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NITROGEN ACCUMULATION IN SCOTS PINE (*Pinus sylvestris* L.) NEEDLES NEAR NITROGEN PLANTS "PUŁAWY"

AKUMULACJA AZOTU W IGŁACH SOSNY ZWYCZAJNEJ (*Pinus sylvestris* L.) W POBLIŻU ZAKŁADÓW AZOTOWYCH „PUŁAWY"

Abstract: The paper concerns nitrogen content in the needles of Scots pine (*Pinus sylvestris* L.) depending on the concentration of this element in the soil and on the distance from the Nitrogen Plant "Pulawy" S.A., which emits air nitrogen pollutions. The studies have shown a significant relationship between the concentrations of nitrate and total nitrogen in the organs of assimilation of scots pine and ammonium and nitrate nitrogen content in soil and the distance from the emission source – Nitrogen Plants "Pulawy".

Keywords: pine needles, nitrogen accumulation, nitrogen plant emissions

Nitrogen Plants "Pulawy" are located inside a forest about 4 km away to the north from the center city of Pulawy. In the first period of activity in the years 1966–1985 there has been intense environmental degradation and death of a lot of pine trees [1–4]. The main reason for such rapid disappearance of forests and expand the borders of individual degradation zones was saturation of the atmosphere and soil with nitrogen compounds [2, 5, 6]. The cause of secondary, but equally important was the poor quality of the soil environment and the resulting nutritional pine trees [7–9].

In January 1990, Nitrogen Plants, "Pulawy" were located by the Minister of Environmental Protection, Natural Resources and Forestry on the list of 80-plus companies in the country – onerous environmental degradation. Ecological friendly actions initiated in 1985 resulted in a significant reduction of pollutants emitted by Nitrogen Plants, "Pulawy", an average of about 65 %, while increasing production by about 50 %.

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The largest reduction was achieved with: ammonia 88 % and 85 % of the fertilizer dust, ash particles 80 %, 62 % nitrogen oxides, sulfur dioxide and 27 % [1, 3, 4]. As a result, there has been a significant reduction in emissions and the negative impact of the factory on the environment.

The aim of this study was to assess the nitrogen content in the needles of Scots pine (*Pinus sylvestris* L.) depending on the content of this component in the soil and on the distance from the Nitrogen Plant "Pulawy", which emits air pollution.

Methods

The study was conducted in the years 2007–2009, in an area located in the zone of influence of the Nitrogen Plant "Pulawy" S.A. Material for the study was taken from various distances from the source of pollution, the transect from the plant, according to the main direction of migration of contaminated air in this area: Control – the south-west (SW) at distance of 11.0 km and northeast (NE) at a distance of 160, 260, 400, 800, 1500, 1900, 2500 m from Nitrogen Plants. Soil and plant material (pine needles) for investigations were collected at three different times: at the beginning of the growing season – first decade of April, in the middle of growing season – first decade of July and the end of the vegetation season – first decade of October.

In the soil were determined: total nitrogen by the Kjeldahl method and mineral nitrogen – $N_{min.}$ ($N\text{-}NH_4^+$ and $N\text{-}NO_3^-$) extracted from soil with 1 % solution of K_2SO_4. The concentration of mineral nitrogen in the extract was determined by the colorimetric method: Ammonium $N\text{-}NH_4^+$ with Nessler reagent and nitrate nitrogen $N\text{-}NO_3^-$ with sodium salicylate.

Pine (*Pinus sylvestris* L.) was selected as an indicator plant to study due to needle existing on the plants for 3–4 years and their actively involving in the uptake of the pollutants from the atmosphere. In the laboratory of Regional Agricultural Chemical Station in Lublin in pine needles were determined: total nitrogen by distillation (KQ/PB-70) and $N\text{-}NO_3^-$ by flow colorimetric method. For the statistical evaluation of results used analysis of variance with Tukey confidence intervals and coefficients of linear correlation (Pearson). Correlation coefficients were calculated between the contents of nitrogen in the soil and the plant. Calculations have been made with program Statgraphics Centurion XV.

Results and discussion

Uptake of nitrogen by plant roots from the soil solution concerns mainly mineral fractions of the element ($N\text{-}NH_4^+$ and $N\text{-}NO_3^-$) known as active forms present in the soil solution, and to a lesser extent, organic-soluble fraction of nitrogen [5, 7, 10–12]. While ammonium is adsorbed by soil colloids, nitrates are present only in the soil solution and are more readily taken up by plants, but also easily leached into groundwater [13–15].

Average ammonium nitrogen content (Table 1) in the soil profile was significantly differentiated depending on the distance from the emission source. The highest

concentration of this form of nitrogen were stated in objects located close to Nitrogen Plants "Pulawy" (160 m) and (260 m).

Table 1

The content of $N\text{-}NH_4^+$ [mg · kg^{-1} d.m.] in the soil profile depending on the depth of soil profile and the distance from source of emission

Distance [m] (A)	Depth [cm] (B)						Means (A)
	0–5	5–20	20–40	40–60	60–80	80–100	
Control	1.1	0.6	0.2	0.2	0.08	1.3	0.6
160	7.0	1.5	1.0	0.4	0.6	1.5	2.0
260	6.1	1.3	0.7	0.5	0.8	0.5	1.7
400	2.2	1.0	1.3	0.5	0.6	0.7	1.1
800	2.1	1.2	1.1	0.6	0.3	0.5	1.0
1500	4.0	1.0	0.7	0.8	0.3	0.8	1.3
1900	2.6	1.2	0.6	0.2	0.4	0.8	1.0
2500	1.8	0.9	0.3	0.6	1.4	0.1	0.9
Means (B)	3.4	1.1	0.8	0.5	0.6	0.8	

$LSD_{0.05}$ for: A = 0.4; B = 0.3; A × B = 0.9.

Ammonium nitrogen content in soil profiles decreased with increasing distance, and the lowest average content was found in control. In the soil profile located close to the emitter average ammonia nitrogen content for all layers was 3.4 times higher than in the control and 2.3 times than the furthest point away from the factory.

The content of $N\text{-}NO_3^-$ in soils (Table 2) was characterized by high volatility and was respectively higher than ammonium content. Mean values for the nitrogen in the form of nitrate are varied in a broad range from 0.6 mg · kg^{-1} and 40.8 mg · kg^{-1}.

Table 2

The content [mg · kg^{-1} d.m.] of $N\text{-}NO_3^-$ in the soil profile depending on the depth of soil profile and distance from source of emission

Distance [m]	Depth [cm]						Means (A)
	0–5	5–20	20–40	40–60	60–80	80–100	
Control	3.4	1.0	0.9	0.6	1.4	1.3	1.4
160	26.8	13.9	13.2	8.9	8.1	2.3	12.2
260	40.8	17.2	13.0	5.4	6.7	7.1	15.1
400	9.2	1.6	3.5	1.1	2.3	2.7	3.4
800	19.0	4.5	3.2	3.1	1.4	1.6	5.5
1500	21.9	3.1	1.9	1.9	1.7	2.5	5.5
1900	24.3	5.0	3.8	2.7	3.0	3.2	7.0
2500	15.2	8.5	5.6	5.9	3.9	2.6	7.0
Means (B)	20.1	6.8	5.6	3.7	3.6	2.9	

$LSD_{0.05}$ for A = 2.4; B = 2.1; A × B = 5.9.

The study showed significant differences between the concentration of nitrate nitrogen, and the distance from the emission source. The highest content of $N\text{-}NO_3^-$ in the soil was found in places closest to the source of emission (160 m and 260 m), and the lowest in control. Also concentration of this form of nitrogen was higher in soil located at the furthest from the emitter than in the control.

Compared to other research objects relatively low levels of nitrates in the soil was found 400 m away from emitter (reclaimed sand dune), which must be combined with favorable conditions for leaching of nitrates and mobile wind erosion associated with terrain, which resulted in the loss of this component outside of the soil environment [3, 4, 16–18].

An important and very useful indicator of changes in the environment is the chemical composition of assimilatory organs of plants, which are more sensitive to environmental and atmospheric pollution in comparison with other components of the ecosystems [5–7, 19, 20]. The availability of different forms of nitrogen in soil and nitrogen metabolism play a key role in ionic balance of plants, which largely controls the uptake and distribution of the cations in the plant [10, 11, 13, 14]. The chemical composition of the plants is dependent on many factors, not only the content of different nutrients in the environment, but also on the mutual balance between them [10, 11, 14–16].

Scots pine (*Pinus sylvestris* L.) has been selected as an indicator of response on air pollution due to existing of the needles on the plants for 3–4 years and are actively involved in the uptake of the pollutants from soils and the atmosphere [5, 6, 19, 20].

Studies have shown significant differences in the nitrogen content of pine needles depending on the distance from the Nitrogen Plants "Pulawy" (Fig. 1). The content of this element in the organs of assimilation of scots pine decreased with increasing distance from emitter, excluding object of 400 m (reclaimed sand dune), which should be associated with poorer habitat. In addition, the soil of the test area was characterized by a lower content of nitrogen in the form of both ammonium and nitrate compared with other objects in the soil. The accumulation of nitrogen in plants was dependent on the concentration of mineral nitrogen in the soil. This confirms the positive correlation coefficient, which in the surface layer of soil (0–5 cm) was significant only for the NH_4^+ ($R = 0.52$), while in the deeper one (5–20 cm) for both forms of nitrogen: NH_4^+

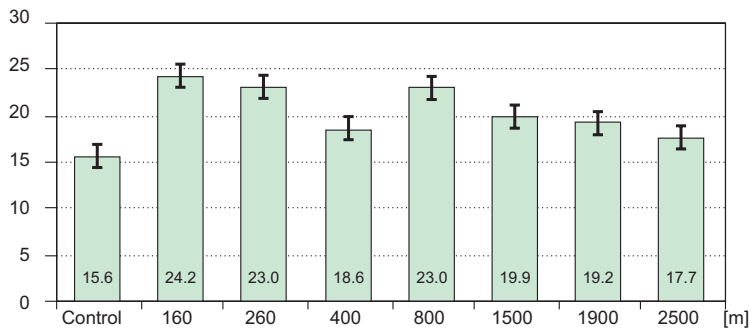

Fig. 1. The average content of total nitrogen [$g \cdot kg^{-1}$ d.m.] in pine needles (y axis), depending on the distance from the emitter (x axis)

(R = 0.40) and NO_3^- (R = 0.26). Many authors [1, 7, 9, 21] indicates that the pine tree in the wild in acidic forest soils is adapted for the use of ammonium ions. The uptake of nitrogen by scots pine is also beneficially affected due to the content of the nitrates in the soil and the balance between NH_4^+ and NO_3^- ions.

Pine trees located in the vicinity of the pollutants emitter characterized by a higher content of nitrogen in the needles, compared with control plants. The highest average content of total nitrogen in pine needles were found in the experimental area closest to Nitrogen Plants "Pulawy" of 160 m (24.2 g · kg^{-1} d.m.), and the lowest at the farthest distance from the emitter 2500 m (17.7 g · kg^{-1} d.m.). Comparative optimum content of nitrogen in the pine needles usually ranges, from 12.0 to 18.0 g · kg^{-1} d.m. [1, 8, 13]. Taking these values as a reference points it must be noted that the content of total nitrogen in the needles of trees from the area of impact of the Nitrogen Plant was higher than optimal [7] and varied in a particular objects from 24.2 to 17.7 g · kg^{-1} d.m.

Only research material from an object far away from the emission source was located in the upper limit of the optimum. Needles of control object corresponded to the optimal content for both ranges and average nitrogen content in the bioindicator research plant material was 15.6 g · kg^{-1} d.m. The nitrogen content in the pine needles in almost all objects in area of nitrogen fertilizers manufactory impact exceeded plant physiological maximum (18.0 g · kg^{-1} d.m.) and could be treated as evidence of negative impact of air pollution on trees.

Statistical analysis revealed significant differences of the nitrogen content in needles depending on the time vegetation season and material download years in the study (Fig. 2). The highest concentrations of this element in the organs of pine assimilation were stated in 2008 year, and the lowest in 2009. High nitrogen accumulation in plant tissues probably was related to the high amounts of rainfall this year and good soil moisture was beneficial for N uptake by plants. In the spring there were significant differences between the content of the element in all years, while in summer and autumn only between the years 2007 and 2008, and the year 2009. According to Parzych [21], small differences in the content of nitrogen and phosphorus in pine needles in the seasons between the years due to the variable availability of nutrients and

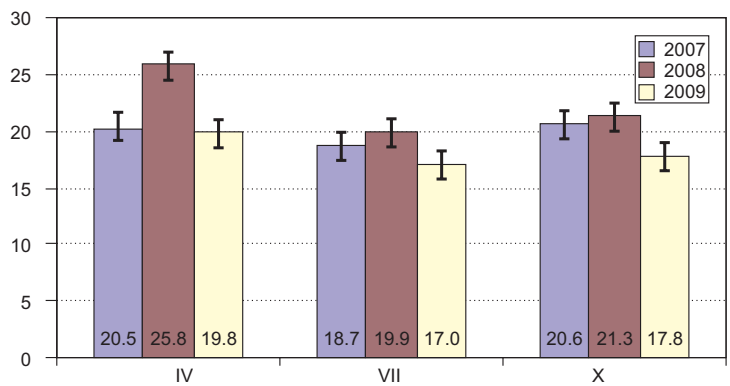

Fig. 2. The total nitrogen content in the needles of pine (y axis) [g · kg^{-1} d.m.] depending on the date and year (x axis)

water in the soil. The decrease of uptake both cations and anions by plants may also be affected the temperature drop. In general, the maximum concentration of nitrogen in the needles were in April (19.8–25.8 g · kg^{-1} d.m.), and the minimum in July (17.0–19.9 g · kg^{-1} d.m.). Low nitrogen content in the needles in July was probably associated with fast growth of biomass weight, and so-called "Dilution effect" and a small water capacity of the soils and drying effect in the summer. The content of N in the needles increased again in October can be associated with the extension of the growing season.

The nitrate content of pine needles (Table 3) showed significant differences depending on the distance from the Nitrogen Plant "Pulawy" and timing of sampling for analysis. The content of nitrate in assimilation organs of trees decreased with increasing distance from the emission source. In April the content of N-NO_3^- was significantly higher in needles of pine located closest to Nitrogen Plant, than in the control and plants from further away. In all the research objects the highest concentration of nitrates in pine needles was recorded in early stages, in the 1st decade of April. During the growing season – 1st decade of July and the end of the vegetation time in October nitrate concentration in pine needles decreased. Nitrate content in the organs of assimilation largely depends on the precipitation, which can wash out the NO_3^- anions from plant tissue [21].

Table 3

The content of nitrate [mg · kg^{-1} d.m.] in the pine needles, depending on the distance from the Nitrogen Plant "Pulawy" and time

Time (A)	Distance [m] (B)								Means (A)
	Control	160	260	400	800	1500	1900	2500	
IV	27.7	157.3	182.1	58.8	36.0	35.9	36.2	15.6	68.7
VII	5.5	133.7	29.6	24.9	14.2	11.5	10.6	4.7	29.3
X	4.8	114.9	14.6	6.4	12.6	14.5	18.8	23.0	26.8
Means (B)	12.7	135.3	75.4	30.0	20.9	20.6	21.9	14.4	

$LSD_{0.05}$: A – 12.4; B – 20.5; A × B – 48.1.

The high content of nitrates in the pine organs of assimilation from the places nearest to the source of emissions, is likely to be related to deposition of nitrogen impurities on needles surface and the possibility of NO_3^- intake through the stomata or outside stomata [1, 5, 20].

Conclusions

The study of the nitrogen content in the needles of Scots pine (*Pinus sylvestris* L.) depending on the content of this component in the soil and the distance from the Nitrogen Plant "Pulawy", which emits air pollution containing nitrogen compounds allowed to draw the following conclusions:

1. Average content of ammonium and nitrate nitrogen in the soil profile were significantly differentiated depending on the distance from the emission source. The

highest concentration of this forms of nitrogen were stated in objects located close to Nitrogen Plants "Pulawy".

2. Scots pine (*Pinus sylvestris* L.) has been given as a bioindicator of response on air pollution due to existing of the needles on the plants for 3–4 years and are actively involved in the uptake of the pollutants from soils and the atmosphere.

3. The concentrations of nitrate and total nitrogen in the organs of assimilation of scots pine decreased with increasing distance from emitter of gaseous and particulate pollutants.

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References

[1] Falkowska K, Filipek T, Badora A. Ecol Chem Eng A. 2012;19(10):1185-1191. DOI: 10.2428/ecea.2012.19(10)112.
[2] Falkowska K, Filipek T. Ochr Środow i Zasob Natural. 2009;40:23-28.
[3] Filipek T, Falkowska K. Nawozy Nawożenie – Fertilizers Fertilization. 2011;42:97-105.
[4] Filipek T, Falkowska K. Ochr Środow i Zasob Natural. 2007;31:115-120.
[5] Dmuchowski W, Bytnerowicz A. Environ Pollut. 1995;87:87-104.
[6] Lamppu J, Huttunen S. Environ Pollut. 2002;122:119-126.
[7] Bajorek-Zydroń K, Krzaklewski W, Pietrzykowski M. Górnictwo i Geoinżynieria. 2007;31(2):67-74.
[8] Migaszewski ZM. Wiad Bot. 1997;42(3/4):79-91.
[9] Stolarska M, Stolarski R, Harabin Z, Krzaklewski W, Pietrzykowski M. Roczn Glebozn. 2006;57(1/2):183-191.
[10] Hangs RD, Knight JD, Van Rees CJ. Can J Forest Res. 2003;33(1):156-163.
[11] Malagoli M, Dal Canal A, Quaggiotti S, Pegoraro P, Bottacin A. Plant Soil. 2000;221(1):1-3.
[12] Pietrzykowski M. Natural Sci. 2010;2(6):590-599.
[13] Millard P. Tree Physiol. 1994;14(7/9):1049-1054.
[14] Ohlund J, Nasholm T. Tree Physiol. 2004;24(12):1397-1402.
[15] Theodorou C, Bowen GD. Forest Ecology Managet. 1993;56(1/4):43-56.
[16] Kuznetsova T, Mandre M, Klõšeiko J, Pärn H. Environ Monit Assess. 2010;166:257-265.
[17] Migaszewski ZM, Gałuszka A, Świercz A, Kucharzyk J. Przegl Geolog. 2001;49(7):621-626.
[18] Pietrzykowski M, Woś B, Huma S. Ochr Środow i Zasob Natural. 2011;49:96-107.
[19] Malzahn E. Biuletyn Monitoringu Przyrody. 2002;1(3):19-31.
[20] Migaszewski ZM, Gałuszka A. Przegl Geolog. 1997;4:403-407.
[21] Parzych A. Ochr Środow i Zasob Natural. 2010;43:45-64.

AKUMULACJA AZOTU W IGŁACH SOSNY ZWYCZAJNEJ (*Pinus sylvestris* L.) W POBLIŻU ZAKŁADÓW AZOTOWYCH „PUŁAWY"

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Abstrakt: Praca dotyczy zawartości azotu w szpilkach sosny (*Pinus sylvestris* L.) w zależności od zawartości tego składnika w glebie i odległości od Zakładów Azotowych „Puławy", które emitują do atmosfery gazowe i pyłowe zanieczyszczenia azotowe. Badania wykazały istotne zależności pomiędzy zawartością azotu azotanowego(V) i ogólnego w organach asymilacyjnych sosny oraz zawartością azotu amonowego i azotanowego w glebie i odległością od źródła emisji z Zakładów Azotowych „Puławy".

Słowa kluczowe: igły sosny, akumulacja azotu, emisje zakładów azotowych