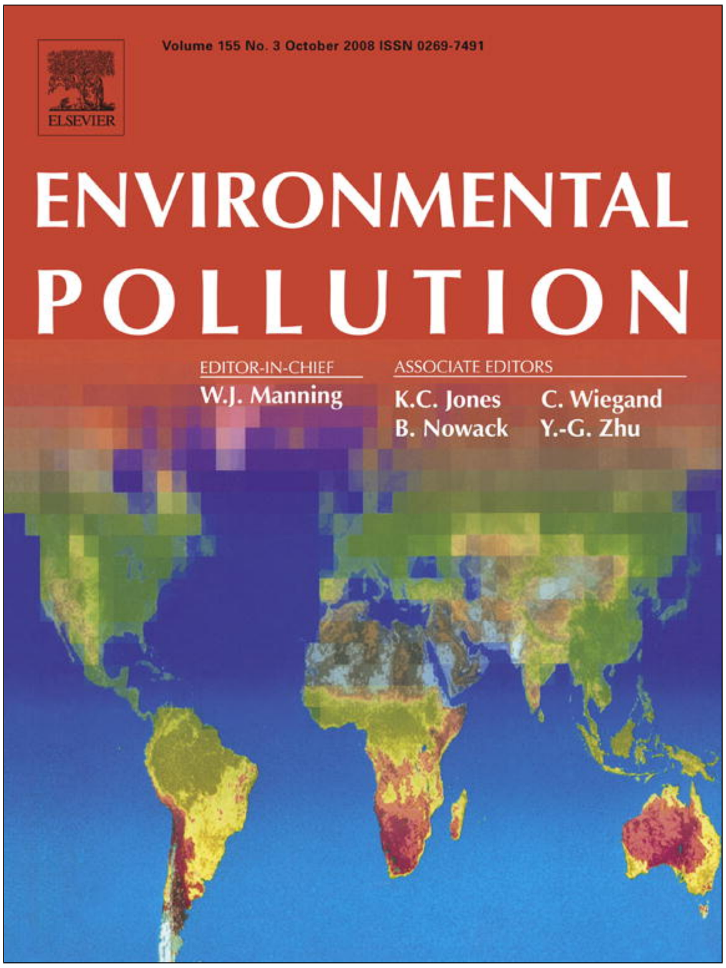
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Throughfall chemistry in a spruce chronosequence in southern Poland

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Ionic concentrations in throughfall and canopy leaching increase whereas acid neutralizing capacity and alkalinity decrease with stand age, which may have implications for the vitality of spruce stands as they age.

Abstract

The chemical composition of throughfall and canopy leaching, as well as the acid neutralizing capacity and alkalinity depended on the age of Norway spruce (*Picea abies* Karst) stands and season of the year. A higher amount of sulphur and strong acids was deposited to the soil in the older age classes. Concentrations of SO_4^{2-}, K^+, H^+, Mn^{2+}, Fe^{2+} and Zn^{2+} in throughfall were higher than in bulk precipitation in any season. This suggests that these ions were washed out or washed from the surface of needles and/or barks. The other ions NO_3^-, NH_4^+, Ca^{2+} and Mg^{2+} were retained by the canopy, in particular Ca^{2+} and Mg^{2+} during the growing season in young stands. Principal component analysis identified five factors responsible for the data structure and suggested the major anthropogenic emission sources were acidic emission ($SO_4^{2-} + NO_3^-$), heavy metals–dust particles ($Fe^{2+} + Mn^{2+} + Zn^{2+}$), ammonium ($NH_4^+$) and H^+, while the natural-origin emission was mineral dust ($Na^+ + K^+ + Ca^{2+} + Mg^{2+}$).

Keywords: Canopy leaching; Acid neutralizing capacity (ANC_{aq}); Alkalinity (ALK); Principal component analysis (PCA); Norway spruce stands

1. Introduction

Cycling of elements in Norway spruce (*Picea abies* Karst) stands, which are affected by industrial emissions, is still a subject of active research (Małek and Astel, 2007). The retention of considerable levels of contaminants by the canopy and their removal or washout from needles by rainfall cause changes in the concentration of anions and cations reaching the soil (Małek, 2004). Earlier investigations were based on both relatively small forested catchments, such as Brenna (Staszewski et al., 1999; Bytnerowicz et al., 1999), and larger ones, such as the Black and the White Vistula (Wróbel, 1998). Their goal was to estimate volume and quality of the deposition of elements and their outflow from the catchment. Several case studies comparing elemental cycling in beech and spruce stands documented that, in general, deposition input to soil and the leaching of sulphur (S), nitrogen (N) and protons are higher in spruce stands (Rothe et al., 2002). Those studies did not usually take into account different development stages of stands or their spatial distribution in catchments. In a couple of the few studies, Małek (2004) investigated the effect of various development stages of spruce stands in the Silesian Beskid and Jussy et al. (2004) compared two spruce age classes (45 and 90 years old) in the Vosges Mountain. Jussy et al. (2004) found lowest N deposition in throughfall and litterfall as well as N leaching below root depth in the youngest spruce stand, while Małek (2004) found systematically increase of concentration and amount of SO_4^{2-} and decrease of pH in throughfall waters with increasing age.

The present study examined the throughfall chemistry in a spruce chronosequence (11–116 years) in the Dupniański Stream Catchment in the Silesian Beskid, southern Poland,

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between 1999 and 2003. The objectives were to determine: (i) whether the chemical composition of throughfall water, canopy leaching, acid neutralizing capacity and alkalinity depends on the age of the spruce stands and season of the year; and (ii) whether the emission sources of the group of pollutants measured in the bulk-precipitation and throughfall can be identified.

2. Materials and methods

2.1. Site description

The Dupniański Stream Catchment of 1.68 km^2 area is located in southern Poland in the Silesian Beskid Mts. (49°34′N, 18°50′E) not far from the main industrial centers. This region of the Polish part of the Carpathian Mountains is affected by air pollution (Bytnerowicz et al., 2002; Maňkovská et al., 2002; Małek et al., 2005). The catchment is covered with Norway spruce stands of different ages growing on dystric cambisols developed on Istebna sandstone. The equipment for measuring throughfall in pure spruce stands (one monitoring plot in each age class) was set up in 1998. According to Polish procedures (ZHL, 2003), from 1st to 6th age-class stands were investigated. Only the 1st, 2nd, 5th and 6th age classes were found in this catchment. In 1999, they were 11, 24, 91, and 116 years old, respectively. The characteristics of the spruce stands are in Table 1.

2.2. Sampling

The studies were conducted in 1999–2003 following standard methods (ICP-Forest Manual, 1998; Małek, 2004). A bulk precipitation (BP) sampler was installed in the middle of the catchment at an elevation of 725 m, within 500 m from the throughfall sampling point. During the vegetation season, i.e. from 1st May to 30th October (the same year), BP samples were collected with special collectors (5 units with 15 cm inlet diameter each) installed 0.5 m above ground in an open area, and connected to a plastic tube with an outlet joining a container and a measuring device installed in a bunker. In winter, i.e. from 1st of November (the previous year) to 30th of April (the following year), six collectors (polyethylene, chemically neutral snow bags with 15 cm inlet diameter each) were installed at 1.3 m above ground in the open area. Those samplers were placed at a distance of 120–150 m from the forest edge. In order to measure volume and quality of throughfall (TF), water was sampled from a sampling system (15 collectors, each with a 15 cm inlet diameter) installed under the canopy, similar to the one installed in the open area during the vegetation season. In winter, six collectors (polyethylene, chemically neutral snow bags with 15 cm inlet diameter each) were installed at 1.3 m above ground, in spruce stands of different age classes, described in detail by Małek (2004). The sampling was performed on the first day of each month.

Table 1
Descriptive characteristics of Norway spruce (*Picea abies* Karst) stands with throughfall plots in the Dupniański Stream Catchment

Age-class plot	Age [year]	Elevation [m a.s.l.]	Diameter [cm]	Height [m]	Number of trees [no ha^{-1}]	LAI (Leaf Area Index)
Year 1999						
1st	11	720	2.2	1.5	20,150	5.0
2nd	24	700	11.7	12.6	2611	5.3
5th	91	660	39.7	37.8	382	5.4
6th	116	700	42.1	36.6	414	5.5
Year 2003						
1st	16		3.6	5	13,758	5.1
2nd	29		14.7	16.2	2070	5.3
5th	96		42.1	39.1	350	5.4
6th	121		45.5	38.8	330	5.5

2.3. Chemical analyses

Water was analyzed using Dionex-320 ion chromatograph (Dionex Corp., Sunnyvale, CA, USA) to determine the concentration of: Cl^-, NO_3^-, SO_4^{2-}, F^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} and Zn^{2+}. A low-pH acid rain sample from southern Ontario (Canada), RAIN.97 – No 409, served as a certified reference material (CRM). When the concentration of analytes was below the limit of detection (LOD), the value of one-third LOD was used in the data set due to chemometric requirements (Astel et al., 2004). Abandon of replacement procedure causes a necessity of particular variable elimination and significantly reduces informative abilities of data set. Replacement values were used for K^+ (0.3% of total samples), Mg^{2+} (1%), Zn^{2+} (9.7%), Mn^{2+} (5.3%), Fe^{2+} (25%), and F^- (49%). In spite of the high number of replacements, Fe^{2+} was subjected to chemometrical evaluation because of the small value of the mean and the median, while F^- was excluded from the analyses.

The canopy leaching (CL) for base cations (K^+, Ca^{2+}, Mg^{2+} and Mn^{2+}) was determined as balance of chemical compound stream passing through the canopy (Ulrich, 1983; Bredemeier, 1988; Draaijers and Erisman, 1995) in agreement with the following formula:

$$CL_{BC}\left[\text{kg ha}^{-1}\ \text{yr}^{-1}\right] = TF_{BC} - \left(BP_{BC} + \left((TF_{Na} - BP_{Na})/BP_{Na}\right)\cdot BP_{BC}\right)$$

(TF – throughfall water, BP – bulk precipitation BC – base cation).

The acid neutralizing capacity – ANC_{aq} (Reuss and Johnson, 1986; Heinrichs et al., 1994) and alkalinity – ALK (Harriman et al., 1990; Block et al., 2000) were calculated by means of the following equations:

$$ANC_{aq}\left[\text{meq L}^{-1}\right] = K^+ + Na^+ + 2Mg^{2+} + 2Ca^{2+} - NO_3^- - Cl^- - 2SO_4^{2-}$$

$$ALK\left[\text{mmol L}^{-1}\right] = \left(K^+ + Na^+ + Mg^{2+} + Ca^{2+}\right) - \left(NO_3^- - Cl^- - SO_4^{2-}\right)$$

2.4. Statistical analyses

Statistica 6.0 for Windows was used for chemometric data mining (StatSoft Inc., 2001; http://www.statsoft.com). Before evaluation, data were normalized by logarithmic transformation in the form $x' = \log(x)$ for ion concentration, due to the considerable asymmetry of values. The effect of stand age on throughfall chemistry was analyzed by analysis of variance (ANOVA). The whole set was divided into two subsets for winter (from November to April) and the growing season (from May to October).

Differences in canopy leaching were tested with the non-parametric Kruskal–Wallis's test which can be used for relatively small groups of results (in this case $n = 60$ for single age of throughfall waters related to whole year and $n = 30$ for single age of throughfall waters related to growing or winter season) drawn from a population that is not normally distributed. Differences in canopy leaching for each combination of subsequent age groups were tested by the non-parametric Mann–Whitney U-test ($p = 0.05$).

The capacity of forest canopies of stands of different ages to modify ionic solutions as they move through the canopy was evaluated by Principal Component Analysis (PCA). PCA as a multivariate statistical method is commonly used to find a small number of factors from a data set of many correlated variables (Brereton, 2003). In monitoring datasets, PCA allows to reduce the number of parameters which are necessary to ecosystem description and thus to mathematical modeling and interpretation. The original data matrix is decomposed into the product of a matrix of factor loadings and a matrix of factor scores plus a residual matrix. The residual matrix contains the part of variance of the data set that cannot be explained by common factors, e.g. analytical uncertainties or feature-own variances. On the basis of the correlation matrix, orthogonal factors, sorted by descending order (Marengo et al., 1995) are extracted solving an eigenvalue problem. In general, the number of extracted factors is lower than the number of measured features. After rotation of the factor loading matrix, the factors can often be interpreted i.e. as origins or common sources of pollutants. In the present study, the autoscalling step was additionally performed prior to PCA evaluation. The validation of the obtained PCA models was performed by consideration of the scree plot (empirical testing) and only those principal components were included in the model which possesses eigenvalue greater than or close to 1. Significance of the component model was additionally tested by applying Bartlett's statistics (Mackiewicz and Ratajczak, 1993). A model with three components was selected for the 5th forest stand age class category, four PCs for BP and five PCs for the 1st, 2nd and 6th forest age class categories, which in general confirms scree plot analysis results. Before final interpretation, factors obtained by PCA were rotated using the orthogonal Varimax Rotation.

3. Results

Five-year average BP of sulphur ($S-SO_4^{2-}$) was 13.7 kg ha^{-1} yr^{-1} in the catchment. The deposition of S via throughfall increased from the 1st to the 5th age class, especially in winter (Table 2), while between 5th and 6th any meaningful changes were not observed. The sum of the strong acids ($S-SO_4^{2-}$ and $N-NO_3^-$) in BP was around 22.7 kg ha^{-1} yr^{-1} and in TF it was around 24.0 in the oldest age classes. After passing through the canopy, pH decreased. This decrease was stronger with increasing stand age, especially in the winter season.

Concentrations of SO_4^{2-}, K^+, H^+, Mn^{2+}, Fe^{2+} and Zn^{2+} in TF were higher than in BP over the whole year, and both growing and winter seasons. The other ions NO_3^-, NH_4^+, Ca^{2+} and Mg^{2+} (especially during the growing season in two young stands) were retained by the canopy (Table 2, Figs. 1 and 2).

For most of the variables (Cl^-, NO_3^-, NH_4^+, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, H^+) stand age resulted in statistically significant differences (Table 3). In the whole year, there were significant differences between the youngest (1st) and oldest (5th and 6th) age classes for most of the elements and water volume, and between the 2nd age class and the 6th age class for all investigated variables excluding Na^+, K^+ and Fe^{2+}. Only a few differences were noticed between the 2nd and 5th age classes (for Cl^-, NH_4^+, SO_4^{2-}, Mn^{2+} and H^+) and between the 1st and 2nd age classes (for Cl^-, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}). Between the 116 year old and the 91 year old stands a significant difference was noticed only for Mn^{2+}. In winter, there was a significant difference between the youngest (1st) and the oldest (6th and 5th) age classes and between the 2nd and the 6th age class for almost all analyzed elements and water amount. Only a few differences were noticed between the 2nd age class and the 5th age class (for NH_4^+, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+} and Mn^{2+}) and between the 1st and the 2nd age class (for SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+}). Between the oldest stands (5th and 6th age classes) a significant difference was noticed only for Mn^{2+}. In the growing period, there was a significant difference in water amount and in the concentration of anions and cations between the youngest age class and the oldest (6th and 5th) (except for K^+ and Fe^{2+}) and the 2nd age class and the oldest one

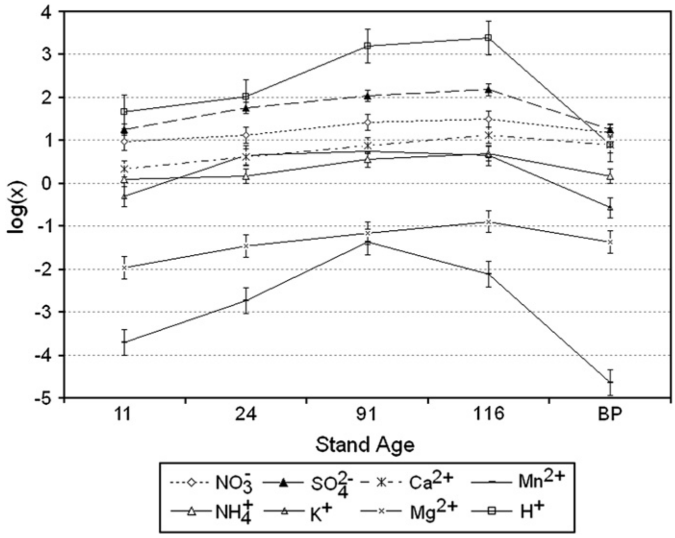

Fig. 1. Distribution of logarithms of mean concentrations of NO_3^-, NH_4^+, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+} [all ions in mg L^{-1}], and H^+ [μg L^{-1}] in throughfall for four Norway spruce (*Picea abies* Karst) forest stand ages and in bulk precipitation for the whole year (vertical lines represent confidence intervals, $p = 0.05$). The lines connecting the mean value points were drawn for illustrative purposes only and do not convey any mathematical meaning.

Table 2
Five-year averages (1999–2003) in bulk precipitation (BP) and throughfall water in Norway spruce (*Picea abies* Karst) stand age classes (1st, 2nd, 5th and 6th)[a] (in kg ha^{-1}) in the Dupniański Stream Catchment in different seasons

Kind of water	Volume	Cl^-	$N-NO_3^-$	$N-NH_4^+$	$S-SO_4^{2-}$	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	H^+	pH
	mm	kg ha^{-1}											g ha^{-1}	
Whole year														
BP	1072	19.70	9.02	12.24	13.67	6.71	9.17	32.73	4.41	0.52	0.17	2.34	70.82	5.18
1st	933	9.27	5.80	9.26	10.98	4.14	11.14	16.13	2.09	0.44	0.45	0.30	92.75	5.00
2nd	833	14.08	8.53	8.30	15.99	5.43	19.59	17.79	2.24	0.49	0.62	0.33	148.28	4.75
5th	696	10.25	6.84	9.61	17.54	3.22	16.00	19.12	2.71	0.34	1.98	0.41	332.30	4.32
6th	624	10.96	6.78	9.50	17.28	3.38	12.87	20.96	3.04	0.41	0.88	0.43	342.00	4.26
Growing season (May–October)														
BP	639	14.43	6.45	7.67	8.60	3.71	6.93	22.87	2.79	0.39	0.11	2.15	35.56	5.25
1st	475	4.41	3.31	5.11	6.88	2.12	9.47	9.53	1.26	0.25	0.35	0.17	43.48	5.04
2nd	412	7.73	5.07	4.95	7.75	3.41	15.10	9.37	1.11	0.27	0.38	0.12	41.71	4.99
5th	399	4.99	4.11	5.86	8.93	1.50	10.68	10.03	1.23	0.22	0.91	0.23	150.72	4.42
6th	364	4.92	3.52	5.82	8.69	1.51	8.52	11.20	1.64	0.25	0.38	0.21	140.52	4.41
Winter season														
BP	432	5.27	2.57	4.56	5.07	2.99	2.24	9.87	1.62	0.13	0.07	0.19	35.26	5.09
1st	457	4.87	2.50	4.15	4.10	2.02	1.68	6.60	0.83	0.19	0.10	0.13	49.27	4.97
2nd	421	6.35	3.46	3.35	8.24	2.01	4.48	8.42	1.13	0.22	0.25	0.20	106.57	4.60
5th	297	5.27	2.72	3.76	8.61	1.72	5.32	9.09	1.48	0.12	1.07	0.18	181.59	4.21
6th	260	6.05	3.27	3.67	8.59	1.87	4.36	9.76	1.40	0.16	0.51	0.22	201.49	4.11

[a] The four stand age categories correspond to 11, 24, 91 and 116 years old stands, respectively.

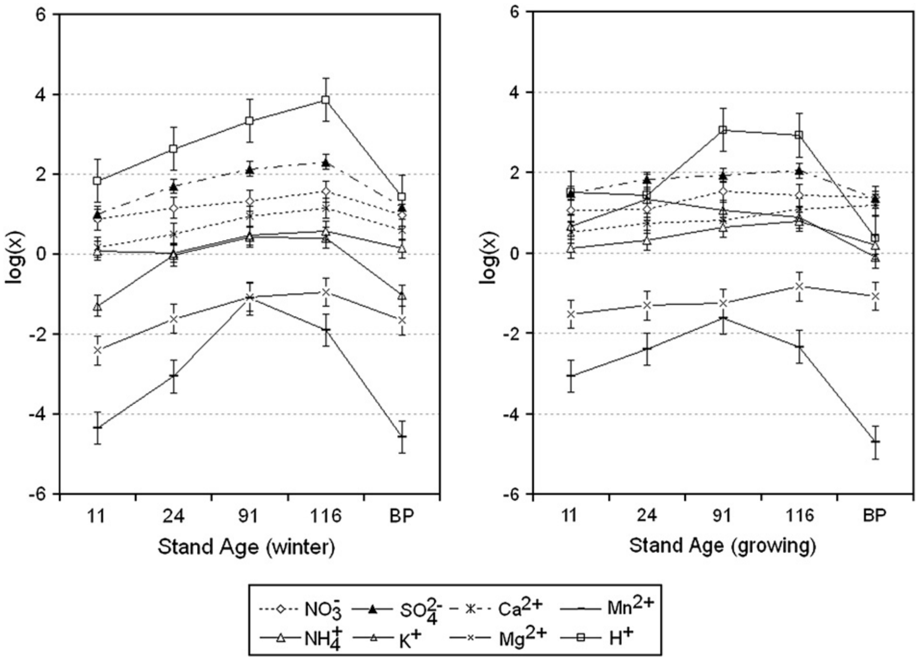

Fig. 2. Distribution of logarithms of mean concentration of NO_3^-, NH_4^+, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+} [all ions in mg L^{-1}], and H^+ [μg L^{-1}] in throughfall for four Norway spruce (*Picea abies* Karst) forest stand ages and in bulk precipitation in (a) winter and in the (b) growing season (May–October) (vertical lines represent confidence intervals, $p = 0.05$). The lines connecting the mean value points were drawn for illustrative purposes only and do not convey any mathematical meaning.

(except for NO_3^-, Na^+, Fe^{2+} and Mn^{2+}). Only a few significant differences were determined between the 2nd age class and the 5th age class (for SO_4^{2-}, K^+, Mn^{2+} and H^+) and between the 1st and the 2nd age classes (for Cl^- and SO_4^{2-}). Between the oldest stands (5th and 6th age classes) there were statistically significant differences for Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+} and Mn^{2+}.

In all age classes, the highest percentage of CL in TF in the whole year was found for Mn^{2+} (70–93%) and K^+ (51–75%) (Table 4). A lower percentage was determined for Mg^{2+} (11–35%) and the lowest for Ca^{2+} (0–17%). Both in the growing season and in the winter, the share of CL in throughfall of Mn^{2+} (78–93%) and K^+ (68–76%) was similar except the youngest age class, where the highest percentage was noted

Table 3
Age-dependent statistically significant differences ("*" yes or "–" not, $p \leq 0.05$, $N = 60$ for the whole year, $N = 30$ for the growing or winter season) among the mean values from 1999 to 2003

Kind of plot	Volume [mm m^{-2}]	Cl^- [mg L^{-1}]	NO_3^-	NH_4^+	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	pH	H^+ [mg L^{-1}]
Whole year														
1st–2nd	–	*	–	–	*	–	*	*	*	–	*	–	–	–
1st–5th	*	*	*	*	*	*	*	*	*	–	*	*	*	*
1st–6th	*	*	*	*	*	*	*	*	*	*	*	*	*	*
2nd–5th	–	*	–	*	*	–	–	–	–	–	*	*	*	*
2nd–6th	*	*	*	*	*	–	–	*	*	–	*	*	*	*
5th–6th	–	–	–	–	–	–	–	–	–	–	*	–	–	–
Growing season (May–October)														
1st–2nd	–	*	–	–	*	–	–	–	–	–	–	–	–	–
1st–5th	*	*	*	*	*	–	–	*	–	–	*	*	*	*
1st–6th	*	*	*	*	*	*	–	*	*	–	*	*	*	*
2nd–5th	–	–	–	–	*	–	*	–	–	–	*	*	*	*
2nd–6th	–	*	–	*	*	–	*	*	*	–	–	*	*	*
5th–6th	–	*	–	–	*	*	*	*	*	–	*	–	–	–
Winter season														
1st–2nd	–	–	–	–	*	–	*	*	*	*	*	–	–	–
1st–5th	*	*	*	*	*	–	*	*	*	*	*	*	*	*
1st–6th	*	*	*	*	*	*	*	*	*	*	*	*	*	*
2nd–5th	–	–	–	*	*	–	*	*	*	–	*	–	–	–
2nd–6th	*	*	*	*	*	–	*	*	*	–	*	*	*	*
5th–6th	–	–	–	–	–	–	–	–	–	–	*	–	–	–

Table 4
Five-year averages (1999–2003) of throughfall water (TF) and canopy leaching (CL) (in kg ha^{-1} yr^{-1}) and percent of leaching of ions from canopy in throughfall water in different stand age classes (1st, 2nd, 5th and 6th) in different seasons

Element	K^+			Ca^{2+}			Mg^{2+}			Mn^{2+}		
Age of stand	TF	CL	%	TF	CL	%	TF	CL	%	TF	CL	%
Whole year												
1st	11.144	5.673	51	16.126	−2.243	−14	2.090	−0.428	−20	0.445	0.312	70
2nd	19.588	14.756	75	17.786	0.049	0	2.240	0.250	11	0.622	0.517	83
5th	15.997	11.320	71	19.122	2.176	11	2.712	0.772	28	1.978	1.833	93
6th	12.873	8.367	65	20.962	3.523	17	3.035	1.049	35	0.881	0.769	87
Growing season												
1st	9.468	5.503	58	9.527	−1.653	−17	1.255	−0.159	−13	0.350	0.275	78
2nd	15.104	11.717	78	9.365	−0.474	−5	1.106	0.055	5	0.375	0.329	88
5th	10.678	7.300	68	10.034	−0.012	0	1.230	0.086	7	0.905	0.837	93
6th	8.517	5.369	63	11.199	1.105	10	1.641	0.522	32	0.377	0.325	86
Winter season												
1st	1.676	0.170	10	6.599	−0.590	−9	0.834	−0.269	−32	0.095	0.037	39
2nd	4.484	3.030	68	8.420	0.522	6	1.134	0.195	17	0.247	0.188	76
5th	5.319	4.020	76	9.088	2.188	24	1.483	0.686	46	1.073	0.996	93
6th	4.356	2.998	69	9.763	2.418	25	1.394	0.527	38	0.505	0.443	88

in the growing season. A considerable share of Ca^{2+} (24–25%) and Mg^{2+} (17–38%) was observed in CL in winter – but only in the oldest age classes; a lack of canopy leaching or retention was noted for Ca^{2+} in the first and second age classes and for Mg^{2+} in the youngest spruce stage of development (Table 4).

For K^+, Ca^{2+} and Mg^{2+}, statistically significant differences ($p < 0.05$) occurred between the youngest stand (1st) and each subsequent older class (2nd, 5th, 6th), especially in winter time, while for Mn^{2+} the differences occurred for each combination of subsequent stand age groups (i.e. 1st–2nd, 1st–5th, 2nd–5th, 5th–6th, etc.) (Table 5).

As results from the calculations performed in the period under research (1999–2003), the waters of bulk precipitation reaching the Dupniański Stream Catchment were characterized by an average positive index ANC_{aq} (0.041 meq L^{-1}), which proves a large acid neutralizing capacity of these waters. The lowest values were noted in winter (0.025) and the highest ones in the growing period (0.057). The precipitation water passing through the canopy became acidic, and the result was a decrease in reaction (Table 2), in the ANC_{aq} and ALK (Table 6). The average annual ANC_{aq} in TF was negative. The minimum values were noted in winter. The average annual ALK in BP was negative (−0.016 mmol L^{-1}). The value of ALK in TF in the growing season decreased with the age of stands. Also for this index, the minimum values were noted in winter (Table 6).

The factor layout obtained by PCA for both BP and TF was similar for four stand age classes. It explained 67.6%, 75.8%, 74.3%, 61.3% and 68.1% of the total variance system for BP in the 1st, 2nd, 5th and 6th age classes, respectively (Table 7). The percentage of variance explained refers not to some definitive environmental events but to the validity of the multivariate statistical model, which tries to indicate possible sources of the deposited ions. Five significant factors were obtained for the 1st and 2nd age classes, four factors for BP and the 6th age class, and three in the case of the 5th age class. Concentration of major analytes classified as components of identified factors were summarized (“acidic emissions”: SO_4^{2-}, NO_3^-; “heavy metals–dust particles”: Fe^{2+}, Mn^{2+}, Zn^{2+}; “natural”: Na^+, K^+, Ca^{2+}, Mg^{2+}; “ammonium”: NH_4^+ and H^+) and presented in Fig. 3 taking into account the division of TF into winter and the growing season. The coefficients of determination were: “acidic emissions” (winter: $R^2 = 0.99$, all: $R^2 = 0.91$); “heavy metals–dust particles” (winter: $R^2 = 0.72$, all: $R^2 = 0.54$); “mineral dust” (winter: $R^2 = 0.98$, all: $R^2 = 0.87$); “H^+” (winter: $R^2 = 0.97$, all: $R^2 = 0.93$); “ammonium” (winter:

Table 5
Season- and age-dependent statistically significant differences (“*” yes or “–” not, $p = 0.05$, $N = 60$ for the whole year, $N = 30$ for the growing or winter season) between mean values of canopy leaching for K^+, Ca^{2+}, Mg^{2+} and Mn^{2+} between different stand age classes (1st, 2nd, 5th, 6th)

	K^+	Ca^{2+}	Mg^{2+}	Mn^{2+}
Kruskal–Wallis's test				
Whole year	*	*	*	*
Growing season	*	–	*	*
Winter	*	*	*	*
Mann–Whitney *U*-test				
Whole year				
1st–2nd	*	–	*	*
1st–5th	*	*	*	*
1st–6th	*	*	*	*
2nd–5th	–	–	–	*
2nd–6th	–	–	*	*
5th–6th	*	–	–	*
Growing season				
1st–2nd	*	–	–	*
1st–5th	–	–	–	*
1st–6th	–	*	*	*
2nd–5th	–	–	–	*
2nd–6th	*	–	–	–
5th–6th	–	–	–	*
Winter				
1st–2nd	*	–	*	*
1st–5th	*	*	*	*
1st–6th	*	*	*	*
2nd–5th	–	–	–	*
2nd–6th	–	–	–	*
5th–6th	–	–	–	*

Table 6
Five-year average (1999–2003) of acid neutralizing capacity – ANC_{aq} (in meq L^{-1}) and alkalinity – ALK (in mmol L^{-1}) in bulk precipitation (BP) and throughfall water (TF) in different stand age classes (1st, 2nd, 5th and 6th) in different seasons

BP		TF							
		1st		2nd		5th		6th	
ANC_{aq}	ALK	ANC_{aq}	ALK	ANC_{aq}	ALK	ANC_{aq}	ALK	ANC_{aq}	ALK
Whole year									
0.047	−0.009	−0.002	−0.015	−0.042	−0.043	−0.042	−0.046	−0.046	−0.059
Growing season									
0.057	−0.024	0.013	0.001	−0.012	−0.018	−0.033	−0.035	−0.006	−0.027
Winter season									
0.038	0.005	−0.016	−0.031	−0.073	−0.069	−0.052	−0.056	−0.085	−0.091

$R^2 = 0.81$, all: $R^2 = 0.91$). As the age of the spruce stands increased together with differences in canopy structure and leachability of foliage with a larger component of older foliage, the sum of anions of strong acids and concentrations of H^+ increased over the whole year, and especially in winter time. The same tendency was also noticed for the sum of cations and heavy metals in winter time. During the growing season this relationship was not so strong. Concentrations of NH_4^+ and H^+ increased with the age of stands in winter and during the growing season.

4. Discussion

Concentrations of SO_4^{2-}, K^+, H^+, Mn^{2+}, Fe^{2+} and Zn^{2+} in throughfall were greater than in bulk precipitation in the Dupniański Stream Catchment over the whole year and in each age classes of spruce stands. The average deposition of S from 1999 to 2003 via throughfall increased from the 1st to the 5th age class, especially in winter time, even if the systematic increase of SO_4^{2-} and decrease of pH in throughfall with increasing age of spruce stands recorded in the year 2000 (Małek, 2004) was not confirmed for SO_4^{2-}.

A substantial absorption of NO_3^-, especially during the growing season, confirms the results of Lovett and Schaefer (1992) and Hansen (1996). In the stands of the 2nd age class, up to 80% of N was absorbed in the tree crowns, a value similar to the one given by Zimka and Stachurski (1996). These reactions make it possible for plants to take up elements directly from rainwater, which causes the removal of Na^+, K^+, and Zn^{2+} from the plants (Stachurski, 1987). K^+ and Mn^{2+} were considered to originate mainly from leaching. The foliar uptake of N in the young stand and the parallel leaching of K^+ from the canopy characterised differences in solution composition between the stands. Differences between stands were related to stem size and LAI (Table 1) and to exposure to the deposition of particles and gases, and were directly related to tree age, like in Marques and Ranger, 1997 and Stachurski and Zimka (2000).

The results obtained in the Dupniański Stream catchment confirm that the Ca^{2+} and Mg^{2+} flux in net throughfall was mainly supplied by dry deposition. The increase in net throughfall fluxes of Ca^{2+} and Mg^{2+} with increasing stand age appeared mainly related to an increase in dry deposition (Novo et al., 1992; Dambrine et al., 1998; Erisman and Draaijers, 2003). Cations like Mg^{2+} and Ca^{2+} were absorbed directly from rainfall in the first and second age classes, possibly compensating for the considerable washout of these elements beyond the reach of the root system (Wróbel, 1998).

In spruce stands (of the 5th and 6th age classes) in southern Poland, the highest percentage of leaching of Mg^{2+} and Ca^{2+} ions (about 70%) in the total load of these ions in throughfall was noted in the Tatra Mts. and in the Low Beskid Mts (Staszewski, 2004). The lowest percentage (15–30%), similar to the Dupniański Stream Catchment, was noted in the Sudety Mts. and in the West Beskid Mts. probably due to higher dust deposition in this region (Staszewski, 2004). In the case of K^+, the percentage of leaching from needles was within 70–88% (this study and Staszewski, 2004). Lower percentages, i.e. 40–50%, were noted in spruce stands of the Cracow-Częstochowa Jura, the West and Low Beskid Mts (Staszewski, 2004). Mn^{2+} ions occur at the highest percentage in the leaching from needles (this study and Staszewski, 2004). An increased leaching of mineral substances (Ca^{2+}, Mg^{2+} and K^+) is one of the consequences of exposure of trees to acid rain, which are described by various authors (e.g. Scherbatskoy and Klein, 1983; Mitterhuber et al., 1989; Paoletti et al., 1989; Adams et al., 1990; Pfirmann et al., 1990; Beier et al., 1993; Knulst, 2004; Polkowska et al., 2005).

On the basis of data from the period 1969–1991, collected in a 105-year-old spruce stand located at an altitude of 500 m in the Sollig Mts. in north-western Germany (Ulrich, 1994), the percentage of canopy leaching in throughfall was: Ca^{2+} – 38%, Mg^{2+} – 21%, K^+ – 73% and Mn^{2+} – 40%. The share of calcium ion leaching in spruce stands located in the Harz and Hills Mts. in southern Germany ranged from 52 to 77% and the absolute values of calcium loads, calculated as leaching from needles, ranged between 10.3 and 25.9 kg $ha^{-1}yr^{-1}$ (Bredemeier, 1988). Such values of Ca^{2+} streams reaching the soil considerably exceed the amounts measured in spruce plots by Staszewski (2004) and in the spruce stands in the Dupniański Stream Catchment.

The water passing through the canopy in the Dupniański Stream catchment became acidic and the result was a decrease in the ANC_{aq} (especially in winter) and ALK. The same tendency towards a seasonal change was noted in the Saint Cross Mts. in Poland, where the values of ANC_{aq} were negative and

Table 7
Factor loading and explained variance for bulk precipitation (BP) and four categories of throughfall solutions collected from Norway spruce (*Picea abies* Karst) stands of different ages (1st, 2nd, 5th, 6th)[a] in the Dupniański Stream Catchment (1999−2003)

	Precipitation				Throughfall solutions																
	BP				1st					2nd					5th			6th			
	PC1	PC2	PC3	PC4	PC2	PC1	PC3	PC5	PC4	PC2	PC3	PC4	PC1	PC5	PC2	PC1	PC3	PC1	PC4	PC2	PC3
	PC1	*PC2*	*PC3*	*PC4*	*PC1*	*PC2*	*PC3*	*PC4*	*PC5*	*PC1*	*PC2*	*PC3*	*PC4*	*PC5*	*PC1*	*PC2*	*PC5*	*PC1*	*PC2*	*PC4*	*PC5*
Volume [mm m^2]	0.18	−0.57	0.04	−0.34	0.18	−0.61	0.05	−0.41	0.01	−0.35	−0.46	−0.18	−0.38	−0.33	−0.07	−0.71	0.30	−0.11	−0.81	−0.29	0.02
Cl^- [mg L^{-1}]	0.21	0.72	0.06	0.12	0.28	−0.02	0.70	0.39	0.26	−0.17	0.87	0.24	0.01	0.10	0.18	0.69	−0.10	0.03	0.61	0.15	0.55
NO_3^- [mg/L^{-1}]	0.11	0.86	−0.08	0.11	0.04	0.81	0.01	−0.04	0.29	0.12	0.87	0.01	−0.01	−0.08	0.24	0.68	0.25	0.42	0.41	−0.30	0.39
NH_4^+ [mg L^{-1}]	−0.17	0.23	0.81	−0.19	−0.22	0.12	0.91	−0.15	−0.12	0.10	0.27	0.64	0.48	−0.22	0.02	0.75	−0.24	0.29	0.71	0.03	−0.16
SO_4^{2-} [mg L^{-1}]	0.35	0.63	0.24	0.16	0.12	0.84	0.26	0.16	0.02	0.17	0.82	0.02	0.19	0.14	0.60	0.65	0.18	0.48	0.59	0.17	0.43
Na^+ [mg L^{-1}]	0.80	−0.13	−0.16	−0.06	0.87	−0.11	−0.12	−0.19	0.14	0.30	0.43	0.16	−0.69	−0.09	0.71	−0.18	0.18	0.63	0.04	−0.26	0.40
K^+ [mg L^{-1}]	0.72	0.42	0.08	−0.12	0.48	0.54	0.21	0.14	−0.43	0.62	0.24	0.50	−0.03	0.20	0.65	0.23	−0.31	0.76	0.20	0.07	−0.16
Ca^{2+} [mg L^{-1}]	0.76	0.28	0.14	0.14	0.30	0.51	−0.30	−0.21	−0.30	0.82	0.00	−0.11	0.05	−0.27	0.78	0.12	0.08	0.86	0.05	0.24	0.14
Mg^{2+} [mg L^{-1}]	0.89	0.12	0.00	−0.09	0.76	0.38	0.04	−0.12	−0.37	0.83	0.04	0.11	−0.14	0.17	0.78	0.07	−0.13	0.77	0.34	−0.38	0.08
Fe^{2+} [mg L^{-1}]	0.00	0.05	−0.34	0.75	−0.12	−0.07	−0.09	0.86	0.05	−0.03	0.04	−0.07	0.06	0.88	−0.24	0.60	0.04	−0.12	0.28	0.69	−0.25
Mn^{2+} [mg L^{-1}]	−0.23	0.19	0.28	0.76	0.02	0.45	0.44	0.61	−0.20	0.19	0.21	0.28	0.60	0.46	0.25	0.70	−0.02	0.14	−0.10	0.87	0.22
Zn^{2+} [mg L^{-1}]	0.11	0.23	−0.08	0.73	−0.15	0.24	0.15	0.63	0.32	−0.07	0.17	−0.16	0.69	0.01	−0.07	0.76	0.17	−0.06	0.32	0.76	0.08
H^+ [μg L^{-1}]	−0.43	0.32	−0.62	−0.07	−0.02	0.14	0.01	0.13	0.88	−0.02	−0.03	−0.84	0.26	−0.03	0.00	0.00	0.92	0.04	−0.07	0.06	0.81
Eigenvalue	3.01	2.51	1.36	1.91	2.68	3.47	1.44	1.06	1.21	2.07	1.59	1.18	3.74	1.08	2.26	4.42	1.28	4.20	1.15	2.55	1.34
Explained variance [%]	27.71	19.98	11.43	8.48	20.59	26.72	11.09	8.14	9.30	15.95	12.28	9.07	28.76	8.28	17.38	34.03	9.85	32.30	8.82	16.64	10.33
Cumulative explained variance [%]	27.71	47.69	59.12	67.60	20.59	47.31	58.40	66.54	75.84	15.95	28.23	37.30	66.06	74.34	17.38	51.41	61.26	32.30	41.12	57.76	68.09
Factors	PC1 − "mineral dust"				PC1 − "mineral dust"					PC1 − "mineral dust"					PC1 − "mineral dust"			PC1 − "mineral dust"			
	PC2 − "acidic emissions"				PC2 − "acidic emissions"					PC2 − "acidic emissions"					PC2 − "acidic emissions" + "heavy metals−dust particles"			PC2 − "acidic emissions"			
	PC3 − "ammonium"				PC3 − "ammonium"					PC3 − "ammonium"								PC4− "heavy metals−dust particles"			
	PC4 − "heavy metals−dust particles"				PC4 − "heavy metals−dust particles"					PC4 − "heavy metals−dust particles"											

PC1, PC2, PC3, PC4, PC5 (regular) − primary notation connected with sequence of PCs sorted by descending percentage of explained variance obtained by PCA. *PC1, PC2, PC3, PC4, PC5* (italic) − notation changed to unify the factor identification (sorted in agreement to pollution origin).

[a] The four stand age categories correspond to 11, 24, 91 and 116 years old stands, respectively.

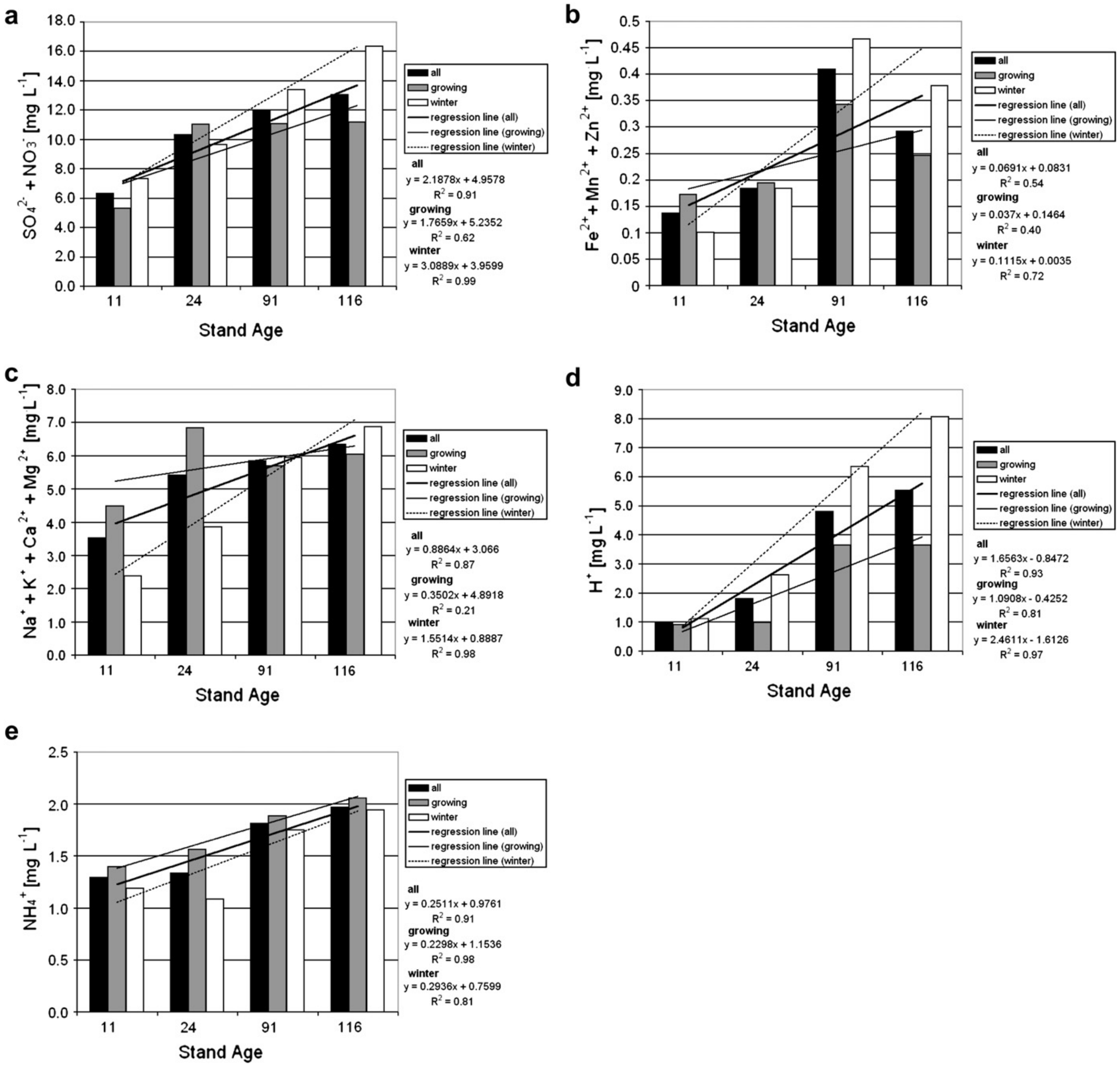

Fig. 3. Linear regressions of a) $\Sigma(SO_4^{2-} + NO_3^-)$; b) $\Sigma(Fe^{2+} + Mn^{2+} + Zn^{2+})$; c) $\Sigma(Na^+ + K^+ + Ca^{2+} + Mg^{2+})$; d) H^+; e) NH_4^+ in throughfall for four Norway spruce (*Picea abies* Karst) stand-age categories for the whole year, and during the winter and growing seasons.

lower than the ones in the Dupniański Stream Catchment (Jóźwiak and Kozłowski, 2004). A smaller acid neutralising capacity in precipitation waters in the Świętokrzyskie Mts. means a greater load of these anions, particularly of sulphates, in this region (Jóźwiak and Kozłowski, 2004). Negative ANC_{aq} values were also noted in central Europe, in the Lysina Catchment in Czech Republic (Hruška et al., 2002). It is known that Ca^{2+} and other cations neutralize the acid deposit on the needle surface and that prolonged exposure to acid precipitation causes damage to needles and leaching due to the loss of buffer capacity (Musselman, 1988; Klumpp and Guderian, 1990; Pucket, 1990).

Data from 121 Intensive Monitoring plots in Europe indicate that SO_4^{2-} is still the dominant source of actual soil acidification despite the generally lower input of S than N, due to the different behaviour of S (near tracer) and N (strong retention) (de Vries et al., 2007) like in the Dupniański Stream Catchment. Unfortunately N deposition ($N-NO_3^- + N-NH_4^+$) in this catchment was above the critical load ($N_{crit} = 15-20$ kg N ha^{-1} yr^{-1}) for coniferous trees, which may change N/macronutrients ratios, decrease K^+ and Mg^{2+} and increase N concentration in foliar tissue (Hall, 2004). Nitrogen deposition fluxes in this study were below the values reported for the heavily polluted Ore Mts. (Czech Republic) (Černý et al., 1997) but above the average monitored over 20 years in ICP Forests plots (Fischer et al., 2007). The effect of N deposition may be an increasing problem in the future unless emissions of

N oxides and especially of ammonium are reduced (Hultberg and Ferm, 2004). Concentrations of ammonium and H^+ increased with the age of spruce stands in the Dupniański Stream catchment. This phenomena is of particular concern because of expected increases in nitrification rates and soil acidification (Jussy et al., 2004; Rosenqvist et al., 2007). Excess N and increasing N:cation ratios may have negative effects on the health of spruce stands (Niemtur et al., 2005) because of a significant relationship between N deposition and crown defoliation (Fischer et al., 2007). Principal component analysis identified five factors responsible for the data structure in the Duniański Stream catchment and suggests the major anthropogenic emission sources were acidic emission ($SO_4^{2-} + NO_3^-$), heavy metals–dust particles ($Fe^{2+} + Mn^{2+} + Zn^{2+}$), ammonium ($NH_4^+$) and H^+, while the natural-origin emission was mineral dust ($Na^+ + K^+ + Ca^{2+} + Mg^{2+}$). The factor named as ''mineral dust'', referring to soil-dust particles, was strongly correlated with Na^+, K^+, Ca^{2+} and Mg^{2+}, especially in the older age classes and for BP. Apart from a lack of correlation between K^+ and Ca^{2+} with other cations, the composition of the ''mineral dust'' factor was quite similar for the various stand age categories. This is in agreement with results obtained by others (Al-Khashman, 2005; Tang et al., 2005). The factor named as ''acidic emissions'', referring to co-emission of SO_4^{2-} and NO_3^- precursors (SO_2, NO_x) associated with the combustion of fossil fuels, burning of biomass and by automobile exhaust was in most cases strongly correlated with Cl^-, SO_4^{2-} and NO_3^-. In the case of the 5th age class category, this factor was strongly correlated with NH_4^+. The factor named as ''heavy metals–dust particles'', referring to heavy metals connected with ash emissions included strong correlations with Fe^{2+}, Mn^{2+} and Zn^{2+}. The PC1 structure for the 5th category indicated an influence of both ''acidic emissions'' and ''heavy metals–dust particles'' sources. For BP and the 1st and 2nd categories in the factor layout there was a factor strongly influenced by NH_4^+. The NH_4^+ present in the atmosphere might come from several sources, including the volatilization of animal residues, human excrements, natural loss by plants, biomass burning, and industrial processes, such as the use or the production of fertilizers and emissions from the combustion of fossil fuels (Spanos et al., 2002; Ugucione et al., 2002). For the 5th and 6th categories, the influence of ammonium was connected with variables belonging to the ''acidic emissions'' factor.

5. Conclusions

Concentrations of SO_4^{2-}, K^+, H^+ and Mn^{2+} in throughfall were greater than in bulk precipitation over the whole year, growing season and winter (together with Fe^{2+} and Zn^{2+}). This suggests that these ions were washed out or washed from the surface of needles and/or barks. The other ions NO_3^-, NH_4^+, Ca^{2+} and Mg^{2+} were retained by the canopy, in particular Ca^{2+} and Mg^{2+} during the growing season in young stands.

The chemical composition of throughfall solutions and canopy leaching, as well as the acid neutralizing capacity and alkalinity depended on the age of the spruce stands and season of the year. For all variables in throughfall, stand age was a significant factor discriminating between the youngest and the two oldest age classes over the whole year and winter time, with exception for K^+, Mg^{2+} and Fe^{2+} in the growing season. The deposition of S via throughfall increased from the 1st to the 5th age class, especially in winter. For canopy leaching of K^+, Ca^{2+} and Mg^{2+}, significantly differences occurred between the youngest stand and each subsequent older class (especially in winter time and over the whole year), while for Mn^{2+} the differences occurred between each stand age group and season. The water passing through the canopy became acidic and the result was a decrease in ANC_{aq} (especially in winter) and ALK. In addition, ALK decreased with increasing age of the stands in the growing season.

Nitrogen deposition was above the critical load for coniferous trees ($N_{crit} = 15–20$ kg N ha^{-1} yr^{-1}). During the passage of precipitation through the canopy, the anions of strong acids from wet and dry deposition, especially in winter, were washed from the surface of needles, shoots, and branches. Even if the leaching of alkaline cations from assimilatory organs was considerable, particularly in the oldest stands, they were unable to neutralize an increased acid inflow from the air.

Over five years, an increasing amount of S and strong acids ($S–SO_4^{2-}$ and $N–NO_3^-$) deposited to the soil was detected in the older spruce age classes, which may have implications for the vitality of spruce stands by increasing the washing out of alkaline cations like Ca^{2+} and Mg^{2+}.

The application of PCA identified five factors responsible for the data structure (''mineral dust'', ''acidic emissions'' ''heavy metals–dust particles'', ''NH_4^+'' and ''H^+''). They explained 61–76% of the total variance system for BP and the 1st, 2nd, 5th, and 6th age classes of spruce. The strong positive correlation between spruce stand age classes and ionic concentrations in throughfall occurred for the whole year and in the winter period. The strength of the relationship decreased in the growing period, probably due to processes occurring in the canopy (adsorption, leaching, etc.).

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