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Sustainability of *Picea abies* of Istebna provenance in Dupniański Stream catchment as dependent on stand age class

Abstract: Ecochemical indexes such as soil buffer reaction (pH), acid neutralising capacity (ANC_{aq}), alkalinity (ALK), soil acidity (Ma%), basic cation saturation (BS), and molar ratios Ca:Al and BC:Al were used to study the sustainability of Norway spruce of Istebna provenance in stands differing in age class. The data were obtained from the research conducted in the Dupniański Stream catchment in the Silesian Beskid Mts. (Poland). The acid neutralising capacity, alkalinity, and soil acidity were found to depend on the age of spruce stands. The increased acidification of deposits was due to the presence of sulphate and nitrate ions which were washed out from the surface of plants. Passing through the canopy caused a decrease in the acid neutralising capacity, alkalinity, and base cation saturation, and an increase in the soil acidity, with the values being dependent on stand age. The soil acid reaction shifted to the range of the aluminium and iron bufferness, but the Ca:Al and BC:Al ratios were still above the level when aluminium stress is probable. The washout of the basic cations beyond the spruce root system, and the low levels of exchangeable Mg^{2+} and Ca^{2+}, basic cation saturation of soil water, and effective base saturation of soil may affect the vitality and health of spruce stands in the future. To maintain the sustainability of Norway spruce stands of Istebna provenance in the Dupniański Stream catchment it is necessary to increase the retention of basic elements, especially Mg^{2+} and Ca^{2+}, by means of stand conversion or fertilisation.

Additional key words: Norway spruce, ecochemical indexes, Silesian Beskid Mts.

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Introduction

The Silesian Beskid Mts. are heavily polluted with immissions coming from various sources, especially from the Karvina and Ostrava regions in the Czech Republic, and the Rybnik and Katowice regions in Poland (Staszewski et al. 1996, 1999; Godzik et al. 1997; Bytnerowicz et al. 1999, 2002; Maňkovská et al. 2002; Kulhavý et al. 2005; Małek et al. 2005, Florek et al. 2007; Małek and Astel 2007b). Both sulphur and nitrogen in the form of NH_4^+ contribute to soil acidification, but the deposition of S tends to decrease, whereas the N deposition seems to be constant or slightly increasing (Małek and Astel 2007a, b, 2008). Therefore, the role of N in forest dieback becomes a cause for growing concern (e.g. van Breemen and van Dijk 1987; Aber 1992; Hornung and Sutton 1995; Flower et al. 2007; Małek and Astel 2007a; Sicard et al. 2007).

Nitrogen is normally the nutrient which limits forest growth, the most distinctly in boreal forest ecosystems (Tamm 1991), but when more N is available through deposition, the growth improves and other nutrients may become growth-limiting. Together with the nutrient loss caused by canopy leaching of K, Ca, Mn and Mg (Ulrich 1983; Bredemeier 1988;

Draaijers and Erisman 1995; Draaijers et al. 1997; Małek and Astel 2007a), the following properties of precipitation, throughfall, and soil water become modified: acid neutralising capacity (Reuss and Johnson 1986; Heinrichs et al. 1994; Jóźwiak and Kozłowski 2004; Małek and Astel 2008), alkalinity (Harriman et al. 1990; Block et al. 2000; Jóźwiak and Kozłowski 2004; Małek and Astel 2008), soil acidity, and basic cation saturation (Ulrich 1988; Kowalkowski 2002) following soil acidification (Falkengren-Grerup et al. 1987), as well as Ca:Al ratio (Cronan and Grigal 1995) and BC:Al ratio (Sverdrup and Warfvinge 1993). These processes may increase the tree demand for mineral nutrients, and may cause nutrient deficiencies in the trees and change the relations between the elements (Cape et al. 1990; Zwoliński 2003). The properties listed above can be good ecochemical indicators of forest soil conditions and stand damage from acidification (Block et al. 2000; Kowalkowski 2002).

The present work aims at determining the sustainability of Norway spruce of Istebna provenance as dependent on stand age class by using ecochemical indexes such as soil buffer reaction (pH), acid neutralising capacity (ANC_{aq}), alkalinity (ALK), soil acidity (Ma%), basic cation saturation (BS), and molar ratios Ca:Al and BC:Al, studied over the period 1999–2003 in the Dupniański Stream catchment in the Silesian Beskid Mts.

Material and methods

Site description

The catchment of the Dupniański Stream has an area of 1.68 km^2 and is located in southern Poland in the Silesian Beskid Mts. (49°34'N, 18°50'E). The catchment is covered with stands of Norway spruce (*Picea abies* (L.) Karst.) of Istebna provenance growing on dystric cambisols developed from Istebna sandstones. The stands of 1st, 2nd, 5th, and 6th age classes (the only age classes found in this catchment) were 11, 24, 91, and 116 years old in 1999. Their descriptive characteristics are provided in Table 1, and the characteristics of the soils are shown in Table 2. The equipment for measuring bulk precipitation, throughfall, and soil water in pure spruce stands (one monitored plot in each age class) was set up in 1998.

Sampling

The studies were conducted in the years 1999–2003 using methods described in the ICP-Forest Manual (1998) and in Małek (2004). Water sampling was performed on the first day of each month. A bulk precipitation (BP) sampler was installed in the central part of the catchment at an elevation of 725 m a.s.l., within 500 m of the throughfall sampling point. During the vegetation season, i.e. from the 1st May to the 30th October, samples of bulk precipitation directly reaching the ground were collected from special collectors (5 units with 15 cm inlet diameter each) installed in an open area 0.5 m above ground level, and connected to a plastic tube with an outlet joining a container and a measuring device installed in a bunker. In winter, from the 1st November (the previous year) to the 30thApril (the following year) six collectors (plastic, chemically neutral snow bags with 15 cm inlet diameter each) were installed at 1.3 m above ground level in an open area at a distance of 120–150 m from the forest edge.

In order to evaluate the volume and quality of throughfall (TF), water was sampled from a sampling system (this time the number of collectors was 15, 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 (plastic, chemically neutral snow bags with 15 cm in-

Table 1. Descriptive characteristics of Norway spruce stands in Dupniański Stream catchment

Age class	Age (years)	Elevation (m a.s.l.)	Diameter (m^2)	Height (m)	Number of trees per ha	Defoliation (%)	Discoloration (%)
1999							
1st	11	720	2.2	1.5	20150	10	5
2nd	24	700	11.7	12.6	2611	30	15
5th	91	660	39.7	37.8	382	31	16
6th	116	700	42.1	36.6	414	33	19
2003							
1st	16		3.6	5.0	13758	15	10*
2nd	29		14.7	16.2	2070	34	22*
5th	96		42.1	39.1	350	35	23*
6th	121		45.5	38.8	330	36	24*

* differences between 2003 and 1999 statistically significant at $p = 0.05$

Table 2. Descriptive characteristics of soils under Norway spruce stands of different age classes in Dupniański Stream catchment

Soil depth (cm)	Soil horizon	pH		Hydrolytic acidity, HA (me 100g^{-1})	Exchangeable cations in CH_3COONH_4 (me 100g^{-1})				Sum of exchangeable cations, EC (me 100g^{-1})	Sorptive capacity SC (me 100g^{-1})	Effective base saturation, EBS (%)
		H_2O	KCl		Na^+	K^+	Ca^{2+}	Mg^{2+}			
1st age class											
0–2	Ol	3.1	2.4	4.04	0.04	0.21	3.17	0.31	3.73	7.77	48.01
2–9	Ofh	3.7	2.9	5.49	0.04	0.08	1.11	0.04	1.27	6.76	18.79
9–14	AEes	3.7	2.9	3.26	0.01	0.09	1.02	0.02	1.14	4.40	25.91
14–36	Bbrfe	4.3	3.5	3.11	0.01	0.09	0.55	0.01	0.66	3.77	17.51
36–51	Bbr	4.0	3.2	3.70	0.02	0.06	0.28	0.01	0.37	4.07	9.09
51–105	B/C	4.3	3.5	2.73	0.02	0.10	0.23	0.01	0.36	3.09	11.65
105–130	C	4.2	3.4	2.78	0.01	0.07	0.15	0.01	0.24	3.02	7.95
2nd age class											
0–1	Ol	3.2	2.4	10.36	0.07	0.25	1.47	0.29	2.08	12.44	16.72
1–7	Ofh	3.8	3.0	8.24	0.01	0.09	0.34	0.01	0.45	8.69	5.18
7–18	AEes	3.7	2.9	6.01	0.01	0.11	0.38	0.02	0.52	6.53	7.96
18–40	Bbrfe	4.1	3.4	2.80	0.01	0.08	0.40	0.01	0.50	3.30	15.15
40–72	Bbr	4.3	3.5	3.70	0.01	0.07	0.27	0.01	0.36	4.06	8.87
72–110	BC	4.5	3.7	6.42	0.01	0.09	0.19	0.01	0.30	6.72	4.46
5th age class											
0–2	Ol	3.0	2.1	14.72	0.02	0.33	2.14	0.29	2.78	17.50	15.89
2–6	Ofh	3.6	2.7	4.56	0.01	0.04	0.27	0.02	0.34	4.90	6.94
6–13	AEes	3.5	2.6	3.97	0.02	0.07	0.27	0.01	0.37	4.34	8.53
13–36	Bbrfe	4.2	3.5	2.84	0.04	0.11	0.28	0.02	0.45	3.29	13.68
36–71	Bbr	4.3	3.5	3.72	0.02	0.05	0.16	0.01	0.24	3.96	6.06
71–120	B/C	4.2	3.4	3.54	0.01	0.07	0.21	0.01	0.30	3.84	7.81
6th age class											
0–3	Ol	3.1	2.2	5.80	0.02	0.19	1.57	0.20	1.98	7.78	25.45
3–9	Ofh	3.6	2.7	5.86	0.01	0.05	0.36	0.04	0.46	6.32	7.28
9–18	AEes	3.5	2.6	3.50	0.02	0.06	0.23	0.01	0.32	3.82	8.38
18–36	Bbrfe	4.1	3.2	2.93	0.02	0.04	0.21	0.01	0.28	3.21	8.72
36–97	Bbr	4.5	3.6	3.63	0.01	0.08	0.11	0.01	0.21	3.84	5.47
97–120	B/C	4.2	3.1	6.60	0.04	0.15	0.21	0.01	0.41	7.01	5.85

SC = HA + EC, EBS = EC/SC · 100

let diameter each) were installed at 1.3 m above ground level in the spruce stands to be studied.

Water percolating through the soil was sampled using four gravity lysimeters (L-(20)) isolated from horizontal water penetration, situated at a depth of 20 cm. Soil water penetrating horizontally and vertically was sampled with four lysimeters (L-20) not isolated from vertical penetration, placed in the soil at the same depth in the stands.

In August 1999 and 2003, thirty permanently numbered trees from I, II, and III canopy classes according to the Kraft system were examined for defoliation and discoloration following the ICP-Forest Manual (1998). Each tree was assessed in 5% intervals (classes) of defoliation and discoloration relative to a healthy tree with full foliage of the same crown type.

Chemical analyses

The soil reaction in H_2O and KCl, hydrolytic acidity (in 1 M $Ca(CH_3COOH)_2 \times H_2O$), exchangeable cations (in 1 M CH_3COONH_4), sum of exchangeable cations, sorptive capacity, and effective base saturation were determined using an atomic absorption spectrophotometer Varian AA-20 (Ogner et al. 1991; Ostrowska et al. 1991). Water was analysed by ion chromatography (Dionex-320) to determine the concentrations of NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, and Al^{3+}. A low-pH acid rain sample from southern Ontario (Canada), RAIN.97 - No 409 served as a certified reference material (CRM) and was analysed as well. When the concentration of analytes was below the limit of detection (LOD) of the analytical technique, the value of one-third LOD was used in the data set due to statistical requirements (Astel et al. 2004).

Calculation of acid neutralising capacity, alkalinity, soil acidity, and basic cation saturation

The acid neutralising capacity, ANC_{aq} (Reuss and Johnson 1986; Schlesinger 1991; Warfvinge and Sverdrup 1992, 1995; Heinrichs et al. 1994; Lorz 1999; Becker et al. 2000), alkalinity, ALK (Harriman et al. 1990; Reuss 1991; Block et al. 2000), soil acidity, Ma% (Ulrich 1988), basic cation saturation, BS (Kowalkowski 2002), molar ratio Ca:Al (Cronan and Grigal 1995), and molar ratio BC:Al (Sverdrup and Warfvinge 1993) were calculated from the following equations:

ANC_{aq} (meq L^{-1}) $= K^+ + Na^+ + 2Mg^{2+} + 2Ca^{2+} - Cl^- - SO_4^{2-}$

ALK (mmol L^{-1}) $= (K^+ + Na^+ + Mg^{2+} + Ca^{2+}) - (NO_3^- + Cl^- + SO_4^{2-})$

$Ma\% = (Ma + H^+)/(Ma + Mb + H^+) \cdot 100$

Ma (mmol L^{-1}) $= (Mn^{2+} + Fe^{2+} + Al^{3+})$

Mb (mmol L^{-1}) $= (K^+ + Na^+ + Mg^{2+} + Ca^{2+})$

BS (%) $= (K^+ + Na^+ + Mg^{2+} + Ca^{2+})/(K^+ + Na^+ + Mg^{2+} + Ca^{2+} + Mn^{2+} + Fe^{2+} + Al^{3+}) \cdot 100$

$Ca:Al = Ca^{2+}/Al^{3+}$

$BC:Al = (K^+ + Mg^{2+} + Ca^{2+})/Al^{3+}$

Statistical analyses

The results were analysed using the STATISTICA 6.0 program (Łomnicki 2002; L. Rutkowska and J. Socha – personal communication). The t-Student test, and the U-Mann-Whitney test in the case of non-normal distribution, at significance level $p = 0.05$ ($n = 60$ for BP and TF, $n = 30$ for L-20 and L-(20)) were employed to compare the average values of ecochemical indexes: acid neutralising capacity (ANC_{aq}), alkalinity (ALK), soil acidity (Ma%), basic cation saturation (BS), as well as molar ratios Ca:Al and BC:Al, in four groups of spruce stands, i.e. 1st, 2nd, 5th, and 6th age classes, and for different kinds of water (bulk precipitation, throughfall, soil water). The defoliation and discoloration indexes were compared between stand age classes, and between years (1999 and 2003).

Results

Acid neutralising capacity (ANC_{aq}) and alkalinity (ALK)

As follows from the calculations performed for the period under research (1999–2003), the precipitation water immediately reaching the Dupniański Stream catchment had a positive average value of ANC_{aq} (0.047 meq L^{-1}), which indicates that its acid neutralising capacity was high. The water which passed through the canopy of a spruce stand became acidic, and the average annual value of ANC_{aq} of throughfall water decreased significantly to negative values ranging from –0.002 in stands of 1st age class to –0.046 in those of 6th age class (Table 3). Statistically significant differences in the throughfall water ANC_{aq} were noted between the youngest age class and the other classes (Table 4).

The average annual value of alkalinity (ALK) in the bulk precipitation was –0.009 mmol L^{-1}. The ALK value in the throughfall was significantly lower, between –0.015 in the 1st age class and –0.059 in the 6th age class (Table 3). There were statistically significant differences in the alkalinity of throughfall water between the youngest age class of stands and the other classes (Table and 4).

The water which passed vertically through the 20 cm layer of top soil under spruce stands became more acidic in each age classes, except the youngest one, with the differences relative to the throughfall water being statistically significant. The average annual value of the acid neutralising capacity of soil water was positive only for the 1st age class of stands (0.068), and was negative in the older age classes (–0.133 in the 2nd age class to –0.182 in the 5th age class; Table 3). Also the alkalinity of soil water had a positive value in the 1st age class (0.041) and negative

Table 3. Five-year (1999–2003) average values of acid neutralising capacity (ANC_{aq}, in meq L^{-1}) and alkalinity (ALK, in mmol L^{-1}) of bulk precipitation, throughfall, and soil water in Norway spruce stands of different age classes in Dupniański Stream catchment

Kind of water	ANC_{aq}	ALK
BP	0.047	–0.009
1st age class		
TF	–0.002	–0.015
L-(20)	0.068	0.041
L-20	0.085	0.041
2nd age class		
TF	–0.042	–0.043
L-(20)	–0.133	–0.099
L-20	–0.033	–0.027
5th age class		
TF	–0.042	–0.046
L-(20)	–0.182	–0.173
L-20	–0.071	–0.040
6th age class		
TF	–0.046	–0.059
L-(20)	–0.127	–0.137
L-20	–0.143	–0.123

BP – bulk precipitation, TF – throughfall, L-(20) – soil water at 20 cm depth penetrating vertically,
L-20 – soil water at 20 cm depth penetrating horizontally and vertically

Table 4. Statistical significance of differences ("*" yes or "–" no; p = 0.05; n = 60 for BP and TF; n = 30 for L-20 and L-(20)) in 1999–2003 average values of acid neutralising capacity (ANC_{aq}) and alkalinity (ALK) of water between age classes of Norway spruce stands in Dupniański Stream catchment and between water kinds

Age class of stand	Kind of water	ANC_{aq}	ALK	Kind of water	ANC_{aq}	ALK	Kind of water	ANC_{aq}	ALK
1st	BP–TF	*	*	TF–L-(20)	*	*	L-20–L-(20)	*	-
2nd	BP–TF	*	*	TF–L-(20)	*	*	L-20–L-(20)	*	*
5th	BP–TF	*	*	TF–L-(20)	*	*	L-20–L-(20)	*	*
6th	BP–TF	*	*	TF–L-(20)	*	*	L-20–L-(20)	–	–
1st–2nd	TF	*	*	L-(20)	*	*	L-20	*	*
1st–5th	TF	*	*	L-(20)	*	*	L-20	*	*
1st–6th	TF	*	*	L-(20)	*	*	L-20	*	*
2nd–5th	TF	–	–	L-(20)	–	–	L-20	*	*
2nd–6th	TF	–	–	L-(20)	–	–	L-20	*	*
5th–6th	TF	–	–	L-(20)	–	–	L-20	*	*

BP – bulk precipitation, TF – throughfall, L-(20) – soil water at 20 cm depth penetrating vertically, L-20 – soil water at 20 cm depth penetrating horizontally and vertically

values in the other classes (–0.099 in the 2nd age class to –0.137 in the 6th age class; Table 3). The differences between the youngest age class and the other classes were statistically significant (Table 4).

The water which passed horizontally and vertically through the 20 cm layer of top soil under spruce stands (L-20) showed significantly higher average annual values of acid neutralising capacity and alkalinity, except the 6th age class, than the water percolating vertically (L-(20)). Compared to the latter, ANC_{aq} increased in the 1st, 2nd, and 5th age class to the values ranging between 0.085 (1st class) and –0.071 (5th class), but decreased in the 6th age class to –0.143 (Table 3). The alkalinity index remained the same in the 1st age class, and increased in the other age classes to the values of –0.027 (2nd class) to –0.123 (6th class; Table 3). Statistically significant differences were noted between all age classes (Table 4).

Soil acidity (Ma%) and basic cation saturation (BS)

The average annual value of soil acidity (Ma%) for water penetrating vertically the 20 cm layer of top soil (L-(20)) was high in all groups of spruce stands, from 52% in the 1st age class to 67% in the 6th age class, so the soil under the stands can be regarded as acid (Ulrich 1988). A statistically significant difference existed between the oldest and the youngest age class. The water that passed horizontally and vertically through the 20 cm layer of top soil (L-20) decreased soil acidity in all age classes, to 34 and 38%, respectively, in the younger stands (statistically significantly) and to 53 and 57% in the older stands. The differences in the Ma% values for L-20 were statistically significant between two older age classes and two younger age classes. Soil acidity tended to rise with the increasing age of spruce stands (Table 5).

The average annual value of basic cation saturation (BS) for the soil water penetrating vertically (L-(20)) was low in all age classes, from 47% in the 1st age class to 33% in the 6th age class. Again, the difference between the older and the younger age classes was statistically significant. The BS values for the water penetrating horizontally and vertically (L-20) exceeded those for L-(20) in all groups of spruce stands, and were from 66% in the 1st age class to 43% in the 6th age class, with the increase being statistically significant for two younger age classes. The differences in the BS values between the two older and two younger age classes were statistically significant. The basic cation saturation decreased with the increasing age of stands (Table 5).

Ca:Al and BC:Al ratios

The average Ca:Al ratio in the soil water penetrating vertically (L-(20)) was high in all groups of spruce stands, from 2.0 in the 5th age class to 5.4 in the 6th age class, and differed significantly between the oldest age class and the other age classes. The water penetrating horizontally and vertically (L-20) increased the Ca:Al ratio in each age class, most substantially in two younger classes, to 4.7 and 5.7, respectively (statistically significantly), and nonsignificantly in two older classes (Table 5).

The average BC:Al ratio in the soil water penetrating vertically (L-(20)) was high in each age class, from 3.3 in the 5th age class to 8.7 in the 6th age class. The oldest class differed significantly from the other age classes. The water penetrating horizontally and vertically (L-20) increased the BC:Al ratio in all groups of spruce stands: more than twofold (to 8.8 and 12.5; statistically significantly) in two younger age classes, and nonsignificantly in two older groups of stands (Table 5).

Table 5. Five-year (1999–2003) average values of soil acidity (Ma%), basic cation saturation (BS), and Ca:Al and BC:Al ratios of soil water at 20 cm depth penetrating vertically (L-(20)) and horizontaly and vertically (L-20), and statistical significance of differences ("*" yes or "–" no; p = 0.05; n = 30 for L-20 and L-(20) in average values between age classes of Norway spruce stands in Dupniański Stream catchment and between soil water kinds

Age of stand	Ma%	BS	Ca:Al	BC:Al
		L-(20)		
1st	52.47	47.23	2.48	3.99
2nd	62.98	37.02	2.27	4.07
5th	58.93	41.07	2.04	3.33
6th	66.88	33.12	5.43	8.74
1st–2nd	–	–	–	–
1st–5th	–	–	–	–
1st–6th	*	*	*	*
2nd–5th	–	–	–	–
2nd–6th	–	–	*	*
5th–6th	–	–	*	*
		L-20		
1st	34.18	65.82	4.67	8.78
2nd	38.42	61.58	5.72	12.49
5th	52.92	47.08	2.47	5.27
6th	57.03	42.97	5.86	10.45
1st–2nd	–	–	–	–
1st–5th	*	*	*	*
1st–6th	*	*	–	–
2nd–5th	*	*	*	*
2nd–6th	*	*	–	–
5th–6th	–	–	*	*
		Statistical difference between L-20 and L-(20)		
1st	*	*	*	*
2nd	*	*	*	*
5th	–	-	–	–
6th	–	-	–	–

Discussion

The nitrogen deposition to the Dupniański Stream catchment over the period 1999–2003 was above the critical load for coniferous trees (Małek and Astel 2007a, 2008), which may have changed the N:macronutrients ratios, decreased K^+ and Mg^{2+}, and increased the N concentration in foliar tissue (Hall 2004).

A low magnesium content of spruce needles is closely connected with a relatively low level of available Mg in the soil (Table 2), and with its being leached beyond the reach of the root system of trees (Nihlgård 1972). The Mg deficiency, which is considered a prime cause of the yellowing damage of Norway spruce, typical of this part of Europe, manifested itself in the discoloration of needles, which increased significantly in all stand age classes between 1999 and 2003, and exceeded 20% in the older stands (Table 1). The sudden occurrence of this symptom may be attributed to a series of dry years which reduced the Mg mineralisation and uptake, as well as to the more intensive tree harvesting (shorter rotation) and the leaching of soils by acid rain (Adams et al. 2000). As demonstrated by studies made in spruce stands in the Central German Uplands (Roberts et al. 1989), the Mg deficiency in needles may to a greater degree be caused by the reduced level of Mg in the soil, resulting from wood harvesting and soil leaching by acid rain, than by the direct washing of Mg from the needles in connection with air pollution (Małek 2004; Małek and Astel 2007a, 2008).

The values of the acid neutralising capacity of bulk precipitation on the Saint Cross Mt. (Świętokrzyskie Mts., Poland; 50°51'20''N, 21°03'10''E) were negative and lower than those noted in the Dupniański Stream catchment. This indicates that precipitation waters in the Świętokrzyskie Mts. have a smaller acid neutralising capacity, which means that this region receives a greater load of sulphates (Jóźwiak and

Kozłowski 2004). Negative values of ANC_{aq} were also observed in Central Europe, in the Lysina catchment in the Czech Republic (Hruška et al. 2002). The acid neutralising capacity as well as alkalinity and soil acidity dropped as water passed the stand canopy both in the Dupniański Stream catchment and the Świętokrzyskie Mts., which means a greater load of sulphates being washed out (Jóźwiak and Kozłowski 2004).

In the Świetokrzyskie Mts., water penetrating acid soils at 15 cm depth showed a decrease in acid neutralising capacity and alkalinity, and an increase in soil acidity, compared to throughfall water (Jóźwiak and Kozłowski 2004). The same pattern was observed for the Dupniański Stream catchment. The slight increase in the acid neutralising capacity, alkalinity, and basic cation saturation of water penetrating vertically and horizontally the soil under spruce stands in the Dupniański Stream catchment, and the decrease in soil acidity can be explained by the leaching of the basic cations from the chemical decomposition of soil mineral particles (Kowalkowski 2002), which could have compensated for the acidic anions. The results suggest that the soils in the Dupniański Stream catchment, especially under the spruce stands of younger age classes, are exposed to very strong acidification but with a low concentration of Al, whereas those under the older spruce stands are exposed to moderate acidification (Block et al. 2000).

The potential effects of N saturation include increased soil acidification (van Breeman et al. 1982), aluminium mobility (Johnson et al. 1991), increased nitrate leaching (Aber et al. 1989), and elevated base cation leaching (Fenn et al. 1998). As the highly mobile nitrate anion moves through the soil solution, base cations are removed from the soil exchange sites and leached from the soil. The nitrate pulses can also result in considerable increases in aluminium in the soil solution, to the levels that may affect the base cation uptake (Johnson et al. 1991; Raynal et al. 1992; Cronan and Grigal 1995). Since the N deposition is expected to increase, the N saturation has become a concern. The sulphate anion also plays an important role in altering the flux of other ions, especially acidic and basic ions, in soil solutions (Reuss and Johnson 1986). Soils that do not adsorb sulphate are most susceptible to base leaching (Cronan et al. 1978). Acidity is the aspect of atmospheric chemistry which may affect soil productivity. The addition of strong mineral acids (e.g. H_2SO_4 and HNO_3) in wet and dry deposition was hypothesised to reduce soil pH and base saturation, with other possible detrimental effects relative to the elevated H^+ activity in soil solutions. The base cation depletion occurs as a result of leaching with counterbalancing sulphate and nitrate, and as a result of fewer cation exchange sites due to lower pH, and decreased base saturation due to higher aluminium availability. When the base saturation is low, Al^{3+} is the dominant cation available for exchange, which results in the release of aluminium in response to acidic deposition. These processes can lead to increased aluminium toxicity or nutrient imbalances (Cronan and Grigal 1995). The values obtained for Ca:Al and BC:Al in the Dupniański Stream catchment were above the level when aluminium stress is probable (Sverdrup and Warfvinge 1993; Cronan and Grigal 1995). On the other hand, according to Cronan and Grigal (1995) and Urlich (1988), these soils at a depth of 20 cm belonged to the acidic horizon with possible Al-stress on sensitive plants.

Despite large reductions in emissions, the Dupniański Stream catchment still suffers from very high loads of acidifying inputs deposited during the past decades. The results obtained in this study confirm that there is an additional inflow of the anions of strong acids. As precipitation water passes through the canopy, the latter components are washed out from the surface of needles, shoots, and branches. Alkaline cations, even if leached from assimilatory organs in considerable amounts, are unable to neutralise an increased acid inflow from the air (Małek and Astel 2007a, 2008). Considerable amounts of ions, especially sulphur and alkaline cations, are carried beyond the reach of the main mass of the root system and then out of the catchment, which may adversely affect the development and health of spruce stands. When the soil reaction in KCl falls below 3.0 (Table 2), the roots are likely to get damaged (Rost-Siebert 1985; Murach 1994). The low effective base saturation (around 10%; see Table 2) observed in the Dupniański Stream catchment and the Świętokrzyski National Park (Kowalkowski 2002), can be considered as a small flexibility in the response to acidic deposition. The sustainability of soils and spruce stands depends on future emissions, especially on the deposition of base cations and NH_4^+ (Ulrich et al. 1979). The recovery will even be slower if the base cation deposition continues to decrease (Małek et al. 2005).

Conclusions

The acid neutralising capacity, alkalinity, soil acidity, and basic cation saturation were found to depend on the age of spruce stands. The variability indicators showed an increasing share of the acidic component in throughfall and soil water. The increased acidification of deposits results from the presence of sulphate and nitrate ions which were washed out from the plant surface.

The acid deposition transformed in throughfall caused a decrease in the acid neutralising capacity, alkalinity, and basic cation saturation, and an increase in soil acidity with the increasing age of spruce stands, which confirms its negative effect.

Long-lasting considerable acidic emissions caused an increase in soil acidity and a decrease in basic cation saturation as well as a shift in the soil acid reaction to the range of aluminium and iron bufferness, but the Ca:Al and BC:Al ratios were above the level when aluminium stress is probable.

The washout of the basic cations beyond the tree root system and the low levels of exchangeable Mg^{2+} and Ca^{2+}, basic cation saturation of soil water, and effective base saturation of soil may have an effect on the future vitality and health of spruce stands. In order to preserve the sustainability of Norway spruce of Istebna provenance in the Dupniański Stream catchment it is necessary to improve the retention of basic elements, especially Mg^{2+} and Ca^{2+}, by stand conversion or fertilisation.

References

Aber J.D. 1992. Nitrogen cycling and nitrogen saturation in temperate forest ecosystems. Trends in Ecology and Evolution 7: 220–223.

Aber J.D., Nadelhoffer K.J., Steudler P. 1989. Nitrogen saturation in northern forest ecosystems. Bioscience 39: 378–386.

Adams M.B., Burger J.A., Jenkins A.B., Zelazny L. 2000. Impact of harvesting and atmospheric pollution on nutrient depletion of eastern US hardwood forests. Forest Ecology and Management 138: 301–319.

Astel A., Mazerski J., Polkowska Ż., Namieśnik J. 2004. Application of PCA and time series analysis in studies of precipitation in Tricity (Poland). Advances in Environmental Research 8: 337–349.

Becker R., Block J., Schimming C.G., Spranger T., Wellbrock N. 2000. Critical loads für Waldökosysteme – Methoden und Ergebnisse für Standorte des Level II Programmes. BELF, BML Bonn.

Block J., Eichborn J., Gehrmann J., Kölling C., Matzner E., Meiwes K.J., Wilpert K., Wolff B. 2000. Kennwerte zur Charakterisierung des ökochemischen Bodenzustandes und des Gefährdungspotentials durch Bodenversauerung und Stickstoffsättigung an Level II-Waldökosystem-Dauerbeobachtungsflächen. Arbeitskreis C, der Bund-Länder Arbeitsgruppe Level II. BML, Bonn.

Bredemeier M. 1988. Forest canopy transformation of atmospheric deposition. Water, Air and Soil Pollution 40: 121–138.

Bytnerowicz A., Godzik S., Poth M., Anderson I., Szdzuj J., Tobias C., Macko S., Kubiesa P., Staszewski T., Fenn M. 1999. Chemical composition of air, soil and vegetation in forests of the Silesian Beskid Mountains, Poland. Water, Air and Soil Pollution 116: 141–150.

Bytnerowicz A., Godzik B., Frączek W., Grodzińska K., Krywult M., Bada O., Barančok P., Blum O., Černy M., Godzik S., Maňkovská B., Manning W., Moravčik P., Musselman R., Oszlányi J., Postelnicu D., Szdżuj J., Varšavova M., Zota M. 2002. Ozone, sulphur dioxide and nitrogen dioxide air pollution in forests of the Carpathian Mountains. In: Effects of Air Pollution on Forest Health and Biodiversity in Forests of the Carpathian Mountains. Szaro R.C. et al. (eds.). IOS Press, pp. 138–160.

Cape J.N., Freer-Smith P.H., Paterson I.S., Parkinson J.A., Wolfenden J. 1990. The nutritional status of *Picea abies* (L.) Karst. across Europe, and implications for 'forest decline'. Trees 4: 211–224.

Cronan C.S., Grigal D.F. 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. Journal of Environmental Quality 24: 209–226.

Cronan C.S., Reynolds R.C. Jr., Lang G.E. 1978. Forest floor leaching: contributions from mineral, organic and carbonic acids in New Hampshire subalpine forests. Science 200: 209–311.

Draaijers G.P.J., Erisman J.W. 1995. A canopy budget model to assess atmospheric deposition from through fall measurement. Water, Air and Soil Pollution 85: 2253–2258.

Draaijers G.P.J., Erismann J.W., Van Leuven N.F.M., Römer F.G., Vinkel 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. Atmospheric Environment 31: 387–397.

Falkengren-Grerup U., Linnermark N., Tyler G. 1987. Changes in acidity and cation pools of south Swedish soils between 1949 and 1985. Chemosphere 16: 2239–2248.

Fenn M.R., Poth M.A., Aber J.D., Baron J.S., Bormann B.T., Johnson D.W., Lemly A.D., McNulty S.G., Ryan D.F., Stottlemeyer R. 1998. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses and management strategies. Ecological Applications 8(3): 706–733.

Florek M., Maňkovská B., Oszlányi J., Frontasyeva M.V., Ermakova E., Pavlov S.S. 2007. The Slovak heavy metals survey by means of the bryophyte technique. Ecologia (Bratislava) 26(1): 99–114.

Flower D., Smith R., Muller J., Cape J.N., Sutton M., Erisman J.W., Fagerli H. 2007. Long-term trends in sulphur and nitrogen deposition in Europe and the cause of non-linearities. Water, Air and Soil Pollution: Focus 7: 41–47.

Godzik S., Kubiesa P., Staszewski T., Szdzuj J. 1997. Air pollution and its possible effects on vegetation in Brenna – the Beskydy mountains. Zpravodaj Beskydy "Vliv imisi na lesy a lesni hospodarstvi Beskyd" (MZLU v Brne) 9: 21–26.

Hall J. 2004. Mapping critical loads. Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risk and trends. www.icpmapping.org

Harriman R., Gillespie E., King D. 1990. Short-term ionic responses as indicators of hydrochemical processes in the Allt a'Mharcaidh catchment, Western Cairngorms, Scotland. Journal of Hydrology 116: 267–285.

Heinrichs H., Siewers U., Böttcher G., Matschullat J., Roostai A.H., Schneider J., Ulrich B. 1994. Auswirkungen von Luftverunreinigungen auf Gewösserim Einzugsgebiet der Seetalsperre. In: Gefahr für Ökosysteme und Wasserqualität. Matschullat J., Heinrichs H., Schneider J., Urlich B. (eds.). Springer Verlag, Berlin, pp. 233–259.

Hornung M., Sutton M.A. 1995. Impact of nitrogen deposition in terrestrial ecosystems. Atmospheric Environment 29: 3395–3396.

Hruška J., Moldan F., Krám P. 2002. Recovery from acidification in central Europe – observed and predicted changes of soil and stream water chemistry in the Lysina Catchment, Czech Republic. Environmental Pollution 120: 261–274.

ICP-Forest Manual. 1998. Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. (4th ed.). UN-ECE, Fed. Res. Centre for Forestry and Forest Products (BFH).

Johnson D.W., Cresser M.S., Nilsson S.I., Turner J., Ulrich B., Binkley D., Cole D.W. 1991. Soil changes in forest ecosystems: evidence for and probable causes. Proceedings of the Royal Society of Edinburgh 97B: 81–116.

Jóźwiak M., Kozłowski R. 2004. Transformacja opadów atmosferycznych w wybranych geoekosystemach w Górach Świętokrzyskich. Regionalny Monitoring Środowiska Przyrodniczego (Kieleckie Towarzystwo Naukowe, Kielce) 5: 199–217.

Kowalkowski A. 2002. Wskaźniki ekochemicznego stanu gleb leśnych zagrożonych przez zakwaszenie. Regionalny Monitoring Środowiska Przyrodniczego (Kieleckie Towarzystwo Naukowe, Kielce) 3: 31–44.

Kulhavý J., Drápelová I., Remeš M., Lesná J. 2005. Depozični toky látek, stav pùdy a minerální výživy ve smrkové monokultuře v horské oblasti (Deposition flow, soil condition and mineral nutrition in spruce monoculture of mountain region). In: Trvale udržitelné hospodačeni v lesích a v krajiné od koncepce k realizacji (Sustainable forest and landscape management from concept to reality). Kulhavý J., Skoupý A., Kantor P., Simon J. (eds.). Sborník významných výsledkù institucionálního výzkumu LDF MOLU v Brne, češeného v letech 1999–2004, Brno, pp. 215–223.

Lorz C. 1999. Gewässerversauerung und Bodenzustand in Westerzgebirge. UFZ Bericht No. 14. (Diss.)

Łomnicki A. 2002. Wprowadzenie do statystyki dla przyrodników. PWN, Warszawa.

Małek S. 2004. The effect of the age of spruce stands on the balance of elements in the Potok Dupnianski catchment. Dendrobiology 51: 61–66.

Małek S., Astel A. 2007a. The effect of stand age on throughfall chemistry in spruce stands in the Potok Dupniański catchment in the Silesian Beskid Mountains, Southern Poland. TheScientificWorldJOURNAL 7(S1): 181–191.

Małek S., Astel A. 2007b. Source apportionment modeling of bulk precipitation chemistry on the Dupniański Stream catchment area (Silesian Beskid – Southern Poland) within 1999–2003. Polish Journal of Environmental Studies 16, 3B: 308–315.

Małek S., Astel A. 2008. Throughfall chemistry in a spruce chronosequence in southern Poland. Environmental Pollution 155, 3: 517–527. doi:10.1016/j.envpol.2008.01.031

Małek S., Martinson L., Sverdrup H. 2005. Modeling future soil chemistry at a highly polluted forest site at Istebna in Southern Poland using the "SAFE" model. Environmental Pollution 3(137): 568–573.

Maňkovská B., Černy M., Moravčik P., Godzik B., Grodzińska K., Badea O., Barančok P., Oszlányi J., Varšavova M., Fleischer P., Blum O., Parpan V., Bytnerowicz A., Szaro R. 2002. Chemical and morphological changes in Carpathian Mountains trees caused by air pollution. In: Effects of Air Pollution on Forest Health and Biodiversity in Forests of the Carpathian Mountains. Szaro R.C. et al. (eds.). IOS Press, pp. 173–184.

Murach D. 1994. Steuerung des Wurzelwachstums und der Jonenaufnahme von Waldbäumen und Waldbodenpflanzen. Berichte des Forschungszentrums Waldökosysteme (Göttingen), Reihe B, 37: 30–40.

Nihlgård B. 1972. Plant biomass, primary production and distribution of chemical elements in a beech and planted spruce forest in South Sweden. Oikos 23, 1: 69–81.

Ogner G., Opem M., Remedios G., Sjotveit G., Sorlie B. 1991. The chemical analysis program of the Norwegian Forest Research Institute. NISK, Aas.

Ostrowska A., Gawlinski S., Szczubiałka Z. 1991. Metody analizy i oceny właściwości gleb i roślin. Instytut Ochrony Środowiska, Warszawa.

Raynal D.J., Foster N.W., Mitchell M.J., Johnson D.W. 1992. Eastern hardwoods. In: Acidic Deposition and Forest Nutrient Cycling. Johnson D.W., Lindberg S.E. (eds.). Springer Verlag, New York, pp. 526–534.

Reuss J.V. 1991. The transfer of acidity from soils to surface waters. In: Soil acidity. Ulrich B., Summer M.E. (eds.). Springer Verlag, Berlin, pp. 203–217.

Reuss J.O., Johnson D.W. 1986. Acid deposition and the acidification of soils and water. Ecological Studies 59: 1–120.

Roberts T.M., Skeffington R.A., Blank L.W. 1989. Causes of spruce decline in Europe. Forestry 62(3): 179–222.

Rost-Siebert K. 1985. Untersuchungen zur H- und Al-Toxizität an Keimpflanzen von Fichte (*Picea abies* Karst.) und Buche (*Fagus sylvatica* L.) in Lösungskultur. Berichte des Forschungszentrums Waldökosysteme/Waldsterben (Göttingen), Band 12: 1–219.

Schlesinger W.H. 1991. Biogeochemistry. Analysis of global change. Academic Press, San Diego.

Sicard P., Coddeville P., Sauvage S., Galloo J.C. 2007. Trends in chemical composition of wet-only precipitation at rural French monitoring stations over the 1990–2003 period. Water, Air and Soil Pollution: Focus 7: 49–58.

Staszewski T., Godzik S., Szdzuj J. 1996. Monitoring spruce stands in Brenna and Salmopol pass in the Polish part of the Beskids. Zpravodaj Beskydy "Vliv imisi na lesy a lesni hospodarstvi Beskyd" (MZLU v Brne) 8: 13–18.

Staszewski T., Godzik S., Kubiesa P., Szdzuj J. 1999. Fate of nitrogen compounds deposited to spruce (*Picea abies* Karst.) and pine (*Pinus silvestris* L.) forests located in different air pollution and climatic conditions. Water, Air and Soil Pollution 116: 121–127.

Sverdrup H., Warfvinge P. 1993. The effect of soil acidification on the growth of trees, grass, herbs and expressed by the (Ca+Mg+K):Al ratio. Reports in Environmental Engineering and Ecology 2, Lund University.

Tamm C.O. 1991. Nitrogen in Terrestrial Ecosystems. Questions of Productivity. Springer Verlag, Berlin.

Ulrich B. 1983. Soil acidity and its relation to acid deposition. In: Effects of Accumulation of Air Pollutants in Forest Ecosystems. Ulrich B., Pankrath J. (eds.). D. Reidel Publishing Company, Dordrecht, pp. 127–146.

Ulrich B. 1988. Ökochemischen Kennwerte des Bodens. Zeitschrift für Pflanzenernahrung und Bodenkunde 157: 171–176.

Ulrich B., Mayer R., Khanna P.K. 1979. Deposition von Luftverunreinigungen und ihre Auswirkungen in Waldökosystemen im Solling. Frankfurt a. M.

van Breemen N., van Dijk H.F.G. 1987. Ecosystem effect of atmospheric deposition of nitrogen in the Netherlands. Environmental Pollution 54: 249–274.

van Breemen N., Burrough P.A., Velthorst E.J., van Dobben H.F., DeWit T., Ridder T.B., Reijnders H.F.R. 1982. Soil acidification from atmospheric ammonium sulphate in forest canopy throughfall. Nature 299, 548–550.

Warfvinge P., Svedrup H. 1992. Calculating critical loads of acid deposition with PROFILE. A steady state soil chemistry model. Water, Air and Soil Pollution 63: 119–143.

Warfvinge P., Svedrup H. 1995. Critical loads of acidity to Swedish forest soils. Methods, data and results. Reports in Environmental Engineering and Ecology 5: 1–104.

Zwoliński J. 2003. Ocena zagrożenia lasów świerkowych w Beskidzie Śląskim przez zanieczyszczenia powietrza atmosferycznego. Prace Instytutu Badawczego Leśnictwa, A, 1(951): 53–68.