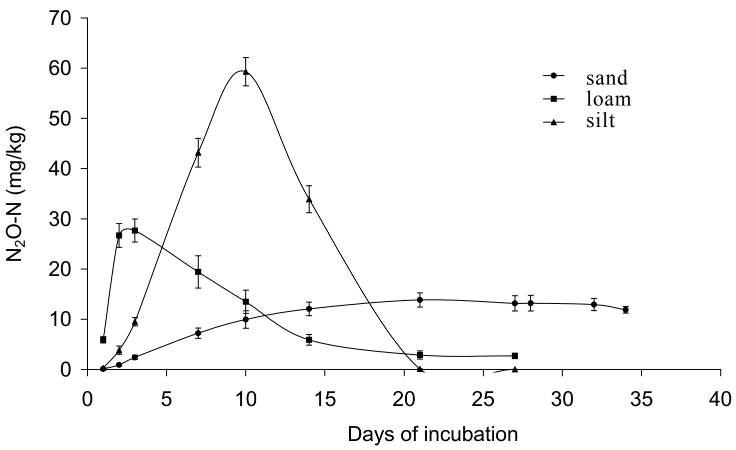


Fig. 7. The course of cumulative N_2O-N content in the headspace during incubation of Cambidols developed from sand, silt and loam under flooding conditions – model experiment in closed vessels (WŁODARCZYK 2000)

reached. Nitrate reduction in soil is generally found to be either a zero- or first order process.

Total denitrification fluxes (N_2O plus N_2) are directly proportional to soil NO_3^- concentrations when the other important component, a readily metabolisable organic substrate, is also present and non rate-limiting described by WŁODARCZYK (2000) and presented in Fig. 5. When a lack of metabolisable organic matter limits potential denitrification, N_2 plus N_2O fluxes do not increase with increasing NO_3^- concentration described by SAHRAWAT and KEENEY (1986).

It is well established that an increase in soil or sediment NO_3^- concentration leads to an increase in the N_2O/N_2 ratio in the product gases. This is attributed to the inhibition of N_2O reductase by NO_3 described by ZUMFT and KRONECK (1990).

2.5. Soil pH

Although denitrification occurs within the range of approximately 3.9–9.0, maximum nitrogen oxide occurs from 7.0–8.0.

Under conditions where NO_3^- concentrations do not limit potential denitrification, the overall rates of both denitrification and nitrification decline with decreasing pH from optima of about pH 7.5 described by WŁODARCZYK (2000) and presented in Fig. 6.

2.6. Soil texture

The soil texture and particle size distribution significantly affected the production of N_2O. Nitrous oxide production from heavier-textured soils exceeds that from coarse-textured soils up to 6-times. A course of the headspace N_2O content depending on the soil texture is presented (as the average values for the three soil groups developed rom sand, silt and loam) in Fig. 7. As it can be seen after the period of the initial increase of the N_2O content to the maximum value a subsequent decrease was observed, which could be attributed to its absorption by the soil. In the loamy soils the period of nitrous oxide production lasted only 3 days, in the silty soils – 10 days, while in the sandy soils – about 21 days described by WŁODARCZYK (2000).

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Emise N_2O z minerálních půd – Studie

ABSTRAKT: Zvýšené ukládání sloučenin dusíku působí ekologické problémy, jako je vyluhování nitrátů nebo zvyšování emisí N_2O. Většina N_2O vzniká odbouráváním nitrátů v prostředí chudém na kyslík, ačkoli také může vznikat chemolitotrofní a heterotrofní nitrifikací a asimilační redukcí nitrátů v aerobních podmínkách. Produkce N_2O je ovlivňována mnoha fyzikálními a biochemickými faktory, jako jsou: povaha a množství organické hmoty disponibilní jako zdroj energie pro denitrifikanty a heterotrofní nitrifikanty, stav provzdušnění a vlhkosti půdy, koncentrace půdních nitrátů, pH půdy a struktura půdy. Tyto faktory na sebe vzájemně působí složitým způsobem s mikroorganismy na mikroúrovni v půdě, vytvářejí velkou prostorovou a časovou variabilitu denitrifikace a ovlivňují poměr N_2O/N. Emise N_2O rostou lineárně s redukcí NO_3^-, křivočaře s obsahem organické hmoty, s aktivitou dehydrogenázy a s hodnotou pH a klesají křivočaře s obsahem kyslíku.

Klíčová slova: asimilační a disimilační redukce nitrátů; nitrifikace a ekologické podmínky

Corresponding author:

Dr. hab. TERESA WŁODARCZYK, Instytut Agrofizyki PAN, ul. Doświadczalna 4, P.O. Box 201, 20-290 Lublin 27, Polska
tel.: + 48 744 50 61, fax: + 48 744 50 67, e-mail: teresa@demeter.ipan.lublin.pl