ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 34 no. 2 pp. 13 - 24 2008

PL ISSN 0324-8461

FLUXES OF BIOGENIC SUBSTANCES IN PRECIPITATION AND THROUGHFALL IN WOODLAND ECOSYSTEMS OF SŁOWIŃSKI NATIONAL PARK

AGNIESZKA PARZYCH, ALEKSANDER ASTEL, JAN TROJANOWSKI

Pomeranian Academy, Institute of Biology and Environmental Protection, Environmental Chemistry Research Unit
ul. Arciszewskiego 22, 76-200 Słupsk, Poland

Keywords: Nitrogen, phosphorus, precipitation, throughfall, forest, Słowiński National Park.

Abstract: In the study the dynamics of concentration level changes was analyzed in the period between 2002 and 2005 concerning N-NH_4^+, N-NO_3^-, P-PO_4^{3-} and pH in bulk precipitation and throughfall in two different woodland ecosystems of Słowiński National Park. Both woodland ecosystems were influenced by the same weather conditions. On the basis of obtained results it was found that chemical variability of throughfall waters is mainly determined by both species composition and the kind of forest stand, as well as its trophic conditions. Comparing to bulk precipitation (collected at an open area) throughfall samples collected at the *Vaccinio uliginosi – Betuletum pubescentis* ecosystem were poor in N-NH_4^+ and P-PO_4^{3-}, enriched in N-NO_3^- and slightly more acidic (by 3.9%), while at the *Empetro nigri – Pinetum* ecosystem were poor in N-NH_4^+, enriched in P-PO_4^{3-} and N-NO_3^- and more acidic (by 4.4%).

INTRODUCTION

Gases and aerosols are taken over by precipitation from the atmosphere and successively deposited onto the soil surface after filtration through vegetation [24, 28, 37]. The contact with plants affects the composition of precipitation and its physical characteristics. Because of large contact area the modification processes are very dynamic, especially in the woodland ecosystems [3, 11, 19, 20, 38]. Rain precipitation is subjected to both physical and chemical transformation processes shifting trees crown area and drifting trees steams [5, 12, 21]. It is immobilized on the leafs, branches and steams and because of this the total amount of precipitation which arrives to the bottom of the forest is decreased by this quantity [4, 8, 35]. Chemical composition of throughfall waters depends on many factors, which the most significant are: atmosphere conditions, precipitation quality and quantity, amount of ions deposited on trees surface, kind of forest species [29, 34] and its age [22, 33]. The structure, thickness, forest floor, shape of the crowns, degree of needles and leafs density [23] as well as the forest health condition [30] play an important role in throughfall chemical profile modification. Throughfall waters are enriched by dry deposition washed off leafs' surface and also by ions leached out from plant tissue. Sulphates and nitrates, responsible for precipitation's acidification, are predominantly swilled off leafs' surface [16, 26]. The chemical composition of throughfall can be modified by individual compounds absorption in the crowns of the trees. Moreover, the throughfall water is more condensed comparing to bulk precipitation collected in an open field [13]. Seasonal concentration variability of some ion levels in throughfall proceeds from biological cycle in woodland ecosystem. Plants are able to replenish deficiency of chemical compounds by absorption processes which dominate in the case of habitat's low trophic condition [38, 39, 40]. Flowing with precipitation, NH_4^+ ions can be absorbed in the crown zone resulting in sodium and potassium equivalent leaching. Because of this, for plants, bulk precipitation becomes a valuable source of scarcely and biogenically important nitrogen. In previous investigations conducted in pine and spruce ecosystems in Łobez and Krzystkowice, Tyszka discovered the fact of immobilization of N-NH_4^+ and N-NO_3^- in the crowns of the trees [42]. Also in the forests of North America [9, 6, 27] and Denmark [11] the phenomenon of nitrogen absorption in the crowns of the trees was observed. In ecosystems with high trophic conditions leaching of some ions from plant tissues during shifting of precipitation through the crowns of the trees plays a dominant role. Some ions are more frequently leached in winter periods comparing to growth period. This phenomenon is connected with plants decreasing nutrition demand [11, 41]. Leaching of nitrogen-contained ions from plant tissue during precipitation's shifting through the crowns of the trees was identified by Stachurski [40], Blond [2] and Walna [44]. Similarly to nitrogen-contained ions very often hydrogen ions are leached resulting in soil acidification, especially in spruce stands [42, 45]. The highest concentration levels of analytes in the water stream shifting by the crown zone occur in the middle part of the crown of pines [42] and spruces [11]. The chemical composition of precipitation is strongly impacted also by atmospheric pollution originating not only from local sources but transferred with air masses universally [7, 8]. Atmospheric precipitation bringing certain amount of components to the biogeochemical circulation accelerates element migration in the catchment by releasing dry deposits from plants surfaces.

The aim of the study was to compare the contents of a nitrogen and phosphorus species in the bulk precipitation and throughfall in chosen woodland ecosystems of Słowiński National Park: *Vaccinio uliginosi – Betuletum pubescentis* and *Empetro nigri – Pinetum* in the period between 2002 and 2005.

MATERIALS AND METHODS

Sampling sites

The studies were carried out on the territory of two forest areas located within the boundaries of Słowiński National Park (SNP). This study area is located in northern Poland, in the region influenced by the Baltic Sea, with very little human activity and relatively free of industrial air pollution. Due to close vicinity of the Baltic Sea the climatic conditions are characterized by mild winters, not so warm summers and high air humidity. Average annual precipitation amount is attained up to 700 mm [29]. The examined plots are located 1.5 km from the coastline of the Baltic Sea, along the road from Smołdziński Las to Czołpino at a distance of 600 m from each other. The vegetation of the research plot I belongs to the group of *Vaccinio uliginosi – Betuletum pubescentis* and covers proper podsol on mineral peat soil. The vegetation of the research plot II covering proper podsol belongs to the group of *Empetro nigri – Pinetum* (dry form). Studied forest stands are diversified by species and age. Research plot I is overgrowed by loose birch-pine stand of 18–19 m height. The participation of a common 60 year-old pine (*Pinus sylvestris* L.) in the stand equals 25%, while 47 year-old mossy birch (*Betula pubescens*) – 75%. Research plot II is overgrown by uniform, 140 year-old pine stand (*Pinus sylvestris* L.) characterized by low (7 m), deformed crowns and leant trunks [31]. Location of the sampling sites and their surroundings with more detailed characteristics are presented in Figure 1.

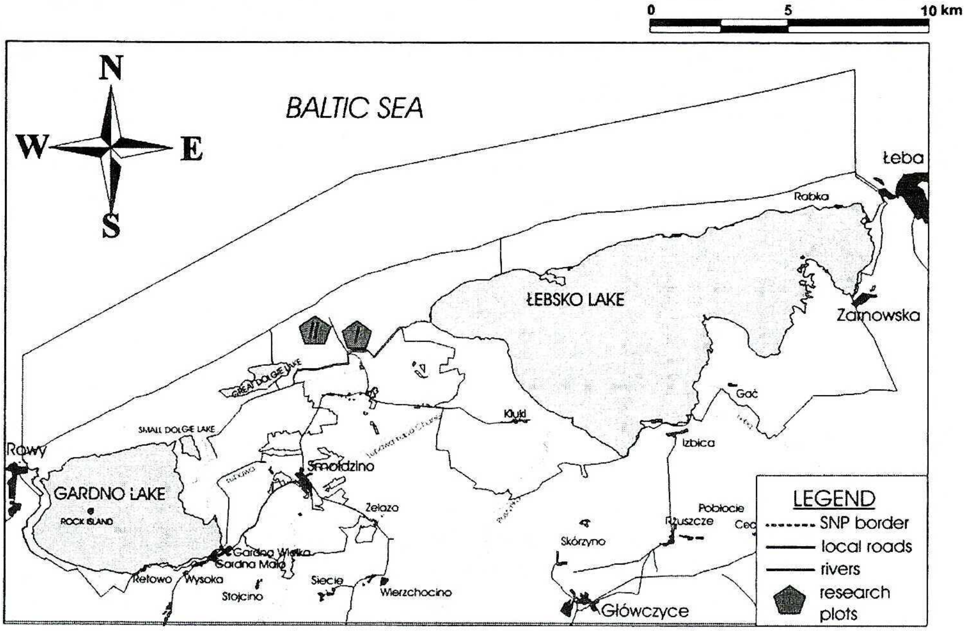

Fig. 1. Situation plan of Słowiński National Park – locations of the study sites

Sampling and analytical procedure

Bulk precipitation and throughfall waters were collected repeatedly during every growing season in the period between 2002 and 2005. Samples were collected in clean, 2 dm^3 polyethylene bottles approximately 1 m above ground level [23] (including ground cover level). Throughfall samples were collected directly below the crowns of trees, while bulk precipitation samples in the near vicinity of the investigated forest area in an open area. Because of close location of the investigated areas bulk precipitation samples were collected only in one location. A new type of rain trap with a double filter system was used [39] for sampling. In both cases once a sampler was set up, it remained at the sampling location for a period of one month. After delivering to the laboratory, the samples were filtered and the investigated analytes (with threefold repetition) were determined in water in agreement with standard methods, described in details before by Hermanowicz [12]. The methodology of determination is depicted in Table 1.

The limit of detection and quantification of the method depend on the purity of the reagents used. In the case of spectrophotometric determinations the calibration solutions were prepared basing on Merck standards with the nominal PO_4^{3-}, NO_3^- and NH_4^+ concentrations as follows: 1002 ± 5 mg/cm^3, 1004 ± 2 mg/cm^3 and 1001 ± 2 mg/cm^3. The limit of quantification for PO_4^{3-}, NO_3^- and NH_4^+ was 0.01 mg/cm^3, 0.02 mg/cm^3 and 0.005 mg/cm^3, respectively. QA/QC was carried out by analyzing field samples fortified with analytes of interest. In general, the determined concentration fell within 15–20% of the true value, which is comparable to the results presented before by Polkowska *et al.* [32]. The repeatability of methodology calculated according to the formulas presented by Konieczka *et al.* [17] reached $RSD(PO_4^{3-})$ = 1.4%, $RSD(NO_3^-)$ = 1.6%, $RSD(NH_4^+)$ = 1.4%, and $RSD(N_{total})$ = 2.1%.

Table 1. Methodology of determination according to Hermanowicz [12]

Determination		Methodology of determination
Total nitrogen	T-N	Kiejdahel's method[1], after mineralization in the mixture of H_2SO_4 and H_2O_2
Ammonia nitrogen	$N\text{-}NH_4^+$	spectrophotometricaly[2] (with Nessler's reagent)
Nitrate nitrogen	$N\text{-}NO_3^-$	spectrophotometricaly[2] (with sodium salicylate)
Phosphate phosphorus	$P\text{-}PO_4^{3-}$	spectrophotometricaly[2] (molybdate method, with ascorbic acid as reducing agent)
Reaction	pH	potentiometricaly[3]

[1] Parnas-Wagner apparatus,
[2] Shimadzu spectrophotometer (UV-VIS 1202),
[3] glass electrode Eurosensor ESAgP-341W No 38.

RESULTS AND DISCUSSION

The total amount of precipitation in respective years in the period between 2002 and 2005 showed substantial variation. Average annual amount of precipitation was equal to 665 mm, which is slightly lower than an average for a multi-year period (1951–1970) average – 705 mm [36]. The highest annual amount of precipitation occurred in 2004 (848 mm), while the lowest in 2003 (552 mm). The variability of chosen meteorological parameters in the period between 2002 and 2005 is summarized in Table 2. The total amount of precipitation showed substantial variation also in monthly cycles. Generally, the highest amount of precipitation was noticed in October (95.3 mm) and July (85.1 mm), while the lowest during spring months: in April (25.9 mm) and in March (34.9 mm). The average values of air temperature kept on a constant level, reaching value 7.7°C in the period between 2003–2004 and 7.8°C in 2005 (Tab. 2). Annual average of relative air humidity in successive years slightly fluctuated, but in general the average was 84%. Variability of chosen meteorological parameters was correlated with concentration levels of nitrogen and phosphorus compounds in bulk precipitation. Highly significant, negative correlation occurred between temperature and $P\text{-}PO_4^{3-}$ concentration ($R = -0.47$, $p < 0.05$, $n = 50$) and also between relative air humidity and $N\text{-}NH_4^+$ concentration ($R = -0.43$, $p < 0.05$, $n = 50$). Positive correlation was found between concentration of $P\text{-}PO_4^{3-}$ and respectively, relative air humidity ($R = 0.34$, $p < 0.05$, $n = 50$) and amount of rain precipitation ($R = 0.30$, $p < 0.05$, $n = 50$).

Table 2. Atmospheric conditions in the period between 2002 and 2005

	2002	2003	2004	2005	Mean
Rainfall [mm]	682	552	848	579	665
Air temperature [°C]	–	7.69	7.68	7.81	7.73
Air humidity [%]	–	83.5	84.5	83.6	83.9

Similar relations were noticed by Żelazny *et al.* in previous research work focused on rain precipitation chemistry conducted in the area of Wiśnickie foot-hills [46]. In investigated woodland ecosystem, both bulk precipitations collected in an open area and throughfall waters, demonstrated changeable reaction. The lowest pH value was noticed for bulk precipitation in 2002 (6.6), while the highest in 2004 (7.0). In Table 3 mean annual pH values both for bulk precipitation and throughfall in the period between 2002 and 2005 are presented. In agreement with Jansen categorization for precipitation waters [15], mean pH is above regular (pH > 6.5). Such low acidity can be related to SNP location, which is in the coastal area, along one of the most important annual paths of birds' migration, taking place both in the spring and autumn periods [1]. Birds' droppings can have a serious impact on the decreasing precipitation waters acidity. Throughfall waters passing through the crown area showed a slightly higher acidity comparing to bulk precipitation collected in an open area in all research years. An acidity increased by 3.9% (2002–2005) in the *Vaccinio uliginosi – Betuletum pubescentis* and by 4.4% in *Empetro nigri – Pinetum,* respectively (Tab. 3). Throughfall waters acidification can be caused by washing SO_4^{2-} and NO_3^- as well as accompanied hydrogens absorbed on the plants surface as a result of dry and wet deposition [26]. An intensity of such process can be related to differences both between the structure and the species composition of forest stand [10]. The *Vaccinio uliginosi – Betuletum pubescentis* stand constitutes 520 trees, with average distance between them 3.10 m, while in *Empetro nigri – Pinetum* 715 trees were stated, with average distance equal to 2.64 m. Higher density of pine stand can cause higher acidification of throughfall waters. An acidification of throughfall waters related to bulk precipitation was discovered also in previous field-works conducted in the Pomeranian Voivodship area [44], Karkonosze Forest [45], the Świętokrzyskie Mts. [16] and also in Łobez and Krzystkowice [42]. The total amount of nitrogen (T-N) in bulk precipitation is limited simultaneously by the amount of nitrates and ammonium ions (Fig. 2).

Table 3. Mean annual pH values in bulk precipitation and throughfall in the period 2002–2005

	2002	2003	2004	2005	Mean 2002–2005
Bulk precipitation	6.64	6.73	7.05	6.87	6.82
Throughfall I	6.50	6.57	6.65	6.52	6.56
Throughfall II	6.31	6.45	6.69	6.66	6.53

Throughfall I – throughfall of the research plot I (*Vaccinio uliginosi – Betuletum pubescentis),*
Throughfall II – throughfall of the research plot II (*Empetro nigri – Pinetum).*

Ammonium ions are immobilized in the trees crowns area of *Empetro nigri – Pinetum* stand in spring to early summer period. From August till October leaching is a dominating process. Considerably higher demand for $N\text{-}NH_4^+$ in the March – September period is shown by the trees of *Vaccinio uliginosi – Betuletum pubescentis* (*Pinus sylvestris* and *Betula pubescens*) stand as compared to *Empetro nigri – Pinetum*. For *Vaccinio uliginosi – Betuletum pubescentis* stand leaching processes were observed only in October, which is related to decreasing demand for biogens (Fig. 3). An average concentration of $N\text{-}NH_4^+$ in bulk precipitation collected in an open area was equal to 1.25 mg/cm^3 and varied in the range of 0.55–2.31 mg/cm^3. The highest concentration of $N\text{-}NH_4^+$ was determined in March (2.22 mg/cm^3) and in summer months (average 1.43 mg/cm^3), while the lowest in October (0.71 mg/cm^3). The variability observed for nitrates differed from those mentioned above. For trophically poor *Empetro nigri – Pinetum* stand the absorption process occurs in the midpoint of a growing season (March-June). From August till

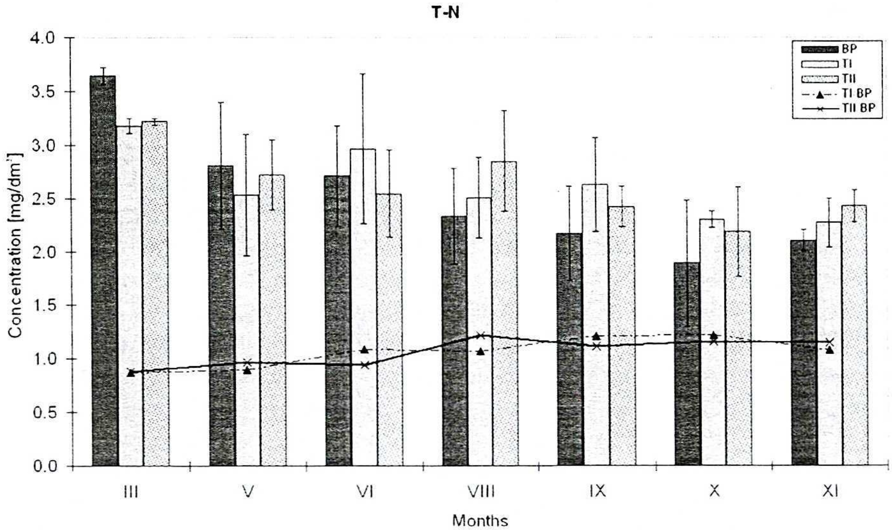

Fig. 2. Concentration of T-N in bulk precipitation (BP) and throughfall waters (I and II, respectively as TI and TII) as well as the ratio value between throughfall and BP (box: mean value, whiskers: standard deviation)

November the predominant processes are related to leaching from the zone of crowns. In the case of slightly more trophic abundant *Vaccinio uliginosi – Betuletum pubescentis* stand the nitrogen absorption process occurs only in May. In the remaining period of investigated growing seasons the leaching of nitrates from plant's issue were dominating (Fig. 4). An average concentration of N-NO_3^- in bulk precipitation was 1.21 mg/cm^3 and varied in the range between 0.59 and 1.77 mg/cm^3. A phenomenon of N-NH_4^+ retention

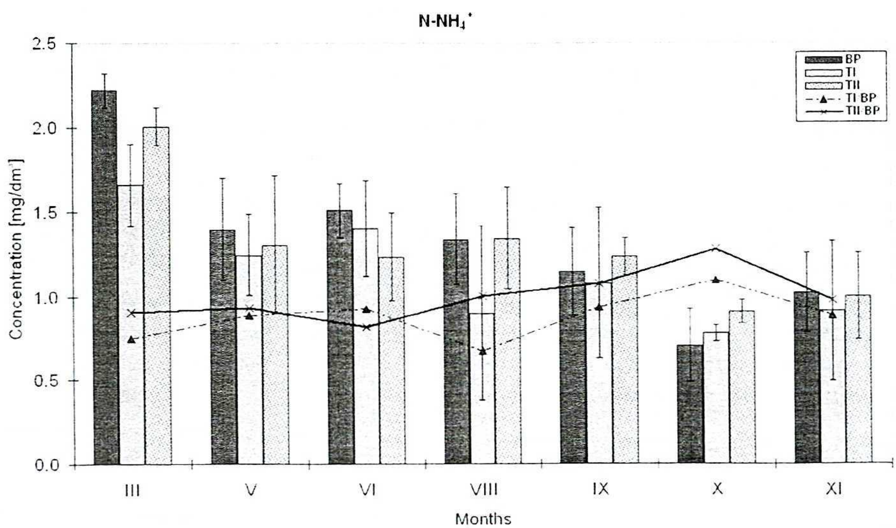

Fig. 3. Concentration of T-NH_4^+ in bulk precipitation (BP) and throughfall waters (I and II, respectively as TI and TII) as well as the ratio value between throughfall and BP (box: mean value, whiskers: standard deviation)

in the zone of pine crowns and leaching of N-NO_3^- in the growing period was observed also in field-works conducted in the Augustowski Forest area [14]. Retention of nitrogen-including ions in the crown area was observed also in the forest of North America [6, 27] and in a pine stand in Denmark [11]. The retention of phosphates in *Vaccinio uliginosi – Betuletum pubescentis* stand in the period between March and June and in November was observed. During summer time P-PO_4^{3-} leaching is a dominating process. Phosphates

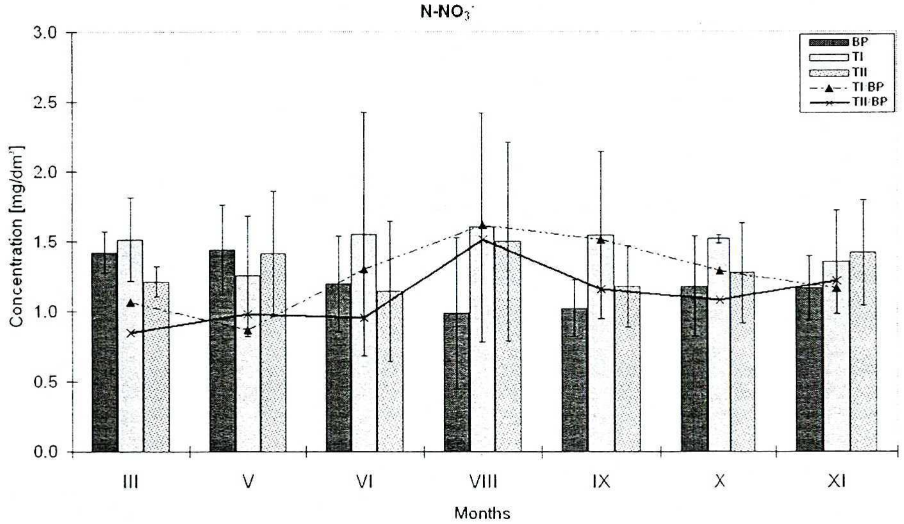

Fig. 4. Concentration of T-NO_3^- in bulk precipitation (BP) and throughfall waters (I and II, respectively as TI and TII) as well as the ratio value between throughfall and BP (box: mean value, whiskers: standard deviation)

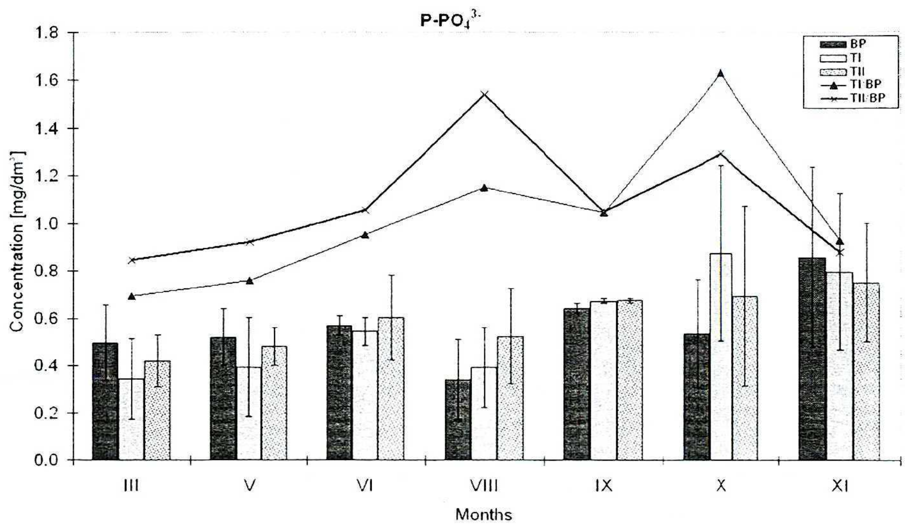

Fig. 5. Concentration of T-PO_4^{3-} in bulk precipitation (BP) and throughfall waters (I and II, respectively as TI and TII) as well as the ratio value between throughfall and BP (box: mean value, whiskers: standard deviation)

are absorbed by the *Empetro nigri – Pinetum* stand in limited amounts only in March, May and November. During remaining time of growing periods leaching processes are prevailing (Fig. 5). An average concentration of P-PO_4^{3-} was 0.58 mg/cm^3 and varied in the range between 0.17 and 1.31 mg/cm^3. Special attention should be paid to increased amount of nitrogen-including compounds in bulk precipitation in the first midpoint of the growing season (Figs 2, 3 and 4) while P-PO_4^{3-} in the second midpoint of the growing season (Fig. 5).

Similar dynamics of biogens in bulk precipitation was observed in southern Poland at Wiśnickie foot-hills [46]. In bulk precipitation ammonium ions predominated quantitatively over nitrates, while nitrates over phosphates: $NH_4^+ > NO_3^- > PO_4^{3-}$ (Tab. 4). The same relationship between contents of the above-mentioned ions was observed in bulk precipitation collected in the area of the Świętokrzyskie Mts. [18].

Table 4. Statistical descriptors of nitrogen and phosphorus content and pH of precipitation and throughfall in the *Vaccinio uliginosi – Betuletum pubescentis* and the *Empetro nigri – Pinetum* in the period 2002–2005

	Mean	Minimum	Maximum	Median	Standard deviation	Variability factor [%]
T-N [mg/cm^3]	2.54 [a]	1.47 [a]	3.72 [a]	2.34 [a]	0.64 [a]	25.18 [a]
	2.61 [b]	1.92 [b]	3.83 [b]	2.55 [b]	0.49 [b]	18.79 [b]
	2.63 [c]	1.88 [c]	3.42 [c]	2.55 [c]	0.40 [c]	32.01 [c]
N-NH_4^+ [mg/cm^3]	1.35 [a]	0.55 [a]	2.31 [a]	1.30 [a]	0.46 [a]	34.15 [a]
	1.14 [b]	0.42 [b]	1.81 [b]	1.24 [b]	0.43 [b]	37.26 [b]
	1.29 [c]	0.66 [c]	2.14 [c]	1.22 [c]	0.39 [c]	43.40 [c]
N-NO_3^- [mg/cm^3]	1.21 [a]	0.59 [a]	1.77 [a]	1.22 [a]	0.34 [a]	27.94 [a]
	1.46 [b]	0.71 [b]	2.79 [b]	1.49 [b]	0.53 [b]	35.86 [b]
	1.32 [c]	0.82 [c]	2.28 [c]	1.27 [c]	0.42 [c]	51.39 [c]
P-PO_4^{3-} [mg/cm^3]	0.58 [a]	0.17 [a]	1.31 [a]	0.58 [a]	0.25 [a]	42.29 [a]
	0.56 [b]	0.10 [b]	1.22 [b]	0.56 [b]	0.27 [b]	47.76 [b]
	0.59 [c]	0.29 [c]	0.98 [c]	0.55 [c]	0.20 [c]	35.93 [c]
pH	6.84 [a]	5.95 [a]	7.30 [a]	6.90 [a]	0.28 [a]	4.09 [a]
	6.57 [b]	5.72 [b]	6.97 [b]	6.60 [b]	0.27 [b]	4.11 [b]
	6.56 [c]	5.80 [c]	6.90 [c]	6.58 [c]	0.27 [c]	26.98 [c]

a – bulk precipitation,

b – throughfall in the *Vaccinio uliginosi – Betuletum pubescentis*,

c – throughfall in the *Empetro nigri – Pinetum*.

In throughfall waters of both forest stands the content of investigated ions varied as follows: $NO_3^- > NH_4^+ > PO_4^{3-}$. Such order can be associated with slightly increased rain acidity. In an open area bulk precipitation indicated pH = 6.8 on average, while below crowns area of both investigated forest stand pH = 6.6, on average. Additional factor which influences the mutual biogens ratio in throughfall water can be the fact, that some of NH_4^+ ions can be oxidized to NO_3^- during rain shifting through the crowns area, especially in the growing season [43]. Among biogens the highest transition dynamics, expressed by temporal variability coefficient (CV), was shown by P-PO_4^{3-} in the *Vaccinio uliginosi – Betuletum pubescentis* stand, which was equal to 42.3% in an open area and 47.8% below crown area. The lowest dynamics was shown by total nitrogen (18.8%). In the *Empetro nigri – Pinetum* stand the highest variability was shown by nitrates (51.4%), while the lowest by total-nitrogen (32.0%). Similar variability of the above-mentioned biogens was observed in bulk precipitation by Żelazny [46]. In total balance leaching of nitrogen-including ions slightly dominates in the trees crowns zone. Higher than one ratio value between concentration of total nitrogen compounds in throughfall and bulk precipitation collected in an open area (Tab. 5) proves such observation. In both investigated stands $N\text{-}NO_3^-$ leaching process is a dominating one. *Vaccinio uliginosi – Betuletum pubescentis* stand (humid habitat, trophically abundant) showed stronger leaching comparing to *Empetro nigri – Pinetum* stand (dry habitat, trophically poor). $N\text{-}NO_3^-$ leaching caused by rain precipitation shifting through the crown area was noticed by Hansen [11] and Walna [44].

Table 5. Ratios of mean nitrogen and phosphorus compounds between fluxes in throughfall and bulk precipitation (2002–2005)

Ratios	T-N	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	$P\text{-}PO_4^{3-}$
Throughfall *Vaccinio uliginos – Betuletum pubescentis* / bulk precipitation	1.03	0.85	1.21	0.96
Throughfall *Empetro nigri – Pinetum* / bulk precipitation	1.04	0.95	1.09	1.02

In the case of $N\text{-}NH_4^+$ a different variability occurs. In both forest stands retention of $N\text{-}NH_4^+$ in the crown zone is dominating. Comparing to *Empetro nigri – Pinetum* higher retention is observed in *Vaccinio uliginosi – Betuletum pubescentis* forest stand. A proof for the above-mentioned statement is a difference of ratio between concentration of ammonium in throughfall and bulk precipitation, which for *Vaccinio uliginosi – Betuletum pubescentis* stand is 0.85, while for *Empetro nigri – Pinetum* 0.95. A parameter which differentiates investigated woodland ecosystems is phosphates sorption. In *Vaccinio uliginosi – Betuletum pubescentis* stand $P\text{-}PO_4^{3-}$ absorption dominates, while in *Empetro nigri – Pinetum* stand a slightly leaching processes is the most significant. Predominance of ammonium ions comparing to nitrates in bulk precipitation is reflected also in the value of ratio of the above-mentioned ions in precipitation, which equals 1.11 (Tab. 6). Similar observations were described earlier by Janek [13], Kram [24] and Walna [44].

Table 6. Ratios of soluble nitrogen and phosphorus ions in throughfall and bulk precipitation (2002–2005)

	$N\text{-}NH_4^+/N\text{-}NO_3^-$	$(N\text{-}NH_4^+ + N\text{-}NO_3^-)/P\text{-}PO_4^{3-}$
Bulk precipitation	1.11	4.35
Throughfall *Vaccinio uliginosi – Betuletum pubescentis*	0.78	4.63
Throughfall *Empetro nigri – Pinetum*	0.97	4.39

On the contrary, in throughfall waters, nitrates dominate quantitatively. Slightly higher amounts of nitrates were determined in throughfall waters of *Vaccinio uliginosi – Betuletum pubescentis* stand, while higher amounts of ammonium in *Empetro nigri – Pinetum* stand (0.97). In general, the concentration level of nitrogen-including compounds is a few times higher than phosphates both in bulk precipitation collected in an open area and throughfall waters. This phenomenon is reflected in the value of ratio between the sum of ammonium and nitrates related to phosphates. The lowest $P\text{-}PO_4^{3-}$ concentration value in throughfall waters was determined in *Vaccinio uliginosi – Betuletum pubescentis* stand, where the ratio of soluble forms of nitrogen comparing to phosphorus equals 4.63.

CONCLUSIONS

Rain precipitation transforms during shifting through the trees crown area. In chosen SNP woodland ecosystems bulk precipitation waters, in the period between 2002 and 2005, according to Jansen categorization [15] concerning pH was above regular (pH > 6.5), with slightly increased N-NH_4^+ concentration (1.35 mg/cm^3) and inconsiderable amounts of N-NO_3^- (1.21 mg/cm^3). Also, P-PO_4^{3-} concentration was low and persisted on the level of 0.58 mg/cm^3 in average. Comparing to bulk precipitation (collected at an open area) throughfall samples collected in the *Vaccinio uliginosi – Betuletum pubescentis* ecosystem (loose birch-pine stand, pine participation – 25%, birch participation – 75%) became poor in N-NH_4^+ and P-PO_4^{3-}, enriched in N-NO_3^- and slightly more acidic (by 3.9%), while at the *Empetro nigri – Pinetum* ecosystem (uniform pine stand) became poor in N-NH_4^+, enriched in P-PO_4^{3-} and N-NO_3^- and more acidic (by 4.4%). Such phenomenon suggests that variability of chemical profile of throughfall waters is mainly determined by species composition and the kind of forest stand, as well as it's trophic conditions.

Acknowledgements

The authors would like to express their sincere gratitude to Ms Beata Sobocka (major specialist of education and GIS in Słowiński National Park) for cooperation and SNP map delivering.

REFERENCES

[1] Bednorz J.: *Animal world*, [in:] H. Piotrowska (eds.), *Nature of Słowiński National Park*, Bogucki, Poznań – Gdańsk 1997.

[2] Blond E.R., W.T. Swank, T. Williams: *Precipitation, throughfall, and stem flow chemistry in a Coastal Loblolly Pine Stand*, Freshwater Wetlands and Wiltwife, 61–78 (1986).

[3] Bochenek W.: *Influence of atmospheric circulation on electrolytic conductivity of precipitation water solutions in the Bystrzanka catchment in the period between 1995–2004*, Nature Environment Monitoring KTN, Kielce 2005, **6**, 49–58.

[4] Bormann F.H., G.E. Likens: *Pattern and Process in a Forested Ecosystem*, Springer Verlag, Berlin, New York 1979.

[5] Butler T.J., G.E. Likens: *A direct comparison of throughfall plus stem flow to estimates of dry and total deposition for sulfur and nitrogen*, Atmos. Environ., **29**, 1253–1265 (1995).

[6] Carleton T.J., T. Kavanagh: *Influence of stand age and spatial location on throughfall chemistry beneath Black spruce*, Can. J. Forest Res., **20**, 1917–1925 (1990).

[7] Charron A., H. Plaisance, S. Saurage, P. Coddeville, I.C. Galloo, R. Guillermo: *A study of the source – receptor relationships influencing the acidity of precipitation collected at a rural site in France*, Atmos. Environ., **34**, 3665–3674 (2000).

[8] Chiwa M., D.H. Kim, H. Sakugawa: *Rainfall, stem flow and throughfall chemistry at urban- and mountain-facing sites at Mt. Gokurakuj, Hiroshima, Western Japan*, Water, Air, Soil Pollut., **146**, 93–109 (2003).

[9] Foster N.W., I.K. Morrison: *Distribution and cycling of nutrients in a natural Pinus Banksiana ecosystem*, Ecology, **57**, 110–120 (1976).

[10] Hansen K.: *Throughfall and canopy interaction in spruce forest*, Forskningsserien 8, Danish Forest and Landscape Research Inst., Lyngby 1994.

[11] Hansen K.: *In-conopy throughfall measurements of ion fluxes in Norway spruce*, Atmos. Environ., **30**, 4065–4076 (1996).

[12] Hermanowicz W., J. Dojlido, W. Dożańska, B. Kosiorowski, J. Zerbe: *Physico-chemical measurements of water and waste-waters*, Arkady Press, Warsaw 1999.

[13] Janek M.: *Influence of coniferous forest stands on bulk precipitation quality*, Works of Institute of Forest Research, **4**, 73–87 (2000).

[14] Janek M.: *Influence of coniferous forest stands on bulk precipitation quality, Part II. Seasonal changes in quantity and chemical profile of precipitation in coniferous forest stands of Augustowska Forest*, Works of Institute of Forest Research, **3**, 73–86 (2002).

[15] Jansen W., A. Block., J. Knack: *Acid rain. History, genesis, effects.* Aura 4 (1998).

[16] Jóźwiak M., R. Kozłowski: *Transformation of bulk precipitation in chosen ecosystems of Świętokrzyskie Mts.*, Regional Monitoring of Natural Environment, KTN Kielce 2004, **5**, 199–217.

[17] Konieczka P., J. Namieśnik , B. Zygmunt, E. Bulska, A. Świtaj-Zawadka, A. Naganowska, E. Kremer, M. Rompa: *Quality assessment and quality control of analytical results – QA/QC*, Centre of Excellence in Environment Analysis and Monitoring, Gdańsk (in Polish) 2004.

[18] Kowalkowski A., M. Jóźwiak: *Chemical composition of bulk precipitation, Świętokrzyski National Park: Nature, Economy, Culture*, Bodzentyn – Krakow 2000.

[19] Kowalkowski A., M. Jóźwiak, R. Kozłowski: *Versauerung der Niederschläge und Bodenzustand im Świętokrzyski National Park*, DBG, Mitteilungen, Band **98**, 49–50 (2002).

[20] Kowalkowski A., M. Jóźwiak, R. Kozłowski: *Changes in quality of bulk precipitation in the Świętokrzyski National Park forest ecosystem*, Environ. Engin. Tech. J., **5**, 97–110 (2002).

[21] Kozłowski R.: *An inflow of mineral compounds together with bulk precipitation to the forest bottom layer in the Base Station of Integrated Monitoring of Natural Integrated Monitoring of Natural Environment. An action and monitoring of geoecosystems considering atmospheric pollution*, Environmental Monitoring Library, Kielce 2001, 207–218.

[22] Kozłowski R.: *Quantitative and qualitative variability of throughfall stem flow in chosen forest ecosystems of Świętokrzyskie Mts.*, Regional Monitoring of Natural Environment, KTN Kielce 2002, **3**, 95–102.

[23] Kozłowski R.: *Spatial variability of throughfall waters in mixed fir-pine forest stand in the central part of Świętokrzyskie Mts.*, Regional Monitoring of Natural Environment, KTN Kielce 2003, **4**, 99–106.

[24] Kram K.J.: *Bulk deposition and aerosol-gaseous input of elements in the forested area of Coastal Region (Pomerania, North Poland)*, Pol. J. Ecol., **53**, 261–268 (2005).

[25] Krzysztofiak L.: *A report of Base Station of Integrated Monitoring of Natural Environment (Krzywe) for the hydrologic period between 1994 and 1997*, [in:] Kostrzewski A. (eds.) Integrated Monitoring of Natural Environment. Geoecosystems condition in the period between 1994 and 1997, Environmental Monitoring Library. PIOŚ, Warsaw 1998, 103–122.

[26] Likens G.E., H.F. Bormann: *Biogeochemistry of a Forested ecosystem*, Springer- Verlag, New York, Berlin, Heidelberg, London, Paris, Tokyo, Hong Kong, Barcelona, Budapest 1995, 1–159.

[27] Lovett G.M., S.E. Lindberg: *Atmospheric deposition and canopy interactions of nitrogen of forest*, Can. J. For. Res., **23**, 1603–1616 (1993).

[28] Malzahn E.: *Monitoring of hazards and pollutions of forest ecosystem of Białowieska Forest*, Cosmos, **51**, 435–441, (2002).

[29] Matuszkiewicz J. M.: *Polish woodland ecosystems*, PWN, Warszawa 2002.

[30] Mazurek M., Z. Zwoliński: *An activity of chosen polish geoecosystems in the framework of monitoring measurements in hydrologic year 1999*, http://main.amu.edu.pl/~zmsp/stan99/stan99.html, Institute of Quaternary Research and Geoecology UAM, Poznań 2000.

[31] *Słowiński National Park protection plan, Forest ecosystems protection procedures for the period between 2002 and 2021, Vol. 7 General description, Vol. 9.1 Taxonomical forest description – Land Compound, Units 1-63*, Jelenia Mt. Office of planning and designing 2003.

[32] Polkowska Ż., A. Astel, M. Grynkiewicz, T. Górecki, J. Namieśnik: *Studies on intercorrelation between ions co-occuring in precipitation in the Gdańsk – Sopot – Gdynia Tricity (Poland)*, J. Atmos. Chem., **41**, 239–264 (2002).

[33] Polkowska Ż., A. Astel, B. Walna, S. Malek, K. Mądrzycka, T. Górecki., J. Siepak, J. Namieśnik: *Chemometric analysis of rainwater and throughfall at several sites in Poland*, Atmos. Environ., **39**, 837–855 (2005).

[34] Pryor S.C., R.J. Barthelmie: *Nutrient fluxes in precipitation, throughfall and stem flow: observations from the deciduous forest*, Geophysic. Res. Abstr., **5**, 1911 (2003).

[35] Pryor S.C., R.J. Barthelmie: *Liquid and chemical fluxes in precipitation, throughfall and stemflow: Observations from a deciduous forest and a red pine plantation in the Midwestern U.S.A.*, Water, Air, Soil Pollut., **163**, 203–227, (2005).

[36] Rabski K.: *Mezoclimatic background of Słowiński National Park*, National Parks and Nature Reservoirs, **11**, 37–54 (1992).

[37] Shubzda J., S.E. Lindberg, C.T. Garten, S.C. Nodvin: *Elevation trends in the fluxes of sulphur and nitrogen in throughfall in the southern Appalachian Mountains: some surprising result*, Water, Air, Soil Pollut., **85**, 2265–2270 (1995).

[38] Stachurski A.: *Nutrient control in throughfall waters of forest ecosystems*, Pol. Ecol., **35**, 3–69 (1987).

[39] Stachurski A., J.R. Zimka: *The budget of nitrogen dissolved in rainfall during its passing through the crown canopy in forest ecosystems*, Pol. Ecol., **32**, 191–218 (1984).

[40] Stachurski A., J.R. Zimka: *Radicals cycle in land ecosystems*, Cosmos, **54**, 391–400 (2004).

[41] Szarek G.: *Sulphur and nitrogen input to the Ratanica forested catchment (Carpathian foothills, Southern Poland)*, Water, Air, Soil Poll., **85**, 1765–1770 (1995).

[42] Tyszka J., T. Wawrzyniak, M. Janek: *Ion fluxes through spruce and pine forest ecosystems in various environmental pollution conditions*, Works of Institute of Forest Research, **864**, 35–56 (1998).

[43] Van Dobeen H.F., J. Mulder, H. van Dam, H. Houweling: *Impact of acid atmospheric deposition on the biogeochemistry of moorland pools and surrounding terrestrial environment*, Agricultural Research Reports 931, Pudoc Scientific Publishers. Wageningen 1992, 1–199.

[44] Walna B., Ż. Polkowska, S. Małek, K. Mędrzycka, J. Namieśnik, J. Siepak: *Tendencies of Change in the Chemistry of Precipitation at Three Monitoring Stations 1996–1999*, Pol. J. Environ. Stud., **12**, 467–472 (2003).

[45] Zimka J.R., A. Stachurski: *Forest decline in Karkonosze Mts. (Poland), Part II, An analysis of acidity and chemistry of atmospheric precipitation, throughfall and forest stream waters*, Pol. Ecol., **44**, 153–177 (1996).

[46] Żelazny M.: *Physical conditions of atmospheric precipitations*, [in:] M. Żelazny (eds.), Dynamics of nutrients in bulk precipitation, surface and underground waters in the catchments characterized by various utilization in the Wiśnickie foothills, Institute of Geography and Space Economy, UJ, Krakow 2005.

Received: October 10, 2007; accepted: March 28, 2008.

PRZEPŁYW SUBSTANCJI BIOGENICZNYCH WRAZ Z OPADAMI ATMOSFERYCZNYMI I PODKORONOWYMI W WYBRANYCH EKOSYSTEMACH LEŚNYCH SŁOWIŃSKIEGO PARKU NARODOWEGO

W pracy przeanalizowano dynamikę zmian poziomów stężeń N-NH_4^+, N-NO_3^-, P-PO_4^{3-} oraz pH w opadach na otwartej przestrzeni i opadach podkoronowych w dwóch różnych ekosystemach leśnych Słowińskiego Parku Narodowego w okresie 2002–2005. Badane ekosystemy leśne znajdowały się pod wpływem takich samych warunków meteorologicznych. Na podstawie uzyskanych wyników stwierdzono, że o zmianie jakości wód podkoronowych decydują przede wszystkim rodzaj i gatunek drzewostanu, a także stan troficzny ekosystemu leśnego. Opady podkoronowe w porównaniu do opadów na otwartej przestrzeni w zespole *Vaccinio uliginosi – Betuletum pubescentis* były uboższe w N-NH_4^+ i P-PO_4^{3-}, wzbogacone w N-NO_3^- oraz nieco bardziej kwaśne (o 3,9%), a w zespole *Empetro nigri – Pinetum* uboższe w N-NH_4^+, wzbogacone w P-PO_4^{3-} i N-NO_3^- oraz bardziej kwaśne (o 4,4%).