

**SEASONAL CHANGES OF N-NH₄⁺, N-NO₃⁻ AND P-PO₄³⁻
IN PROPER PODZOL SOIL IN THE SLOVINSKI NATIONAL PARK**

Agnieszka Parzych, Jan Trojanowski, Katarzyna Bigus

*Department of Environmental Chemistry,
Institute of Biology and Environmental Protection,
Pomeranian University in Słupsk,
ul. Arciszewskiego 22b, 76-200 Słupsk, Poland
e-mail: parzychal@op.pl*

Abstract

The paper presents seasonal changes in the concentrations of ammonia, nitrate and phosphate ions in podzolic soils under the *Vaccinio uliginosi*-*Betuletum pubescentis* and *Empetro nigri*-*Pinetum* plant communities. It results from the conducted investigations that the distribution and accumulation of mineral forms of nitrogen and phosphorus are considerably affected by atmospheric conditions such as temperature, humidity and precipitation. Analysed soils were characterised by a strongly acid reaction, which decreases with the depth of the soil profiles. A statistically significant correlation was found between the content of biogenic substances in soil and litterfall. The highest concentration of biogenic substances was observed in spring and summer months. Among analysed ions the ammonia form predominated, which mean content remained within the range from 0.12 to 6.69 mg/100 g d.m. Concentration of nitrates ranged from 0.05 to 0.13 mg/100 g d.m., while that of phosphates – from 0.04 to 3.09 mg/100 g d.m. The predominance of the ammonia and phosphate forms over the nitrate form in the organic horizons may result from their retention by the sorption complex. Nitrate ions exhibit greater mobility and are leached deeper into the analysed soil profiles.

Key words: forest, soil, nitrogen, phosphorus

INTRODUCTION

Abundance of nitrogen and phosphorus compounds in forest soils is a major factor determining their fertility. These elements are found primarily in organic forms (Bielek 1998), contained mainly in the soil humus. Organic nitrogen and phosphorus compounds are degraded (mineralization) and their final products are mineral forms of nitrogen and phosphorus, mainly NH₄⁺, NO₃⁻ and HPO₄²⁻, H₂PO₄⁻ (Brożek 1985).

Mineral compounds of nitrogen and phosphorus are formed in the degradation processes of organic matter and constitute an important link in the nutrient cycle in forest ecosystems (Czepińska-Kamińska et al. 1999). The process of their release in soil is closely dependent on forest site conditions, on soil moisture content and on continuously occurring nitrification and denitrification processes. Nitrates found in the soil solution are absorbed much more intensively by plants than the ammonia and phosphate forms, partly connected with the sorption complex of soil. The nitrate form does not undergo exchange sorption as NH_4^+ , HPO_4^{2-} and H_2PO_4^- ions do and it is much easier washed deeper into the profile. Changes in nitrogen and phosphorus compounds in the soil are very dynamic, exhibiting seasonal variation (Czepińska-Kamińska et al. 1999).

The aim of this study was to compare the dynamics of concentrations of mineral nitrogen and phosphorus forms in the genetic horizons of podzolic soils, formed on loose dune sands, covered by an old forest stand, taking into account the impact of weather conditions.

MATERIALS AND METHODS

Study site

The studies were carried out in two different forest ecosystems in the Slovinski National Park (SNP), (Fig. 1). The vegetation of sample plot I belonged to the group of *Vaccinio uliginosi-Betuletum pubescentis* (*Vu-Bp*) with 60-years-old pines (*Pinus sylvestris* L.) and 47-years-old mossy birches (*Betula pubescens*) and it covered proper podzol on mineral peat soil (Ol-Ofh-AEes-Bhfe-C-Otni). The vegetation of sample plot II covering proper podzol (Ol-Ofh-AEes-Bhfe-C) belonged to the group of *Empetro nigri-Pinetum* (*En-P*) with a 140-years-old pine stand (*Pinus sylvestris* L.). Analysed forest associations were found within the range of a high and variable groundwater level (Table 1), which influenced soil properties, particularly the dynamics of nitrogen and phosphorus compounds in selected forest ecosystems.

Table 1
Atmospheric conditions and average ground water levels in the years 2002-2005

		2002	2003	2004	2005	Mean 2002-2005
Precipitation [mm]		682(±39.5)	552(±28.9)	848(±36.4)	579(±21.5)	665(±32.8)
Air temperature [°C]		-	7.69(±7.4)	7.68(±6.7)	7.81(±6.6)	7.73(±6.7)
Air humidity [%]		-	83.5(±5.8)	84.5(±5.2)	83.6(±5.1)	83.9(±5.2)
Average under-ground water level [cm]	<i>Vu-Bp</i>	79.8(±18.0)	79.1(±17.2)	60.8(±24.9)	73.7(±18.7)	73.3(±20.1)
	<i>En-P</i>	93.8(±20.9)	93.6(±18.5)	79.3(±36.9)	94.3(±31.7)	90.2(±28.4)

(±) – standard deviation

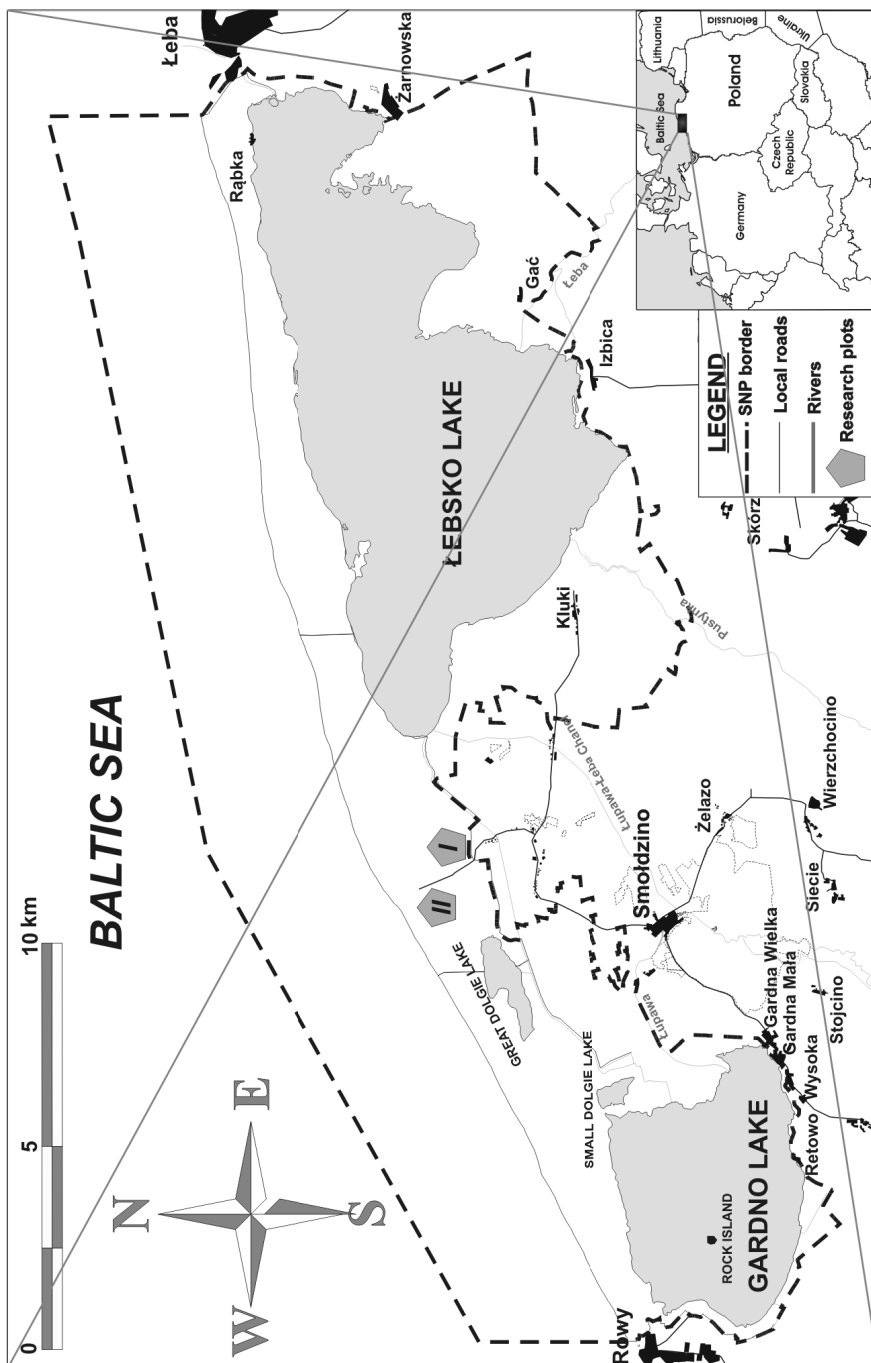


Fig. 1. Situation plan of the Slovinski National Park – locations of the study sites I – research plot I (*Yu-Bp*), II – research plot II (*En-P*)

Sample collection and analysis

Concentrations of nitrogen and phosphorus compounds in soil were determined on average every 5-7 weeks in the vegetation seasons of 2002-2005. Samples were collected several times during each vegetation season from March to November: 5 times in 2002, 6 times in 2004, 7 times in 2003 and 2005 each, a total of 25 times. Bulk soil samples were collected from around a dozen randomly selected locations in each forest community. In all samples the following parameters were determined: pH by potentiometry in an aqueous solution and in 0.1 n KCl solution, saturation with bases Vs (%), organic carbon according to Tiurin, total nitrogen (T-N) – according to Kjeldahl. Contents of NH_4^+ , NO_3^- and PO_4^{3-} ions were determined by spectrophotometry, using 1% K_2SO_4 as a displacement solution (Nowosielski 1974), with NH_4^+ determined using the Nessler reagent, NO_3^- – with sodium salicylate, PO_4^{3-} – using the molybdate method with ascorbic acid as a reducer. All analyses were performed in 3 replications. Mean values, as well standard deviations, coefficients of variation (CV) and Pearson's correlation coefficients (R) were calculated from the recorded data for $n=25$, at $p<0.05$. Dynamics of concentrations of nitrogen and phosphorus compounds in the organic, humus-eluvial horizons and in the enrichment horizons of *Vaccinio uliginosi-Betuletum pubescentis* and *Empetro nigri-Pinetum* were compared using a non-parametric U Mann-Whitney test.

RESULTS AND DISCUSSION

Fluctuations in the concentrations of mineral nitrogen and phosphorus forms in forest soils are affected by weather conditions. The sum at precipitation in the analysed years varied considerably. The biggest rainfall was recorded in 2004 (848 mm), while the lowest in 2003 (552 mm), (Table 1). Much smaller variation was found for mean annual temperatures and humidity, which in successive years of the experiment were on average $7.73(\pm 6.7)^\circ\text{C}$ and $83.90(\pm 5.2)\%$.

Analysed podzolic soils differed in the thickness of genetic horizons and chemical properties (Table 2). Soils in *Vu-Bp* and *En-P* had an acid and strongly acid reaction, which decreased with the depth of the soil profiles. Slightly greater acidity was found for organic horizons of pine coniferous forest (*En-P*).

The degree of saturation with bases (V) in the organic horizons of *Vaccinio uliginosi-Betuletum pubescentis* was on average by 25.9% higher than V in the organic horizons in *Empetro nigri-Pinetum* (Table 2). With an increase in the degree of humification of organic matter accumulated in the successive organic horizons (Ol, Ofh) the value of V decreases on both experimental plots. Such a dependence was found for the soil under *Vaccinio uliginosi-Betuletum pubescentis*, in which V decreased from 46.1% the ectohumus subhorizon (Ol) to 17.5 % in the humus-eluvial horizon (AEes), and next it gradually increased in the successive mineral horizons, reaching maximum saturation with bases in the organic soil horizon (Otni, 84.7%). A different situation was observed in the soil profile of *Empetro nigri-Pinetum*, maximum V was recorded in the AEes horizon (56.5%) and in horizon C₂ (51.3%). The highest concentrations of nitrogen and phosphorus compounds, and carbon were recorded in the

Table 2
Selected physical and chemical properties of soil (mean for growing season) under *Vu-Bp* and *En-P*

Soil horizon	Depth [cm]	Thickness of soil [cm]	pH _{H2O}	pH _{KCl}	Vs [%]	C [%]	N [%]	C:N
<i>Vaccinio uliginosi-Betuletum pubescentis</i>								
Ol	8-4	4	4.4(±0.5)	3.6(±0.4)	46.1	27.6	1.069(±0.159)	25.8
Ofh	4-0	4	4.6(±0.6)	3.8(±0.5)	39.0	26.6	1.011(±0.318)	26.3
AEes	0-13	13	4.8(±0.4)	4.0(±0.5)	17.5	0.95	0.064(±0.019)	14.8
Bhfe	13-41	28	5.1(±0.5)	4.4(±0.6)	45.4	0.24	0.021(±0.007)	11.4
C ₁	41-72	31	5.3(±0.5)	4.6(±0.6)	46.0	0.10	0.016(±0.006)	6.2
C ₂	72-104	32	5.3(±0.5)	4.6(±0.6)	53.8	0.06	0.026(±0.013)	2.3
Otni	104-150	38	5.3(±0.5)	4.6(±0.6)	84.7	36.6	2.848(±0.612)	12.8
<i>Empetro nigri-Pinetum</i>								
Ol	8-5	3	4.1(±0.4)	3.4(±0.5)	38.8	38.5	1.071(±0.132)	35.9
Ofh	5-0	5	4.1(±0.6)	3.3(±0.4)	29.0	39.6	1.078(±0.251)	36.7
AEes	0-18	18	4.8(±0.5)	4.0(±0.5)	56.5	0.63	0.028(±0.012)	22.5
Bhfe	18-48	30	5.1(±0.5)	4.3(±0.4)	44.4	0.23	0.015(±0.004)	15.3
C ₁	48-72	24	5.4(±0.5)	4.6(±0.3)	47.4	0.10	0.013(±0.004)	7.1
C ₂	72-102	30	5.7(±0.5)	4.8(±0.4)	51.3	0.06	0.012(±0.003)	5.0
C ₃	102-150	40	5.6(±0.6)	4.9(±0.4)	34.7	0.02	0.013(±0.003)	1.5

(±) – standard deviation

Ol – fresh forest litter subhorizon, Ofh – detritus subhorizon, AEes – albic horizon with humic horizon feature, Bhfe – spodic horizon, C – mother rock, Otni – histic horizon of buried peat soil (Konecka-Bentley et al. 1999)

Table 3
Average content of nitrogen and phosphorus [mg/100 g d.m.] in forest soil communities in 2002-2005, n = 25

Soil horizon	N-NH ₄		N-NO ₃		P-PO ₄	
	average	CV [%]	average	CV [%]	average	CV [%]
<i>Vaccinio uliginosi-Betuletum pubescentis</i>						
OI	6.69(±3.11)	46.6	0.13(±0.14)	104.4	3.09(±0.61)	19.7
Ofh	4.50(±2.06)	58.0	0.08(±0.08)	91.4	2.69(±0.73)	27.2
AEes	0.16(±0.09)	56.5	0.06(±0.05)	90.7	0.10(±0.11)	104.4
Bhfe	0.13(±0.09)	69.7	0.05(±0.02)	49.9	0.07(±0.09)	134.6
C ₁	0.13(±0.09)	70.1	0.05(±0.03)	55.4	0.06(±0.08)	134.7
C ₂	0.16(±0.11)	68.4	0.05(±0.02)	52.7	0.04(±0.02)	58.4
Otni	0.25(±0.13)	52.1	0.06(±0.04)	73.2	0.09(±0.08)	89.3
<i>Empetro nigri-Pinetum</i>						
OI	5.19(±2.14)	41.4	0.12(±0.07)	58.4	3.06(±1.19)	39.1
Ofh	3.99(±1.79)	44.7	0.09(±0.08)	82.3	2.59(±1.24)	47.8
AEes	0.18(±0.12)	68.2	0.05(±0.02)	46.6	0.07(±0.06)	87.4
Bhfe	0.13(±0.07)	49.7	0.04(±0.03)	67.7	0.06(±0.07)	119.5
C ₁	0.18(±0.15)	141.7	0.05(±0.03)	60.7	0.05(±0.06)	123.2
C ₂	0.12(±0.06)	44.9	0.05(±0.02)	52.5	0.05(±0.07)	149.6
C ₃	0.12(±0.04)	34.6	0.05(±0.03)	51.8	0.05(±0.05)	100.2

(±) – standard deviation, CV – coefficient of variation

fossil soil horizon (Otni) of *Vaccinio uliginosi-Betuletum pubescentis* and in the upper organic horizons of both analysed soil profiles (Table 2). Concentrations of the above mentioned elements decreased gradually with the depth into the profiles, with the smallest values being found in the parent rock horizon.

In all analysed vegetation seasons ammonia ions slightly predominated over other ions (Table 3). Their mean content in the organic horizons ranged from 4.5 to 6.6 mg/100 g d.m. in *Vu-Bp* and from 3.9 to 5.1 mg/100 g d.m. in *En-P*. The concentration of phosphate and nitrate ions was lower. In the organic horizons of the analysed forest communities it amounted from 2.5 to 3.0 mg/100 g d.m. and from 0.08 to 0.13 mg/100g d.m., respectively. Much smaller concentration of ammonia and phosphate ions was recorded for the mineral horizons of analysed soil profiles, which did not exceed 0.18 mg/100 g d.m. (N-NH₄) and 0.10 mg/100 g d.m. (P-PO₄). The fossil soil horizon (Otni) contained slightly higher concentrations of ammonia and phosphate ions than those in the mineral horizons.

Mean concentrations of N and P compounds in the soil exhibited slight variation in the vegetation seasons of 2002-2005, probably due to their high absorption by plants, despite different volumes of precipitation (Figs. 2, 3 and 4). Content of mineral nitrogen in soil, available to plants, affects the volume of primary production in forests (Prescott et al. 2000).

Dynamics of soluble ions is evident in the values of the coefficients of variation (CV), assuming as high values as over 100%. The highest variation in the organic horizons was found in the concentration of NO₃⁻ ions (104.4% in *Vu-Bp* and 82.3% in *En-P*). In the mineral horizons the highest value of the coefficient of variation was recorded for the concentration of the PO₄³⁻ ion, which in *Vu-Bp* was 134.7%, and in *En-P* 149.6%. In the first half of the vegetation period (March-August, Figs. 2-4) the concentration of NH₄⁺ ions was found to decrease in the organic horizons of *Vaccinio uliginosi-Betuletum pubescentis* by as much as 72% and by approx. 25% each for NO₃⁻ and PO₄³⁻ ions. In *Empetro nigri-Pinetum* the highest requirement of vegetation was observed for NH₄⁺ (63%) and PO₄³⁻ ions (58%). A bigger depletion of

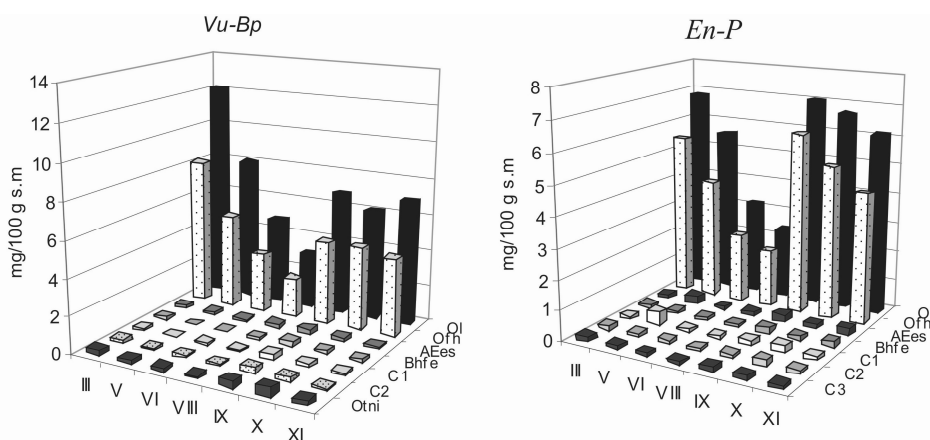


Fig. 2. Seasonal dynamics of N-NH₄ concentration in genetic horizons of the soil *Vu-Bp* and *En-P* (2002-2005)

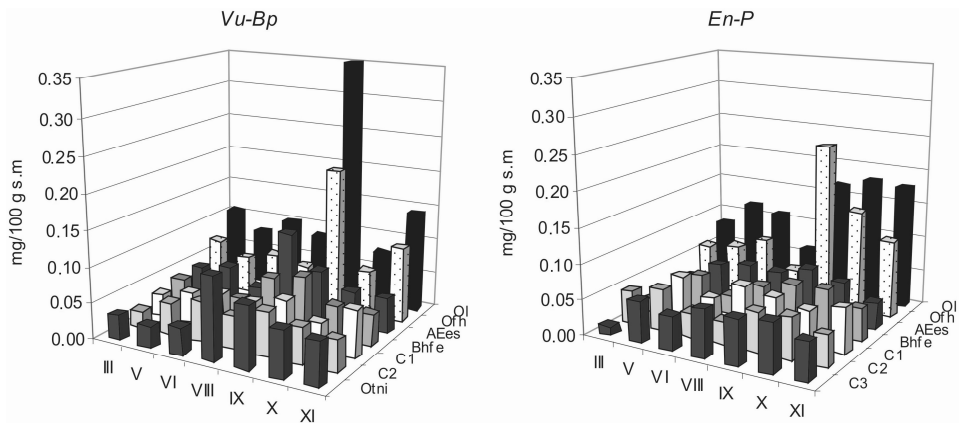


Fig. 3. Seasonal dynamics of N-NO₃ concentration in genetic horizons of the soil *Vu-Bp* and *En-P* (2002-2005)

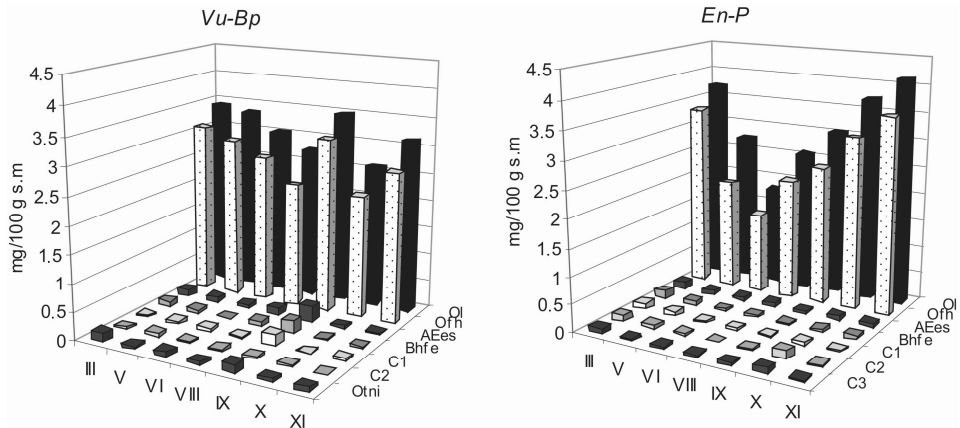


Fig. 4. Seasonal dynamics of P-PO₄ concentration in genetic horizons of the soil *Vu-Bp* and *En-P* (2002-2005)

ammonia ions from the soil in the pine-birch forest than from the pine coniferous forest resulted from the higher frequency and density of the vegetation cover (Parzych and Sobisz 2010). Much higher requirement of *Vaccinio uliginosi-Betuletum pubescentis* for ammonia ions was also evident in the much bigger depletion of ammonia ions from groundwaters in this ecosystem than from groundwaters of pine coniferous forest of *Empetro nigri-Pinetum* (Parzych and Trojanowski 2007). Among other things, strong positive correlations were observed between the content of PO₄³⁻ ions in the OI and Ofh horizons of podzolic soils in *En-P* and litterfall (needles, twigs, bark, seeds, ...), (Parzych 2008). Values of Spearman's coefficients of correlation were $R=0.67$ and $R=0.60$, respectively ($p<0.05$, $n=20$).

Dynamics of NH₄⁺, NO₃⁻ and PO₄³⁻ ions in the soil was a consequence of not only different atmospheric conditions, but resulted first of all from the variable requirement of the vegetation cover for biogens and it is to a bigger or smaller degree corre-

lated with litterfall. According to Czepińska-Kamińska et al. (1999), the dynamics of the amounts of mineral nitrogen compounds in the soil depends on the diversity and maturity of plant associations. Absorption of nutrients by root systems of plants and trees is indicated by the profile distribution of ammonia, nitrate and phosphate ions (Table 3), which concentrations decrease with depth (Kram et al. 1997). The biggest concentrations of analysed biogens were recorded in soil in the early spring (March-May), and in the autumn months (September-November), (Figs. 2, 3, 4). It is a consequence of the accumulation of nutrients as a result of continuously occurring mineralization processes and additionally supplied with precipitation and litterfall (Parzych and Trojanowski 2006).

The lowest concentration of the above mentioned ions was recorded in summer months, which was connected with a strong uptake of nitrogen and phosphorus compounds by the vegetation cover. Slightly different dynamics was only found for nitrates, particularly in *Vaccinio uliginosi-Betuletum pubescentis* (Fig. 2). This difference most probably results from the considerable dependence of N-NO₃ on the climatically determined microbial activity (Banaszuk 1997). Recorded results are confirmed by studies of Banaszuk (1997), in which two maximums of contents of ions easily leached from the organic horizons of forest soils, observed in the spring and early summer period and early autumn, separated by the period of a significant reduction in their concentrations.

The biggest amplitudes of changes in the concentrations of nitrogen and phosphorus compounds were observed in the organic horizons. In deeper lying genetic horizons depletion of ions was found in the spring and summer period, but due to the slight

Table 4
Ratios of soluble nitrogen and phosphorus ions in soils genetic level in 2002-2005

Forest association	Soil genetic horizon	$\frac{\text{N-NH}_4}{\text{N-NO}_3}$	$\frac{\text{N-NH}_4 + \text{N-NO}_3}{\text{P-PO}_4}$
<i>Vu-Bp</i>	Ol	50.60	2.20
	Ofh	52.85	1.69
	AEes	2.81	2.15
	Bhfe	2.69	2.56
	C ₁	2.59	3.13
	C ₂	3.56	5.96
	Otni	4.12	3.42
<i>En-P</i>	Ol	42.59	1.73
	Ofh	40.04	1.58
	AEes	3.73	3.51
	Bhfe	3.09	3.06
	C ₁	3.38	4.65
	C ₂	2.69	3.53
	C ₃	2.28	3.60

amounts of analysed ions in these horizons the dynamics of their changes was much smaller (Figs. 2-4).

In the analysed soils the ammonia form predominated markedly over the nitrate form (Table 4). The broadest range of the N-NH₄/N-NO₃ ratio was found in the organic horizons, being broader in the organic horizons of *Vaccinio uliginosi-Betuletum pubescentis* than those of *Empetro nigri-Pinetum*. Similar proportions between these nitrogen forms in soils were reported e.g. by Bielińska and Domżał 1998, Brożek 1985, Chichester and Hauser 1991, Curtin and Wen 1999, Kozanecka 1995, Kubik-Dobosz 1998, Murphy et al. 2000, Vestgarden and Kjønnaas 2003. The predominance of NH₄⁺ ions over NO₃⁻, amounting to several tens of times, in the organic horizons results from the retention of ammonia ions by the sorption complex. The absence of leaching of ammonia ions into the deeper soil horizons is evident in Fig. 2. Nitrate ions due to their high mobility are transported with precipitation into the soil profiles, which is shown in Fig. 3. Soluble nitrogen compounds are found to predominate over phosphate ions available to plants. Their ratio increases with the depth of both analysed soil profiles, reaching maximum values in the parent rock horizon (Table 4).

Statistical analysis (U Mann-Whitney test) did not show statistically significant differences in the dynamics of N-NH₄⁺, N-NO₃⁻ and P-PO₄³⁻, both in the organic and mineral horizons of the analysed forest ecosystems.

CONCLUDING REMARKS

1. Contents of NH₄⁺, NO₃⁻ and PO₄³⁻ ions in soils of the analysed forest complexes are dependent on atmospheric conditions.
2. The highest concentrations of ammonia, nitrate and phosphate ions were found in the spring and summer months.
3. In both analysed forest ecosystems the biggest concentrations of biogenic substances are recorded in the organic horizons.
4. In the analysed soils ammonia ions predominate markedly over nitrate ions.
5. Nitrate ions exhibit high mobility, thus their concentration is comparable in all analyzed genetic horizons of soil profiles under *Vaccinio uliginosi-Betuletum pubescentis* and *Empetro nigri-Pinetum*.
6. Strong positive correlations between contents of PO₄³⁻ ions in the O_l and O_{fh} horizons of podzolic soils in *En-P* and litterfall.
7. No statistically significant differences were found in the dynamics of N-NH₄⁺, N-NO₃⁻ and P-PO₄³⁻, in podzolic soils under *Vaccinio uliginosi-Betuletum pubescentis* and *Empetro nigri-Pinetum*.

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SEZONOWE ZMIANY N-NH₄⁺, N-NO₃ I P-PO₄³⁻ W GLEBACH BIELICOWYCH SŁOWIŃSKIEGO PARKU NARODOWEGO

Streszczenie

W pracy przedstawiono sezonowe zmiany koncentracji jonów amonowych, azotanowych i fosforanowych w glebach bielicowych pod zbiorowiskami *Vaccinio uliginosi-Betuletum pubescentis* i *Empetro nigri-Pinetum*. Z przeprowadzonych badań wynika, że na rozmieszczenie i kumulację mineralnych form azotu i fosforu duży wpływ wywierają warunki atmosferyczne, takie jak temperatura, wilgotność powietrza i opady atmosferyczne. Badane gleby charakteryzują się silnie kwaśnym odczynem, który maleje w głąb profili glebowych. Wykazano istotną statystycznie korelację między zawartością substancji biogenicznych w glebie a opadem materii organicznej. Największa koncentracja substancji biogenicznych występowała w miesiącach wiosennych i letnich. Wśród badanych jonów przeważała forma amonowa, której średnia zawartość utrzymywała się na poziomie od 0,12 do 6,69 mg/100 g s.m. Koncentracja azotanów utrzymywała się na poziomie 0,05-0,13 mg/100 g s.m., a fosforanów od 0,04 do 3,09 mg/100 g s.m. Przewaga formy amonowej i fosforanowej nad azotanową w poziomach organicznych może wynikać z zatrzymywania ich przez kompleks sorpcyjny. Jony azotanowe wykazują większą mobilność i są wmywane w głąb badanych profili glebowych.