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Nitrification Potential of Soils under Pollution of a Fertilizer Plant

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Nitrogen compounds found in soil in the form of mineral and organic bonds are available to microbes and plants as NO_3^- and NH_4^+, produced in consequence of ammonification, nitrification and N fixation. The laboratory experiment was conducted on samples of podzolic sandy soils. Soil samples were taken in the surroundings of a nitrogen fertilizer plant Achema, situated in the center of Lithuania. The objective of the study was to determine the effect of soil contamination on the nitrification process. Nitrification generally proceeded more rapidly in control soils than in soils under the Achema pollution. On the average, 0.004 μg NO_2-N was nitrified per g N mineralized per hour in the plots under the influence of the nitrogen fertilizer producing plant pollution. In comparison with nitrified N in reference soils the values were significantly higher – 0.253 ($p < 0.05$). Soils from background ecosystems had, on the average, 63 times higher nitrification rate than in polluted soils. The eutrophication of pine sandy soils stimulated biological processes and that was likely related to higher soil pH and initial NH_4^+.

Keywords: *nitrification, nitrogen deposition, pollution, soil.*

1. Introduction

Availability of nitrogen to plants is determined by the rate at which ammonium and nitrate are produced through the processes of nitrogen mineralization and nitrification in the soil. Potential net nitrification is often used as an indicator of nitrogen availability in ecosystems (Bai et al. 2010). Nitrogen is a limiting element in many natural ecosystems (Tamm 1991). Increase in nitrogen deposition in the parts of Europe and America has changed the nutrient balance, now nitrogen is frequently found in excess of other nutrients (Bobbink et al. 1998, Falkengren-Grerup et al. 1998). Accumulation of nitrogen through the deposition in forest soils may therefore cause considerable changes in the ecosystem structure and function (Falkengren-Grerup & Schöttelndreier 2004).

Nitrogen deposition often increases the nitrogen content of the litter. Litter decomposition and nitrogen mineralization rate is known to increase in soils affected by nitrogen deposition (Falkengren-Grerup et al. 1998). Other studies have shown a positive effect of nitrogen deposition on potential nitrification (McNulty et al. 1991). But in short-term experiments such effects are usually not found (Prescot 1995). It is possible that prolonged nitrogen deposition and acidification allows for a microbial community to adapt to more acid and nitrogen-rich conditions, a capacity that may not have had time to develop in the shorter experiments (Månsson & Falkengren-Grerup 2003).

The present study concerns the extent to which nitrogen deposition in the vicinity of Achema – one of the main pollution sources in Lithuania – in coniferous forests can account for variations in potential nitrification in the upper root horizon. The objective of this study was to determine the potential nitrification rate under the influence of nitrogen deposition in coniferous forests soil.

2. Material and methods

Achema is situated in the center of Lithuania (55°4′ N, 24°20′ E). It began operating since 1965. The main activity of the plant is the production of nitrogen fertilizers, ammonia, nitric acid, methanol, formalin, glues, carbonic acid and aluminium sulphate solution. Nitrogen fertilizer is produced by fixing nitrogen from the air. A large amount of energy is needed for this endothermic process and emission of ammonia, sulphur, nitrogen and carbon oxides comprise the main part of emission.

The entire area has been under air pollution stress since 1980 where the total annual deposition of sulphur at a distance of 1-2 km from the plant comprised about 50 kg and at a distance of 20-22 km - over 30 kg, currently it was reduced up to 15 and 9 kg ha^{-1}, respectively. Annual deposition of nitrogen decreased also and it constitutes 15-17 kg ha^{-1} 20-22 km from the plant (Armolaitis 1998). Air pollution is considered to be the main cause of a massive forest dieback that peaked in the beginning of the 1980s. The total quantity of pollutants decreased to only 5-7 thousands tones annually from 1980 in comparison with 40 thousand t in the beginning of the 1980s (Juknys et al. 2003).

The soil used in this experiment was chosen from the region in the study of coniferous forests. The sampled soil layer of these coniferous forest soils, being 10-15 cm soil below the litter layer, consisted of mineral soil. The soil was sampled in October, 2009.

The soil from this region was selected as it is under the continuous nitrogen deposition. Soil samples were taken from the plots at different distances (2-9 km) to the east from the nitrogen fertilizers producer plant Achema. Soil was collected in adjacent matured pine forest from Dubrava Experimental and Training Forest Enterprise. The enterprise is in the region with background deposition and was chosen as a control.

Potential nitrification was determined according to ISO/DIS 15685 (2001). Potential net nitrogen nitrification was measured in 6 hours laboratory incubation (25°C), the soil was kept at 60% water holding capacity (WHC) by regular additions of distilled water. Incubation experiments were set up using 10 g dry weight of soil in 150 ml bottles using three replicates of each sample. Initial (0 h) and after 2, 4 and 6 h levels of nitrite were measured spectrometrically at 540 nm.

For analyzing pH, 10 g fresh soil was extracted with using 50 ml H_2O, shaken for 2 hours and measured after sedimentation by means of a glass electrode.

Significant differences in the rates of nitrification were determined by analysis of variance (ANOVA) using Tukey‘s test.

3. Results and discussion

The potential nitrification rate is the nitrification rate that occurs under ideal conditions in which ample NH_4^+ is present, the soil is well aerated, and NH_4^+ diffusion is not restricted. In this assay, the nitrification rate is mainly controlled by the size of the nitrifier population. On the average, 0.004 µg NO_2-N was nitrified per g N mineralized per hour in the plots under the influence of the nitrogen fertilizer producing plant pollution. In comparison with nitrified N in reference soils the values were significantly higher – 0.253 ($p < 0.05$). Soils from background ecosystems had, on the average, 63 times higher nitrification rate than in polluted soils. Differences in the nitrification rate between control soils and soils under the Achema pollution could also be related to initial NH_4^+ and CO_3^- contents.

There was a clear spatial trend with a distance from the pollution source (Table 1). The highest observed potential nitrification rate was in the soil taken nearest the plant (1 km) – the value was about 2.2 times lower than in the control soil.

Table 1. Potential nitrification rate (PAO, µg NO_2^--N g^{-1}_{dw} h^{-1}) in coniferous forest soil under the influence of the nitrogen fertilizer producing plant pollution. Values are means (± SE) of 3 replicates

Soil	PAO (µg NO_2^--N g^{-1}_{dw} h^{-1})	pHH_2O
Control	0.253 ± 0.033 (100.0)	3.45
1.0	0.114 ± 0.044 (45.0)	2.01
3.1	0.007 ± 0.037 (2.8)	2.80
3.9	0.004 ± 0.017 (1.6)	2.51
5.7	0.001 ± 0.084 (0.4)	2.74
6.3	< 0[a]	4.57
8.1	< 0[a]	5.62
9.0	< 0[a]	4.90

[a] Negative nitrification rates of examined soils are denoted by < 0. Values in soil column represent the distance to the pollution source (1.0-9.0 km).

Very low nitrification rate was found in soils taken at a distance 3.1-5.7 km away from the plant and almost no nitrification was detected in soils taken at 6.3-9.0 km distance (Table 1).

Since soils differed in the pH values at different distances (Table 1), it was important to examine to what extent pH was related to the potential nitrification rate. In all examined soils as a whole, a slight negative correlation was found ($p > 0.05$). The nitrification rate was the highest at pH 3.45 (control soil) and was almost absent at pH > 4.90. A very low potential nitrification rate was in acid soil, there pH values were in the range of 2.01-2.80. Our results indicating almost complete nitrification at pH > 4.5 support earlier findings obtained in transect studies (e.g. Falkengren-Grerup et al. 1998). Taking into account that soil pH was the main variable which determined the nitrification process, the soil pH values measured in other studies also imply on the contrary. Our results are in accordance with those of the other studies (Persson, Wirén 1995) which determined that potential nitrification in the mineral soil was inhibited at pH 4.0-4.5.

Despite initially identical soils from the same forest site type, there was a clear pattern of change. K.Armolaitis et al. (1999) also measured pH_{KCl} at a number of study sites downwinds of the plant and found that pH was relatively low up to 1 km distance and showed a significant increase with the distance from Achema, being 3.3 at 0.2-0.5 km and 6.8 units at 10-14 km. Therefore the explanation that soil pH is the main determinant of the nitrification rate is inappropriate.

The sum loading of nitrogen up to 0.2-1.5 km from the source was 2-4 times greater than in non-industrial areas of Lithuania (Armolaitis et al. 1999). Thus, the increased nitrification rate near the pollution source indicated that the load of nitrogen mainly as ammonium was very high. In the vicinity of Achema species preferring less acid and nutrient-rich soil increased in frequency (Sujetovienė 2006). Less acid-tolerant species, which usually prefer nitrate or a mixture of ammonium and nitrate in hydroponic culture, should have a higher potential nitrification due to a low uptake of ammonium since ammonium is relatively immobile. Acid-tolerant species should have a high uptake of ammonium and thereby lower or equal potential nitrification (Olsson & Falkengren-Grerup 2000). Thus increased frequency of less acid tolerant and nitrophilous species and enhanced nitrification in the closest vicinity of Achema (1 km) could be due to increased nitrogen availability.

Previous studies (Sujetovienė 2006) showed that in the farthest from the pollution source the studied forest sites were rich in low fertility species (*Vaccinium vitis-idaea*, *Vaccinium myrtillus*, *Maianthemium bifolium*), consequently they could slow down the N cycle. This was in accordance with our results that the nitrification rate was very low under a lower pollution load away from the plant with low nitrogen availability. During succession the species from fertile habitats caused an increase in N mineralization, whereas species from much less fertile habitats had a relatively negative effect on the N release from the soil (van der Krift & Berendse 2001). Bengtson et al. (2006) demonstrated that spatial distribution of vegetation and gross N transformation rates were closely related within a distance of a few meters. That means that plant diversity and productivity had a major influence on the rates of N transformations.

The nitrogen mineralization rate is known to increase in soils affected by nitrogen deposition. In Swedish deciduous forests a difference in deposition of 10 kg N^{-1} y^{-1} seemed to cause up to an 80% higher soil nitrogen mineralization rate and a 90% higher nitrification rate (Falkengren-Grerup et al. 1998). To determine the influence of nitrogen deposition was difficult due to the long-term nitrogen deposition and the succession of coniferous forests in the vicinity of Achema that have caused soil acidification. More knowledge about the below-ground status is needed to obtain a deeper insight into the effects of factors on nitrogen mineralization.

4. Conclusions

Potential nitrification rate responded to deposited and accumulated N in coniferous forests in the vicinity of Achema. Low nitrification rates in soil farther from the nitrogen pollution source could be related to very acid conditions, low nitrogen availability. Nitrification in soils was enhanced when the nitrogen availability increased up to 4-5 km from the pollution source. Nitrification generally proceeded more rapidly in control soils than in soils under the pollution of the fertilizers producer plant. The eutrophication of pine sandy soils stimulated biological processes and that was likely related to higher soil pH and initial NH_4^+.

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Nitrifikacijos intensyvumo pokyčiai azotinių trąšų gamyklos poveikio zonos dirvožemyje

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Azoto junginiai, dirvožemyje esantys organinės ir mineralinės formos, yra prieinami mikroorganizmams ir augalams nitratų (NO_3^-) ir amonio (NH_4^+) formos, kurios susidaro dėl amonifikacijos, nitrifikacijos ir azoto fiksacijos procesų. Eksperimentas atliktas naudojant AB „Achema“ taršos poveikio aplinkoje paimtus smėlžemių dirvožemio bandinius. Tyrimų tikslas – nustatyti dirvožemio taršos poveikį nitrifikacijos proceso intensyvumui. Nitrifikacijos procesas buvo patikimai intensyvesnis kontroliniame dirvožemyje (0,253 μg NO_2^--N g^{-1} val^{-1}) nei „Achemos“ taršos poveikio aplinkos dirvožemyje (0,004 μg NO_2^--N g^{-1} val^{-1}, $p<0,05$). Tolstant nuo taršos šaltinio, nitrifikacijos procesas patikimai mažėjo ($p < 0,05$). Nitrifikacijos proceso kaitos tendencijos parodė, kad smėlžemių eutrofikacija intensyvios taršos azoto junginiais poveikio zonoje (1–5 km atstumu nuo azotinių trąšų gamyklos) skatino nitrifikacijos procesą. Tai gali būti susiję su šioje poveikio zonoje nustatytu didesniu dirvožemio pH ir pradiniu NH_4^+ kiekiu.