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MODIFICATION OF THE ATMOSPHERIC LOAD OF ELEMENTS DURING PASSAGE THROUGH FOLIAGED CANOPIES OF FIVE TREE SPECIES OF TEMPERATE ZONE FORESTS

ABSTRACT: Atmospheric load is an important source of nutrients and pollutants to ecosystems. During the flux through forest canopies that deposition is intensively modified enriching in some elements and pooring in others. Both, atmospheric load and flux of elements through forest canopies, were investigated in the Kampinos National Park (central Poland) during vegetative seasons (April–October) of the years 1998 and 2000. Throughfall was compared with atmospheric deposition in five different forest ecosystems: pine, birch, locust tree, alder, and oak. Atmospheric deposition data was obtained from rain collectors equipped with artificial foliage of an area similar to the actual leaf surface area in a given ecosystem. Results showed that H^+ and Pb^{2+} flowed passively through tree canopies. NO_3^-, PO_4^{3-}, SO_4^{2-}, NH_4^+, Na^+, Cd^{2+}, Zn^{2+} and Cu^{2+} were retained in the canopies (the process was the most intensive for ammonium – 58%, and phosphorus – 60% retained), while Cl^-, Mg^{2+}, K^+ and Ca^{2+} were leached out of canopies (throughfall, in comparison to bulk precipitation, was enriched by up to 109% in case of potassium). These processes all occurred more vigorously in deciduous trees, like alder and oak, and less intensively or not at all in pine tree stands. Trees living in symbiosis with nitrogen-fixing microorganisms (alder and locust tree) were equally effective at trapping nitrogen from atmospheric loads, as at non-symbiotic tree species. The calendar day has no influence on the throughfall balance of elements with the only exception for calcium (only in alder forest also magnesium and chlorine), which was more intensively leached out during the autumn then on the beginning of vegetation season.

KEY WORDS: bulk precipitation, throughfall, uptake, leaching, aerosol-gaseous load of elements, artificial foliage, Central Poland

1. INTRODUCTION

The modifying effects of plants on the chemical composition of atmospheric precipitation have been highlighted by many previous studies. As compared to atmospheric deposition, throughfall is usually enriched in elements such as potassium, calcium, magnesium and sodium (Madgwick and Ovington 1959, Morris *et al.* 2003). In some cases, elements that are usually leached out from tree crowns are instead retained, as reported for calcium (Alcock and Morton 1985) and magnesium (White and Turner 1970). The process is not uniform in nature and many factors may affect it, including the type of plant cover (Madgwick and Ovington 1959, Parzych *et al.* 2008), age of foliage (Stenlid 1958), canopy closure (Žaltauskaitė and Juknys 2007), or the plants' nutrient supply (Robertson *et al.* 2000). The elemental pool in throughfall may also be increased by biotic or abiotic factors, such as herbivorous insects (Stadler *et al.* 2001), drought or extreme temperatures (Tukey and Morgan 1963). High concentrations of some gases in the air (Ulrich 1983) or hydrogen ions in the rainfall (Mecklenburg *et al.* 1966) might also increase the pool of elements in throughfall. Additionally, acid fog can dramatically enhance leaching of calcium from leaves, often eventually leading to the death of young trees (Igawa *et al.* 2002).

The main elemental loads to be considered when studying the patterns of precipitation flowing through forest canopies are rainfall and throughflow. However, an additional notable source is the aerosol-gaseous load, the amount of which varies relative to the leaf surface area in particular tree stands (Stachurski and Zimka 2000, Kram 2001, 2005).

Ion exchange is usually the mechanism responsible for retaining or leaching ions from foliage. Foliage absorption of hydrogen (Cronan and Reiners 1983) or ammonium ions (Roelofs *et al.* 1985) is accompanied by a release of other cations by the leaves (e.g., potassium, sodium, magnesium, calcium or zinc). Lovett and co-workers (1985) found that 40–60% of the K^+, Mg^{2+} and Ca^{2+} leached from foliage originated from ion exchange for H^+ and NH_4^+ cations.

Uptake of nitrogen from rainfall in the oak forest canopy was noted by Voigh (1960), and further confirmed by many authors in various ecosystems (Carlisle *et al.* 1966, Stachurski and Zimka 1984, Neirynck *et al.* 2007). Unusually high levels of nitrogen originating from human activities result in an increased rate of nitrogen uptake by trees, which may in turn disturb the elemental equilibrium and cause dying-off of forests through the severe deficit of other elements like magnesium and potassium (Roelofs *et al.* 1985) or phosphorus (Mohren *et al.* 1988).

Sulphur is another important atmospheric element. It is commonly recognised that SO_4^{2-} ions flow passively through tree canopies – they are neither leached nor retained (Ulrich 1983). This result was confirmed by Lindberg and Garten (1988), who used radioactive sulphur isotopes to determine that only 5% of the sulphur in throughfall had been leached from leaves.

The present study was undertaken to answer several lingering questions about elemental flux through forest canopies: Which elements are retained in canopies, and which are leached from foliage during flow through forest canopies and how intensive is this process? How important is the form in which the elements reach the forest canopies? That is, can differences in retention or leaching be detected between the rainfall form and the aerosol-gaseous form of a given element? And is it important season of the year for intensity of processes of leaching and retention?

Answers to these questions may contribute the construction some of general rules for processes occurring in forest canopies. However, these rules may not account for all of the discrepancies in the data collected to date by different authors. These differences may arise not only from different geographic or climatic conditions but also from the fact that these studies were performed in different tree species. Such tree-specific differences were recognized early on, as the earliest papers in the field (i.e., Madgwick and Ovington 1959) included as many as twelve tree species in their comparative analyses of plant modifications of atmospheric deposition. Similar studies have been performed in the meantime, using progressively more modern methods (Lovett and Lindberg 1993, Houle *et al.* 1999, Lovett *et al.* 2004).

Coniferous and deciduous tree species display the most obvious and best-known differences of this type, namely in their differential capacities for retention and leaching of elements (Houle *et al.* 1999). Coniferous tree stands are known to acidify water more than deciduous trees (Parker 1983). Deposition of various ions, however, is greater in deciduous tree stands (Parker 1983).

Another factor of potential importance for these processes is the nutrient quality of the soil. Supplying plants with an abundant amount of nitrogen resulted in increased leaching of the element from forest canopies (Tietema *et al.* 1998). Therefore, the final question addressed in this study was whether the patterns of nitrogen retention and leaching differ between species associated with nitrogen-fixing organisms and those that lack a symbiotic partner.

2. STUDY AREA

The study was carried out in the Kampinos National Park during vegetative seasons (April–October) of the years 1998 and 2000. All forest study plots were located in a small area near the reserve "Zamczysko" (52°18'N and 20°32'E) (Fig. 1). Stands in open areas were situated in the village "Granica", *ca.* 5 km west of the forest sites. According to meteorological data collected in this village, the year 1998 was characterised by precipitation similar to the long term average (annual sum of precipitation = 556.5 mm) and was rather warm (annual mean air temperature = 8.5°C). The year 2000 was characterised by one of the highest annual mean temperatures (9.4°C) and the lowest sum of precipitation (413.9 mm) since 1990 (Andrzejewska 2003).

Five different forest ecosystems were selected for studies of element flux through tree crowns. The tree stands were dominated by pine, birch, locust tree, alder or oak. To simplify the nomenclature, particular tree stands will be referred to by the name of the dominant tree species. It should be remembered, however, that these studies pertained to the whole ecosystem and that sometimes the composition of throughfall was also affected by other trees or shrubs present there.

– Pine forest: monospecific and even-aged (*ca.* 70–80 years) tree stand of Scots pine (*Pinus sylvestris* L.) of the association *Leucobryo-Pinetum* W. Mat. (1962) 1973, with bilberry (*Vaccinium myrtillus* L.), red bilberry (*V. vitis-idaea* L.) and cow-wheat (*Melampyrum pratense* L.) dominating the forest floor.

– Birch forest: monospecific and even-aged (*ca.* 40–50 years) tree stand of the common birch (*Betula pendula* Roth) in the highly degenerated association *Betula pen-*

Fig. 1. Location of study site.

dula-Agrostis capillaris. The floor was dominated by grasses, mainly bent grass (*Agrostis capillaris* L.), reed grass (*Calamagrostis epigeios* (L.) Roth) and apetalous sandwort (*Moechringia trinervia* (L.) Clairv.).

– Locust tree forest: monospecific and multi-aged stand of locust trees (*Robinia pseudoacacia* L.), probably self-sown and on a sandy hill. Association *Robinia pseudoacacia-Calamagrostis epigeios*. The floor was dominated by reed grass (*Calamagrostis epigeios* (L.) Roth), bent grass (*Agrostis capillaris* L.) and blackberry (*Rubus plicatus* W. et N.).

– Alder forest: unmanaged alder wood with distinct clumps of trees classified under the association *Ribeso nigri-Alnetum* Sol.-Górn. (1975) 1987. The tree layer was composed exclusively of black alder (*Alnus glutinosa* (L.) Gaertn.) and the well-developed shrub layer contained bird cherry (*Prunus padus* Mill.), rowan (*Sorbus aucuparia* L.), alder buckthorn (*Frangula alnus* Mill.), and black currant (*Ribes nigrum* L.), among others. The floor was richly diversified, featuring the lesser pond sedge (*Carex acutiformis* L.), marsh fern (*Thelypteris palustris* Schott), climbing nightshade (*Solanum dulcamara* L.) and bedstraw (*Galium palustre* L.).

– Oak forest: natural fresh ground forest island (*Tilio-Carpinetum*) surrounded by alder wood; a unmanaged mixed tree stand with the common oak (*Quercus robur* L.) and aspen (*Populus tremula* L.) dominating among the trees. Hazel (*Corylus avellana* L.) dominated a very dense shrub layer and the yellow archangel (*Galeobdolon luteum* Huds.) and lily of the valley (*Convallaria majalis* L.) comprised much of the poorly developed but diversified forest floor.

Studied tree species included three that grow in nutrient-poor habitats (pine, locust, birch) and two that are found in richer stands (oak, alder). The trees were also classified as deciduous (oak, alder, locust tree and birch) or coniferous (pine). Some species grow in symbiosis with nitrogen-fixing microorganisms (alder with Actinomycetes, and locust tree with bacteria of the genus *Rhizobium*), while the others (pine, birch, oak) lack such interactions. This trait diversity allowed for the determination of the features of particular tree species that are important for the processes analysed within this study.

3. METHODS

3.1. Sampling

To estimate the real load of elements to the five studied ecosystems, it was necessary to estimate their respective surface areas. Surface area is similar to leaf area index (LAI), which is expressed as the surface area of leaves per unit ground area (usually in $m^2\ m^{-2}$). In this study, LAI was measured in every tree stand using the optical device Li-Cor LAI-2000, which determines LAI in a fast, simple and relatively accurate manner (Chason *et al.* 1991). Measurements were performed in August of both years, as this is commonly considered to be the period of maximum foliage area.

According to Gower and Norman (1991), Li-Cor LAI-2000 undervalues the leaf area in coniferous forests by *ca.* 30–40%. Therefore, the LAI values determined for the pine forests were multiplied by a factor of 1.5, as calculated by these authors for similar pine species.

For deciduous tree species LAI was measured also using a method based on measurements of fallen leaves in autumn (method described in details by Stachurski and Zimka 1975), which confirmed Li-Cor LAI-2000 results.

All species of trees and shrubs that participated in the interception of the aerosol-gaseous load and in modification of the throughfall, rather than only the dominant species, were considered when measuring LAI. Stemflow was not considered in this study because of the great labour load necessary for its measurement and its generally low contribution to the total ion load, i.e., less than 10% (Eaton *et al.* 1973).

According to recent views, reliable measurements of the atmospheric load of elements into a given ecosystem should take into account the aerosol-gaseous load. Standard rain collection methods do not catch this type of load, implying that the total load may often be severely underestimated (Lindberg *et al.* 1986). In the present study, an "artificial foliage" method was used to measure both the amount of rain and the aerosol-gaseous deposition in a simple but precise way. The method consists of using modified rain collectors equipped with so-called artificial foliage of a known surface area (LAI) mounted above the trap (Stachurski and Zimka 2000). Four types of traps were used:

Variant "0" – typical rain collector without artificial foliage. The trap is built of a plastic canister with a funnel to collect the rainfall. The funnel is protected from above by a net to catch larger impurities and organisms, and, at the outlet, by a nylon filter that enables separation of dust pollutants and other small particles (e.g., herbivore faeces).

Variant "2" – trap additionally equipped with artificial foliage covering an area of 2 m^2 m^{-2}.

Variant "6" – trap equipped with artificial foliage covering an area of 6 m^2 m^{-2}.

Variant "12" – trap equipped with artificial foliage covering an area of 12 m^2 m^{-2}.

This gradient of surface areas falls within the range of the foliage cover found in forest ecosystems (Gower and Norman 1991). Three traps of each variant ("0", "2", "6", "12") were placed in open areas. Traps of the variant "0" were placed also under trees. Five of these regular rain collectors (two in the oak forest in 1998) were set up in every studied tree stand in random distribution. To sum seasonal load of elements and to use statistical analyses samples from every canister were collected and analysed separately.

Once every three weeks, collected water was sampled and nylon filters and canisters were exchanged for clean materials. To avoid solar radiation and the development of algae and microorganisms in collected water, every canister was wrapped with aluminium foil. The amount of water in traps was measured in the field.

3.2. Chemical analyses

pH was measured potentiometrically with the ion meter Orion Analyzer 940 (USA) and the electrode ROSS Sure-Flow (Thermo Orion, USA). Concentrations of cations (NH_4^+, Na^+, Mg^{2+}, K^+ and Ca^{2+}) and anions (NO_3^-, SO_4^{2-} and Cl^-) were determined in two analytical cycles with the ion chromatograph Metrohm IC System 690 (Switzerland). The samples were filtered through 0.45 μm Teflon filters prior to analysis. Concentrations of cadmium, lead and copper were measured with the inverse voltamperometric (DPASV) method with a Metrohm 646 VA Processor polarograph equipped with a Metrohm 675 VA sample changer (Switzerland). Before analysis, samples were filtered through 0.45 μm Teflon filters, acidified with HNO_3 (Aristar BDH, UK) and mineralized in ultraviolet light for seven hours. P-PO_4 concentrations were determined colorimetrically with the molybdenum blue method in a UV-VIS spectrophotometer (Shimadzu, Japan).

3.3. Statistical data processing

The modifying role of tree canopies was evaluated by comparing the pool of elements contained in throughfall with that in rainfall obtained in rain collectors equipped with artificial intercepting surfaces. For these comparisons, data obtained from traps with an area most similar to the real leaf area of a given tree stand were used. For example, the load of elements in throughfall from pine, birch and locust forests was compared with the load obtained from traps with a foliage area of 2 m^2 m^{-2} and from the oak forest with traps with a foliage area of 6 m^2 m^{-2}. Throughfall in the alder forest was compared with the loads collected in traps with foliage areas of both 2 and 6 m^2 m^{-2}, as the mean intercepting area (4 m^2 m^{-2}) was closest to actual leaf area in the alder ecosystem.

The Student t-test for matched pairs was used to determine whether a given element was retained, leached or passed unchanged through forest canopies. For every sampling date, mean values from under the canopies were compared with mean values obtained from traps with artificial foliage. Thirteen such pairs were examined (seven sampling dates in 1998 and six in 2000), totalling 65 pairs for all examined forests. Since the time intervals between consecutive sampling occasions were not identical (24 days on average), every mean value was divided by the actual number of days and multiplied by 30 to obtain the load in kg ha^{-1} $month^{-1}$.

Multifactor analysis was used to determine whether element uptake by forest canopies was associated more with rainfall or with the aerosol-gaseous load. Possible insignificance was confirmed by forward and backward selection. Load data for this analysis were mean values from particular sampling dates. Independent variables were the loads of a given ion in aerosol-gaseous form, rainfall and the dependent variable was the element's retention in or leaching from forest canopies.

After calculating the total load of elements to particular tree stands, the balance between atmospheric load and throughfall was calculated, thus making it possible to estimate which elements were retained in forest canopies and which were leached out.

4. RESULTS

Throughfall in all studied tree stands contained significantly less water than precipitation from neighbouring open areas. Interception for all tree stands was 8.95 mm per month (i.e. 19% of the total water load; Table 1).

Both forms of nitrogen, ammonium and nitrates, were retained in forest canopies. The intensity of retention ranged from 31% for nitrate ions to 58% for ammonium ions. This result signifies that tree crowns retained 0.13 kg N-NO_3 ha^{-1} month^{-1} and 0.51 kg N-NH_4 ha^{-1} month^{-1} (Table 1).

Other elements retained in forest canopies were sodium, potassium and the heavy metals zinc, cadmium and copper. Sulphur, one of the most important elements in atmospheric deposition, was also significantly retained in canopies, though in small amounts

Table 1. Balance of elements flowing through canopies of the forest ecosystems. Data were calculated from means of particular sampling dates during vegetative seasons of the years 1998 and 2000. A – atmospheric input (rain collectors with artificial foliage of an LAI similar to the LAI of tree stands); T – throughfall. Significance of the differences between A and T was calculated with the Student's t-test for dependent variables. Negative values indicate retention and positive values indicate leaching; *P* – significance, NS – non-significant ($P > 0.05$), n = 65.

Parameter	Unit	A	±SD	T	±SD	*P*	T–A	% (T-A)/A
water	(mm month^{-1})	48.48	±34.92	39.53	±30.42	<0.001	–8.95	–19
H^+	(g ha^{-1} month^{-1})	12.96	±17.86	8.43	±13.04	NS	–	–
Na^+	(kg ha^{-1} month^{-1})	0.209	±0.116	0.150	±0.096	<0.001	–0.059	–28
N-NH_4^+	(kg ha^{-1} month^{-1})	0.875	±1.060	0.367	±0.324	<0.001	–0.508	–58
K^+	(kg ha^{-1} month^{-1})	0.412	±0.349	0.864	±0.680	<0.001	0.452	110
Mg^{2+}	(kg ha^{-1} month^{-1})	0.105	±0.055	0.186	±0.128	<0.001	0.081	77
Ca^{2+}	(kg ha^{-1} month^{-1})	0.774	±0.278	0.922	±0.481	<0.01	0.148	19
Cl^-	(kg ha^{-1} month^{-1})	0.323	±0.206	0.480	±0.448	<0.001	0.157	49
N-NO_3^-	(kg ha^{-1} month^{-1})	0.439	±0.221	0.305	±0.202	<0.001	–0.134	–31
S-SO_4^{2-}	(kg ha^{-1} month^{-1})	0.716	±0.331	0.652	±0.392	<0.01	–0.064	–9
P-PO_4^{3-}	(kg ha^{-1} month^{-1})	0.151	±0.151	0.060	±0.062	<0.001	–0.091	–60
Zn^{2+}	(g ha^{-1} month^{-1})	57.0	±24.7	43.1	±30.1	<0.001	–13.9	–24
Cd^{2+}	(g ha^{-1} month^{-1})	0.061	±0.046	0.037	±0.031	<0.001	–0.024	–39
Pb^{2+}	(g ha^{-1} month^{-1})	0.72	±0.71	0.79	±0.67	NS	–	–
Cu^{2+}	(g ha^{-1} month^{-1})	4.40	±2.44	3.49	±1.75	<0.001	–0.91	–21

Table 2. Coefficients of the linear regression of retention (negative values) or leaching (positive values) of elements from forest canopies for their input as aerosol-gaseous or rainfall forms. Calculations were based on means from particular sampling occasions during vegetative seasons of the years 1998 and 2000, combined for all five studied tree stands. A lack of significance in the multifactor analysis was confirmed by forward and backward selection. b – regression coefficient.

Type of input	N-NO_3^-			N-NH_4^+			S-SO_4^{2-}		
	b	±SE	*P*	b	±SE	*P*	b	±SE	*P*
Aerosol-gaseous input	–0.918	±0.072	<0.001	–0.686	±0.098	<0.001	–0.886	±0.119	<0.001
Rainfall input	0.146	±0.086	NS	–1.195	±0.127	<0.001	0.315	±0.086	<0.001
Regression constant	–0.018	±0.019	NS	0.244	±0.041	<0.001	–0.069	±0.037	NS
			<0.001			<0.001			<0.001
			$r^2 = 76\%$			$r^2 = 91\%$			$r^2 = 48\%$

(0.06 kg ha^{-1} month^{-1} on average; i.e., 9% as compared to open areas; Table 1).

Hydrogen ions were neither retained in nor leached out of forest canopies. Hence, the acidity of throughfall was not different than that of atmospheric deposition (Table 1).

Potassium and magnesium exhibited clear signs of leaching. There was as much as 77% (0.08 kg ha^{-1} month^{-1}) more magnesium and 110% (0.45 kg ha^{-1} month^{-1}) more potassium in throughfall than in atmospheric precipitation. Leaching of calcium (0.15 kg ha^{-1} month^{-1}; i.e., an increase of 19%) and chlorine (0.16 kg ha^{-1} month^{-1}; i.e., an increase of 49%), though statistically significant, was less intense than that of potassium or magnesium (Table 1).

The methods used allowed for differentiation between rainfall and aerosol-gaseous loads, as rain collectors intercepted only rainfall, while those equipped with artificial foliage caught both rain and aerosol-gaseous loads. It was therefore possible to compare the roles of each form in retaining nitrates, ammonium ions and sulphates in forest canopies. The comparison showed that canopies retained only the aerosol-gaseous form of nitrates (Table 2). There was a close positive relationship (r^2 = 0.76, P <0.001) between the aerosol-gaseous load of nitrates and the amount retained in tree crowns (Fig. 2). Conversely, ammonium ions retained in tree crowns originated from both load forms (Table 2). This comparison yielded different results for sulphate-sulphur. Both load forms had significant impacts on the flux through the canopy, but their behaviour was contradictory. Aerosol-gaseous loads of sulphate-sulphur were retained in canopy, similar to the aerosol-gaseous loads of nitrates and ammonium ions. Rain loads, however, resulted in leaching of sulphates and increased sulphate content in throughfall. The relationships (r^2 = 0.48) were somewhat weaker than those for nitrates, but still statistically significant (P <0.001) (Table 2).

An interesting question is whether leaching from or retention in forest canopies of various elements is constant or varies throughout the vegetative season. Different demands for various nutrients between spring and autumn might affect the intensity of leaching and retention. Therefore, the budget of elements under the canopy (the difference between atmospheric load and throughfall) was tested for differences between particular datasets. Data combined from all studied ecosystems (n = 65) were used for this analysis. Contrary to expectations, it appeared that the season did not consistently affect analysed processes (Table 3). Nitrogen, the element vitally important for plant growth, was taken up in similar amounts across the entire vegetative season (Fig. 3). Significant seasonal changes in the intensity of retention or leaching were

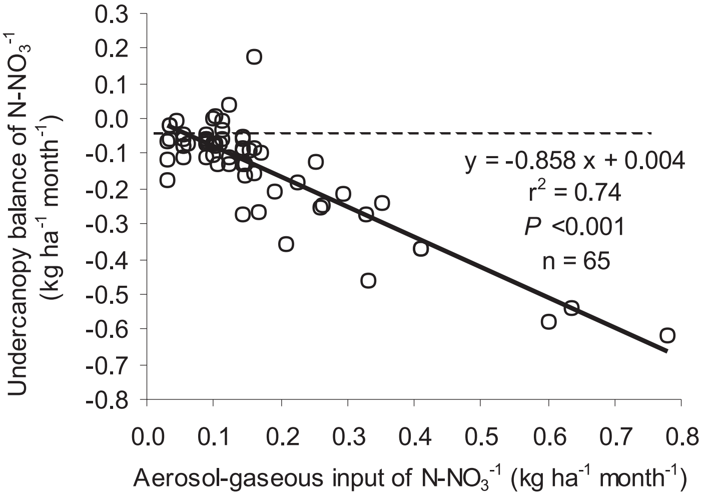

Fig. 2. Throughfall balance of nitrate-nitrogen in relation to input in the aerosol-gaseous form. The relationship was based on data from all five studied tree stands obtained during vegetative seasons of the years 1998 and 2000.

observed only for calcium. More calcium was retained than leached out in the spring. In autumn, leaching predominated over retention (Fig. 4).

For the atmospheric load of all analysed elements, only the process of water loss in throughfall in comparison with atmospheric deposition proceeded identically in all studied ecosystems. The loss was statistically significant in all tree stands and varied from 14% in birch to 30% in oak wood (Table 4). There were, however, differences between tree species in other components of the throughfall. In some species, retention or leaching proceeded vigorously, whereas in others no such processes were observed (Table 4).

Apart from a strong retention of ammonium and phosphorus, the flow of elements through canopies in pine forest was passive and the throughfall did not differ signifi-

Table 3. Coefficients of linear regression of the throughfall balance of elements in relation to calendar days. Calculations were based on results obtained during vegetative seasons of the years 1998 and 2000.

Element	Unit	a	b	±SE	r	*P*
Na^+	(kg ha^{-1} $month^{-1}$)	−0.005	−0.0003	0.0003	−0.12	NS
$N\text{-}NH_4^+$	(kg ha^{-1} $month^{-1}$)	−0.081	−0.0018	0.0021	−0.11	NS
K^+	(kg ha^{-1} $month^{-1}$)	0.845	−0.0025	0.0015	−0.21	NS
Mg^{2+}	(kg ha^{-1} $month^{-1}$)	−0.035	0.0005	0.0002	0.23	NS
Ca^{2+}	(kg ha^{-1} $month^{-1}$)	−0.553	0.0031	0.0008	0.43	<0.001
Cl^-	(kg ha^{-1} $month^{-1}$)	0.155	−0.0003	0.0008	−0.04	NS
$N\text{-}NO_3^-$	(kg ha^{-1} $month^{-1}$)	−0.130	−0.00003	0.0004	−0.01	NS
$S\text{-}SO_4^{2-}$	(kg ha^{-1} $month^{-1}$)	−0.058	−0.0001	0.0005	−0.03	NS
$P\text{-}PO_4^{3-}$	(kg ha^{-1} $month^{-1}$)	0.068	−0.0007	0.0004	−0.21	NS

Table 4. Throughfall balance of elements in particular tree stands. Retention (negative values) and leaching (positive values) of elements by forest canopies are given in percent of atmospheric input. Results were calculated from mean data from particular sampling dates during the growing seasons of 1998 and 2000. NS – change not significant (*P*> 0.05); $^{*}P$ <0.05, $^{**}P$ <0.01, $^{***}P$ <0.001, n = 13 (for all tree stands, n = 65).

Parameter	All stands	Pine	Birch	Locust tree	Alder	Oak
water	−19***	−15**	−14**	−16**	−17*	−30**
H^+	NS	NS	NS	NS	NS	−98*
Na^+	−28***	NS	−35**	NS	−28**	−42**
$N\text{-}NH_4^+$	−58***	−70*	NS	NS	−79*	NS
K^+	110***	NS	NS	268**	65**	138**
Mg^{2+}	77***	NS	NS	NS	192***	97**
Ca^{2+}	19**	NS	NS	41*	47*	NS
Cl^-	49***	NS	NS	95**	73***	NS
$N\text{-}NO_3^-$	−31***	NS	−26***	−28***	−40***	−41***
$S\text{-}SO_4^{2-}$	−9**	NS	−22***	NS	−17***	−20**
$P\text{-}PO_4^{3-}$	−60***	−84*	NS	NS	−84*	NS
Zn^{2+}	−24***	NS	NS	NS	−29*	−54***
Cd^{2+}	−39***	NS	NS	NS	−64***	−76**
Pb^{2+}	NS	99*	NS	NS	NS	−52*
Cu^{2+}	−21***	NS	NS	NS	−28*	−45*

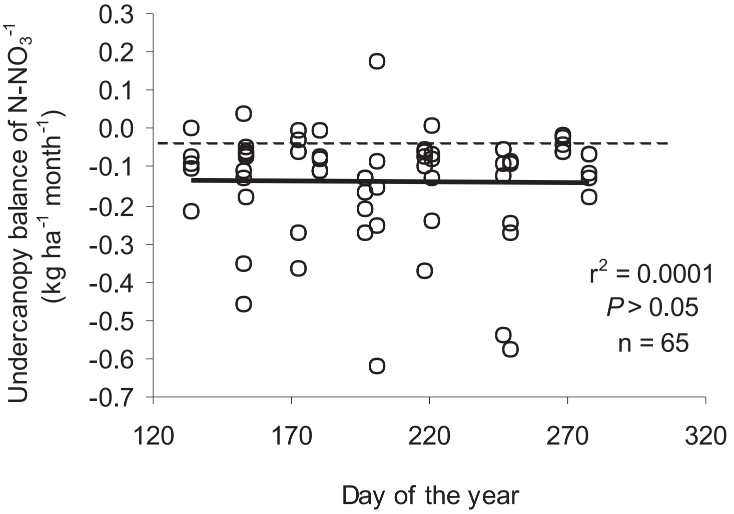

Fig. 3. Seasonal variability of the throughfall balance of nitrate-nitrogen. The relationship was based on data from all five studied tree stands obtained during vegetative seasons of the years 1998 and 2000.

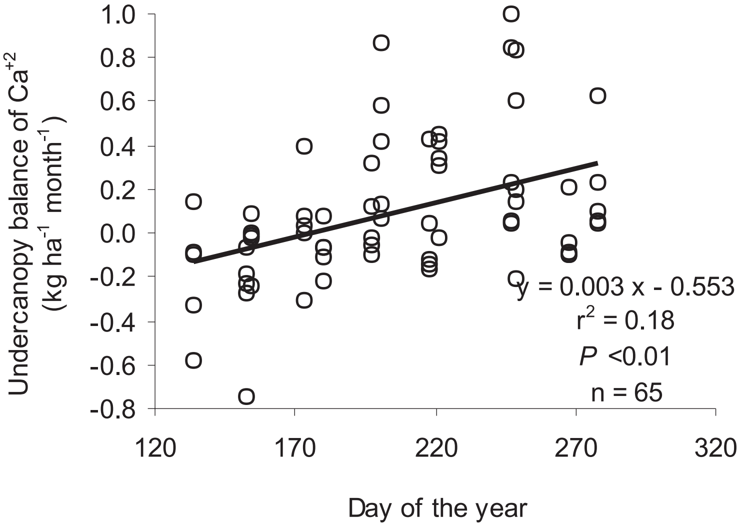

Fig. 4. Seasonal variability of the throughfall balance of calcium. The relationship was based on data from all five studied tree stands obtained during vegetative seasons of the years 1998 and 2000.

cantly from atmospheric load (Table 4). More statistically significant processes of retention and leaching were observed in birch and locust tree stands, though passive flow through forest canopies also dominated in these ecosystems (Table 4). Retention and leaching of elements were intense and statistically significant in forest canopies of alder and oak trees (Table 4).

It should be noted that differences between particular tree stands consisted in the significance or insignificance of a given process and not in the direction. Only lead, which generally flew passively trough forest canopies, was leached out in one forest (pine) and retained in the other (oak) (Table 4).

It was expected that tree species living in symbiosis with nitrogen-fixing organisms (alder and locust) would less carefully manage nitrogen than other species (oak, birch, pine) and therefore more weakly retain the ionic forms delivered from the atmosphere. To determine whether this hypothesis was supported, the retention of total inorganic nitrogen and nitrate and ammonium ions was compared between nitrogen-fixing and non-fixing tree species. The comparison showed that inorganic nitrogen as well as nitrates and ammonium ions were retained in both groups of trees at similar intensities and with no statistically significant differences (Table 5).

A comparison of total nitrogen (NO_3^- + NH_4^+) retention by particular tree species showed that, in spite of specific differences in the retention of particular ions, the total pool of retained nitrogen was similar. Nitrogen was most intensely taken up by the alder tree stand and least intensely by the oak forest; the differences were statistically significant only between these two tree species (Table 6).

Tests to determine which form of nitrogen load (rain *vs.* aerosol-gaseous) was retained in forest canopies showed that ammonium from the rain load was retained in canopies of all tree species, as was the aerosol-gaseous load form in birch, alder, and pine (Table 7). Nitrates retained in forest canopies originated exclusively from the aerosol-gaseous load, as that from rain was lost (Table 7). Pine and locust tree stands, however, retained neither aerosol-gaseous nitrates nor rain-deposited nitrates (Table 7).

Seasonal differences in the intensity of interception or leaching of elements were also tested in all five tree stands. Similar to the general rules, in most cases the results were not statistically significant. The only exception was the alder tree, from which calcium, magnesium and chlorine were much more intensively leached in autumn than in spring (Table 8).

Table 5. Comparison of the intensity of nitrogen retention by forest canopies of species living in symbiosis with nitrogen-fixing microorganisms (alder and locust tree) with species lacking such symbiosis (pine, birch, and oak) (kg ha^{-1} $month^{-1}$). Significance of differences was calculated with the Student t-test for independent variables. n = 26 and 39, respectively. TIN – total inorganic nitrogen (N-NO_3^- + N-NH_4^+); NS – non-significant differences ($P > 0.05$).

Form of nitrogen	Symbiotic		Non-symbiotic			
		±SD		±SD	t	*P*
TIN	−0.69	±1.11	−0.61	±0.98	−0.32	NS
N-NO_3^-	−0.15	±0.11	−0.12	±0.12	−0.96	NS
N-NH_4^+	−0.54	±1.06	−0.49	±1.00	−0.21	NS

Table 6. Retention of total inorganic nitrogen (N-NO_3^- + N-NH_4^+) in forest canopies of particular ecosystems (kg ha^{-1} $month^{-1}$). Significance of differences was calculated with the Student t-test for dependent variables. NS – non-significant differences ($P > 0.05$).

Tree species	Retention	±SD	Tree species	Retention	±SD	t	*P*
Pine	−0.70	±1.00	Birch	−0.74	±1.21	0.53	NS
Oak	−0.38	±0.71	Locust tree	−0.54	±1.21	0.73	NS
Birch	−0.74	±1.21	Alder	−0.85	±1.02	0.98	NS
Locust tree	−0.54	±1.21	Pine	−0.70	±1.00	1.37	NS
Oak	−0.38	±0.71	Birch	−0.74	±1.21	1.59	NS
Oak	−0.38	±0.71	Pine	−0.70	±1.00	1.92	NS
Locust tree	−0.54	±1.21	Alder	−0.85	±1.02	1.92	NS
Pine	−0.70	±1.00	Alder	−0.85	±1.02	1.94	NS
Locust tree	−0.54	±1.21	Birch	−0.74	±1.21	2.06	NS
Oak	−0.38	±0.71	Alder	−0.85	±1.02	2.76	<0.05

Table 7. Coefficients of linear regression of retention (negative values) or leaching (positive values) of inorganic nitrogen from forest canopies for input in aerosol-gaseous form and rain. Calculations were based on mean values from particular sampling dates during the growing seasons of 1998 and 2000. Lack of significance of the multifactor analysis was confirmed by forward and backward stage selection. b – regression coefficient.

Type of input	Pine			Birch			Locust tree			Alder			Oak		
of N-NO_3^-	b	SE	*P*	b	SE	*P*	b	SE	*P*	b	SE	*P*	b	SE	*P*
Aerosol-gaseous input	0.350	±0.938	NS	–0.774	±0.311	<0.05	0.373	±0.735	NS	–1.347	±0.544	<0.01	–0.585	±0.182	<0.001
Rainfall input	0.070	±0.327	NS	0.095	±0.109	NS	–0.229	±0.256	NS	0.225	±0.340	NS	–0.449	±0.320	NS
Regression constant	–0.091	±0.067	NS	–0.025	±0.022	NS	–0.084	±0.052	NS	0.015	±0.049	NS	–0.015	±0.035	NS
			NS $r^2 = 7\%$			<0.05 $r^2 = 47\%$			NS $r^2 = 8\%$			<0.01 r^2=59%			<0.001 $r^2 = 91\%$
Type of input of N-NH_4^+															
Aerosol-gaseous input	–0.910	±0.156	<0.001	–1.054	±0.208	<0.001	–0.677	±0.341	NS	–1.197	±0.192	<0.001	–0.390	±0.205	NS
Rainfall input	–0.794	±0.225	<0.01	–0.743	±0.300	<0.05	–1.307	±0.449	<0.001	–0.835	±0.170	<0.001	–1.364	±0.215	<0.001
Regression constant	0.126	±0.058	NS	0.184	±0.078	<0.05	0.384	±0.127	<0.05	0.147	±0.051	<0.05	0.263	±0.116	NS
			<0.001 $r^2 = 97\%$			<0.001 $r^2 = 96\%$			<0.001 $r^2 = 89\%$			<0.001 r^2=97%			<0.001 $r^2 = 88\%$

Table 8. Correlation coefficients (r) between the throughfall balance of elements and calendar day. Relationships were based on data collected in the growing seasons of 1998 and 2000. n = 13 (for all tree stands, n = 65). Significance: * *P* <0.05, ** *P* <0.01, *** *P* <0.001, NS – non-significant relationship (*P*> 0.05).

Element	All stands	Pine	Birch	Locust tree	Alder	Oak
Na^+	NS	NS	NS	NS	NS	NS
N-NH_4^+	NS	NS	NS	NS	NS	NS
K^+	NS	NS	NS	NS	NS	–0.60*
Mg^{2+}	NS	NS	NS	NS	0.83***	NS
Ca^{2+}	0.43**	NS	NS	NS	0.73**	0.64*
Cl^-	NS	NS	NS	NS	0.69**	NS
N-NO_3^-	NS	NS	NS	NS	NS	NS
S-SO_4^{2-}	NS	NS	NS	NS	NS	NS
P-PO_4^{3-}	NS	NS	NS	NS	NS	NS

5. DISCUSSION

The methods applied in this study measured the different loads of ions to particular forest ecosystems, allowing for precise determination of the intensity of processes taking place within the canopy.

It is commonly assumed that coniferous forests acidify throughfall (Parker 1990) and that deciduous forests neutralise acid rains (Freedman and Prager 1986). Neutralisation might occur through an ion exchange in which retained hydrogen ions are exchanged for NH_4^+, K^+ or Mg^{2+} (Potter *et al.* 1991). Although these cations were leached from canopies, hydrogen ion concentrations did not change after passage through tree canopies.

Most field studies have shown a passive flux of sulphate-sulphur through forest canopies (Urlich 1983, Lindberg and Garten 1988). Some studies, however, were based on radioactive sulphur isotopes and demonstrated the possibility of leaching small amounts of this element from plants (Lindberg *et al.* 1992, Mitchel *et al.* 1992). Others suggested the opposite process, or interception, as the presence of atmospheric sulphur was demonstrated in pine needles (Manninen *et al.* 1998). The field measurement methods and statistical analysis used in the present study showed that sulphate-sulphur from aerosol-gaseous loads was retained in forest canopies, while rainfall leached this element as it passed through the canopy. Similar results were obtained by Dutch researchers using different methods: experiments using the ^{35}S isotope and the model of stomatal absorption showed a retention of gaseous SO_2 through stomata and simultaneous leaching of SO_4^{2-} (of soil origin) from tree crowns (Draaijers *et al.* 1997). Such antagonistic actions of retention and leaching might result in a nearly equilibrated sulphur balance. In that case, measurements might erroneously suggest a lack of either process and, as reported by most authors, passive flow of sulphur through the canopy.

Significant contributions of aerosol-gaseous loads to the retention of both forms of nitrogen (NO_3^- and NH_4^+) were described by in canopies of beech (Stachurski and Zimka 2002), and of birch (Kram 2008). The present study confirms this finding, but also shows the lesser importance of rain loads in the retention of nitrate-nitrogen (Table 2). This may be evidence for a decisive role of aerosol-gaseous loads in supplying trees with airborne nitrogen.

Environmental resources and the nitrogen content in leaves are also of importance for the retention of nitrogen in forest canopies. According to Tietema *et al.* (1998), at high concentrations of nitrogen in leaves and soil, the element is not retained, but rather is leached out of tree crowns. Contrary to expectations, nitrogen in the Kampinos National Park was intensively taken up by alder, the species that theoretically should have the highest trophic status given its rich habitat and symbiosis with nitrogen-fixing organisms. A lower intensity of nitrogen uptake was observed in pine, the species growing in the poorest soils and without nitrogen-fixing symbionts.

Three types of airborne element management can be distinguished in the studied forest ecosystems. The first type, with intensive retention and leaching of elements, was characteristic of alder and oak tree stands. The second, in which these processes were limited or absent, was found in pine forest. The third type, of intermediate intensity, was typical of birch and locust tree stands.

A greater intensity of element leaching from the canopies of oak than from those of pine and Colorado Douglas fir was previously described (Draaijers *et al.* 1992). Studies carried out in Sweden with several deciduous tree species pointed to the relationship between leaching of elements from forest canopies and soil richness. The richer the soil, the greater was the contribution of many elements in throughfall. Soil richness was more important in that case than the tree species (Norden 1991).

Nevertheless, genetic adaptations of different species to different soil conditions and nutrient availabilities are likely to be very important. For example, pine trees that usually live in nutrient-poor conditions protect against nutrient loss by isolating themselves from the surrounding environment. Pine needles have thicker cuticles and a smaller number of stomata than deciduous species. Such protection against loss of calcium, magnesium and potassium has the secondary effect of decreasing nitrogen retention. In contrast, oaks living in nutritionally rich conditions could permit the loss of some elements in exchange for nitrogen.

6. CONCLUSIONS

Atmospheric deposition was modified during flow through forest canopies:

- NH_4^+, PO_4^{3-}, Cd^{2+}, NO_3^-, Na^+, Zn^{2+}, Cu^{2+} and SO_4^{2-} were retained,
- K^+, Mg^{2+}, Cl^- and Ca^{2+} were leached out,
- H^+ and Pb^{2+} flowed through passively,
- SO_4^{2-} was both retained in and leached out of canopies.

Ammonium ions retained in tree crowns originated from both, rainfall and aerosol-gaseous, forms of load, while nitrate ions came only from the aerosol-gaseous form.

For the majority of elements, retention and leaching proceeded at similar intensities across the whole vegetative season. Notably, the intensity of calcium leaching was low in the spring, but increased to attain its maximum in the period when dry leaves were falling.

Processes of retention or leaching of elements in tree crowns proceeded robustly in deciduous trees like alder and oak and less strongly or not at all in pine forest canopies.

Tree species that fix atmospheric nitrogen (alder, locust tree) intercepted atmospheric load of nitrogen with an equal efficiency as other tree species.

Intensification of calcium, magnesium and chlorine leaching during the growing season was more distinct in alder than in other tree species.

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7. REFERENCES

Alcock M.R., Morton A.J. 1985 – Nutrient Content of Throughfall and Stem-flow in woodland Recently Established on Heathland – J. Ecol. 73: 625–632.

Andrzejewska A. 2003 – Klimat [Climate] (In: Kampinoski Park Narodowy [Kampinoski National Park] Ed. R. Andrzejewski) – Izabelin, pp. 41–68 (in Polish).

Carlisle A., Brown A.H.F., White E.J. 1966 – The Organic Matter and Nutrient Elements in the Precipitation beneath a Sessile Oak (*Quercus petraea*) canopy – J. Ecol. 54: 87–98.

Chason J.W., Baldocchi D.D., Huston M.A. 1991 – A comparison of direct and indirect methods for estimating forest canopy leaf area – Agric. For. Meteorol. 57: 107–128.

Cronan G.S., Reiners W.A. 1983 – Canopy processing of acid precipitation by coniferous and hardwood forest in New England – Oecologia, 59: 216–223.

Draaijers G.P.J., Erisman J.W., Van Leeuwen N.F.M., Römer F.G., Te Winkel B.H., Veltkamp A.C., Vermeulen A.T., Wyers G.P. 1997 – The impact of canopy exchange on differences observed between atmospheric deposition and throughfall fluxes – Atmos. Environ. 31: 387–397.

Eaton J.S., Likens G.E., Bormann F.H. 1973 – Throughfall and stemflow chemistry in a northern hardwood forest – J. Ecol. 61: 495–508.

Freedman B., Prager U. 1986 – Ambient bulk deposition, throughfall, and stemflow in a variety of forest stands in Nova Scotia – Can. J. For. Res. 16: 854–860.

Gower S.T., Norman J.M. 1991 – Rapid estimation of leaf area index in conifer and broadleaf plantations – Ecology, 72: 1896–1900.

Houle D., Ouimet R., Paquin R., Laflamme J.-G. 1999 – Interactions of atmospheric deposition with a mixed hardwood and a coniferous forest canopy at the Lake Clair Watershed (Duchesnay, Quebec) – Can. J. For. Res. 29: 1944–1957.

Igawa M., Kase T., Satake K., Okochi H. 2002 – Severe leaching of calcium ions from fir needles caused by acid fog – Environ. Pollut. 119: 375–382.

Kram K.J. 2001 – Influence of leaf area on atmospheric input of elements to the ecosystems of the Kampinos National Park (central Poland) – Pol. J. Ecol. 49: 327–337.

Kram K.J. 2005 – Bulk precipitation and aerosol-gaseous input of elements in the forested area of coastal region (Pomerania, north Poland) – Pol. J. Ecol. 53: 261–268.

Kram K.J. 2008 – Nitrogen deposition and flux through birch stands (*Betula pubescens* Ehrh.) in the Kampinos National Park (Central Poland) – Pol. J. Ecol. 56: 605–612.

Lindberg S.E., Garten C.T. Jr 1988 – Sources of sulphur in forest canopy throughfall – Nature, 336: 148–151.

Lindberg S.E., Johnson D.W., Bondietti E.A. 1992 – Background on Research Sites and Methods (In: Atmospheric Deposition and Forest Nutrient Cycling, Eds: D.W. Johnson, S.E. Lindberg) – Ecological Studies

91. Springer-Verlag, New York, NY USA, pp. 8–26.

Lindberg S.E., Lovett G.M., Richter D.D., Johnson D.W. 1986 – Atmospheric Deposition and Canopy Interactions of Major Ions in a Forest – Science, 231: 141–145.

Lovett G.M., Lindberg S.E. 1993 – Atmospheric deposition and canopy interactions of nitrogen in forests – Can. J. For. Res. 23: 1603–1616.

Lovett G.M., Lindberg S.E., Richter D.D., Johnson D.W. 1985 – The effects of acidic deposition on cation leaching from three deciduous forest canopies – Can. J. For. Res. 15: 1055–1060.

Lovett G.M., Weathers K.C., Arthur M.A., Schulth J.C. 2004 – Nitrogen cycling in a hardwood forest: Do species matter? – Biogeochemistry, 67: 289–308.

Madgwick H.A.I., Ovington J.D. 1959 – The Chemical Composition of Precipitation in Adjacent Forest and Open Plots – Forestry, 32: 14–22.

Manninen S., Huttonen S., Peramaki P. 1998 – Effect of ambient SO_2 levels on S fractions in *Pinus sylvestris* foliage growing in the subarctic – Scand. J. For. Res. 13: 306–316.

Mecklenburg R.A., Tukey H.B., Morgan J.V. 1966 – A mechanism for the leaching of calcium from foliage – Plant Physiol. 41: 610–613.

Mitchel M.J., Burke M.K., Shepard J.P. 1992 – Seasonal and spatial patterns of S, Ca and N dynamics of a Northern hardwood forest ecosystem – Biogeochemistry, 17: 165–189.

Mohren G.M.J., Van den Burg J., Burger F.W. 1988 – Phosphorus deficiency induced by nitrogen input in Douglas fir in the Netherlands – Plant Soil, 95: 91–200.

Morris D.M., Gordon A.G., Gordon A.M. 2003 – Patterns of canopy interception and throughfall along a topographic sequence for black spruce dominated forest ecosystems in northwestern Ontario – Can. J. For. Res. 33: 1046–1060.

Neirynck J., Kowalski A.S., Carrara A., Genouw G., Berghmans P., Ceulemans R. 2007 – Fluxes of oxidised and reduced nitrogen above a mixed coniferous forest exposed to various nitrogen emission sources – Environ. Pollut. 149: 31–43.

Norden U. 1991 – Acid Deposition and Throughfall Fluxes of Elements as Related to Tree Species in Deciduous Forests of South Sweden – Water Air Soil Pollut. 60: 209–230.

Parker G.G. 1983 – Throughfall and stemflow in the forest nutrient cycle – Adv. Ecol. Res. 13: 57–133.

Parker G.G. 1990 – Evaluation of dry deposition, pollutant damage, and forest health with throughfall studies (In: Mechanisms of forest response to acid deposition, Eds: A.A. Lucier, S.G. Haines) – Springer-Verlag, New York-Berlin-Heidelberg-London-Paris-Hong Kong, pp. 5–32.

Parzych A., Astel A., Trojanowski J. 2008 – Fluxes of biogenic substances in precipitation and throughfall in woodland ecosystems of Slowinski National Park – Arch. Environ. Prot. 34: 13–24.

Potter C.S., Ragsdale H.L., Swank W.T. 1991 – Atmospheric deposition and foliar leaching in regenerating southern Appalachian forest canopy – J. Ecol. 79: 97–115.

Robertson S.M.C., Hornung M., Kennedy V.H. 2000 – Water chemistry of throughfall and soil water under four tree species at Gisburn, northwest England, before and after felling – For. Ecol. Manage. 129: 101–117.

Roelofs J.G.M., Kempers A.J., Houdijk A.L.F.M., Jansen J. 1985 – The effect of air-borne ammonium sulphate on *Pinus nigra* var. *maritima* in the Netherlands – Plant Soil, 84: 45–56.

Stachurski A., Zimka J.R. 1975 – Methods of studying forest ecosystems: leaf area, leaf production and withdrawal of nutrients form leaves of trees – Ekol pol. 23: 637–648.

Stachurski A., Zimka J.R. 1984 – The budget of nitrogen dissolved in rainfall during its passing through the crown canopy in forest ecosystems – Ekol. pol. 32: 191–218.

Stachurski A., Zimka J.R. 2000 – Atmospheric input of elements to forest ecosystems: a method of estimation using artificial foliage placed above rain collectors – Environ. Pollut. 110: 345–356.

Stachurski A., Zimka J.R. 2002 – Atmospheric deposition and ionic interactions within a beech canopy in the Karkonosze Mountains – Environ. Pollut. 118: 75–87.

Stadler B., Solinger S., Michalzik B. 2001 – Insect herbivores and the nutrient flow from the canopy to the soil in coniferous and deciduous forests – Oecologia, 126: 104–113.

Stenlid S. 1958 – Salt losses and restitution of salts in higher plants (In: Encyclopaedia of plant physiology, Ed. W. Ruhland) – Springer Verlag, Berlin-Göttingen-Heidelberg, pp. 615–637.

Tietema A., Boxman A.W., Bredemeier M., Emmett B.A., Moldan F., Gundersen P., Schleppi P., Wright R.F. 1998 – Nitrogen saturation experiments (NITREX) in coniferous forest ecosystems in Europe: a summary of results – Environ. Pollut. 102, S1: 433–437.

Tukey H.B., Morgan J.V. 1963 – Injury to foliage and its effect upon the leaching of nutrients from aboveground plant parts – Plant Physiol. 16: 557–564.

Ulrich B. 1983 – Interaction of forest canopies with atmospheric constituents: SO_2, alkali and earth alkali cations and chloride (In: Effects of Accumulation of Air Pollutants in Forest Ecosystems, Eds: B. Ulrich, J. Pankrath) – D. Reidel Publ., Dordrecht, pp. 33–45.

Voigh G.K. 1960 – Alteration of the composition of rainwater by trees – Am. Midl. Nat. 63: 321–326.

White E.J., Turner F. 1970 – A method of estimating income of nutrient in a catch of airborne particles by woodland canopy – J. Appl. Ecol. 7: 441–459.

Žaltauskaitė J., Juknys R. 2007 – Atmospheric deposition and canopy interactions in urban Scots pine forest – Baltic Forestry, 13: 68–73.

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