Original Research

Changes in Element Content of Birch Leaves (*Betula pendula* Roth) in Polluted Air

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Abstract

The content of elements in leaves of birch (*Betula pendula* Roth) growing in the anthropogenicly contaminated conditions surrounding the towns of Olkusz and Niepołomice was determined in 1995, 1998, 2001, 2004, and 2007. Based on the dynamics of changes, the content of sulphur decreased. Contents of phosphorus, calcium, and magnesium fluctuated. Contents of nitrogen, potassium, and copper were insufficient, and that of manganese and zinc optimized to be increased. The content of lead and cadmium was excessive, and the content of aluminium was at the background level.

Keywords: *Betula pendula* Roth, macroelements, microelements, non-nutrient element, pollution

Introduction

The degree of stability disturbance of forest ecosystems depends on the species, amount, and length of the effects of pollutants, site conditions, and the actual conditions of forest stands. In the Czech Republic in the area of the Krušné hory and Jizerské hory mountains, the long-term effects of mainly sulphur oxides have required fundamental changes in forest management in mountain forest ecosystems [1]. The region of Katowice, Poland, is characterized by the long-term effect of industrial air pollutants coming from the metallurgical processing of zinc and lead [2-6]. Due to the high content of heavy metals in forest soils, the nutrition and growth processes of forest trees are altered [7]. The accumulation of heavy metals in tissues represents, at the same time, a threat because toxic heavy metals can come into the food chain [8].

It is known in some species (*Picea abies* [L.] Karst., *Pinus sylvestris* L., *Betula pendula* Roth, etc.) that air pollution load is also related to changes in the content of elements in assimilatory organs [1, 9-11]. In areas contaminated by heavy metals, degradation ecosystem changes occur, namely of vegetation in undergrowth [4].

Birch (*Betula pendula* Roth) used at the reforestation of clear-cut areas in the Czech Republic and other sites heavily disturbed by man contributed to the ecological stability and creation of conditions for the revitalization of soil [12]. Birch is a suitable species for the long-term monitoring of changes in the development of air pollution situation due to its resistance and tolerance to sites contaminated by air pollution [11]. Monitoring air pollution effects through other species was used in studied areas [10].

The aim of our paper is to specify the development of air pollution load (1995-2007) in the area of Olkusz-Niepołomice affected by metallurgical works and the dynamics of the level of macro-, micro-, and non-nutrient elements in assimilatory organs of birch (*Betula pendula* Roth).

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Table 1. Study sites and locations.

Site	Mark	Latitude (N)	Longitude (E)	Altitude (m)
Pakuska	PA	50º15' 57"	19º36' 11"	382
Bolesław – I	BI	50º17' 38"	19º29' 40"	320
Bolesław – II	BII	50º17' 12"	19º30' 30"	319
Bolesław – III	BIII	50º17' 49"	19º30' 00"	318
Klucze	KL	50º21' 31"	19º 33' 05"	356
Bukowno	BU	50º15' 46"	19º28' 40"	310
Niepołomice	NI	50º00' 24"	20º14' 58"	240

Table 2. Annual mean atmospheric SO_2 and NO_x concentrations and amounts of PM10 in station of region (µg·m^{-3}·year^{-1}; [17]).

Year	Olkusz			Niepolomice	
	SO_2	NO_x	PM10	SO_2	NO_x
1999	35	NA	NA	NA	NA
2000	23	16	43	NA	NA
2001	21	22	42	NA	NA
2002	20	NA	35	NA	NA
2003	18	49	38	NA	NA
2004	25	29	42	11	8
2005	16	50	39	12	12
2006	25	55	56	21	23
2007	19	NA	46	14	18

NA – not available

Methods and Material

Research Area

The two research areas were located in the Krakowsko-Częstochowska upland, first near the town of Olkusz (E 19º34', N 50º17'; six plots) and second near the town of Niepołomice (E 20º15', N 50º00; one plot) (for details see Table 1). The upland is built of Upper Jurassic rocks covered by glacial sands and loess. On the sands, particularly poor podzolic soils have developed [13] with low reserves of nutrients and a deep-situated groundwater level that is also disturbed by mining operations [14, 15]. The area climate is characterized by the high amplitude of mean annual air temperatures, relatively high precipitation in the summer season, and the high number of frosty days [16]. Although the area is affected by air pollutants from various sources, metallurgical emissions from works serving to process non-ferrous metals "Bolesław" (Zakłady Górniczo-Hutnicze "Bolesław" S.A.) show decisive position and in the past also a pulp mill (near Klucze). The area of Niepołomice is affected by iron works (Arcelor Mittal Poland S.A, Kraków). The actual air pollution situation in the area of Olkusz (1999-2007) is characterized by SO_2 (16-35 µg·m^{-3}·year^{-1}) and NO_x (16-55 µg·m^{-3}·year^{-1}) concentrations, and the amount of air borne dust (PM10) (35-56 µg·m^{-3}·year^{-1}) [17]. The airborne dust (80% particles <4 pm) is 53% soluble components. Compounds of Zn, Pb, and Cd (Dorling in [4]) are the most important proportion of them. The air pollution situation in the area of Niepołomice (2004-07) is similar to the concentration of SO_2 (11-21 µg·m^{-3}·year^{-1}) and NO_x (8-23 µg·m^{-3}·year^{-1}) (Table 2).

Soil and Leaves Sample Preparations and Analysis

In each of the monitored stands, a borrow pit was dug (2000) and soil samples were taken from particular horizons from a profile 0-100 cm. Metals (Mn, Zn, Cu, Pb, Cd) were analyzed using AAS method after extraction by HNO_3 (c=2 mol·l^{-1}) in the accredited laboratory Laboratoř Morava s.r.o., Studénka. With respect to the surface root system of birch, the site was characterized by Ah horizon from a depth of 2-3 cm.

Sampling the assimilatory organs of birch took place in 1995, 1998, 2001, 2004, and 2007 in plots Klucze (KL), Pakuska (PA), Bukowno (BU), and Bolesław I (BI), and in 2001, 2004, and 2007 in plots Bolesław II (BII), Bolesław III (BIII), and Niepołomice (NI). Samples of assimilatory organs of birch were obtained from the upper released part of crowns of three permanent sample trees from each of the stands at the end of the growing season (August). In particular samples, the content of nitrogen (Kjeldahl method, Tecator system), sulphur (LECO – analyzer), phosphorus (spectrophotometry, molybdenum-vanadium method), potassium (method of flame atomic emissions), calcium, magnesium, manganese, zinc, copper, lead, aluminum (AAS method), and cadmium (ETAAS), was determined [18].

Data Treatment

Values and changes in the content of macroelements (N, S, P, Ca, Mg, and K; mg·g^{-1}) and microelements (Mn, Zn, and Cu; µg·g^{-1}), (Table 4) were assessed from the aspect of limit values inevitable to ensure the nutrition and growth of birch (Table 5; classes: CC1 – insufficient, CC2 – sufficient, CC3 – optimum/higher). The content of Pb, Cd, and Al (µg·g^{-1}) (Table 4) was assessed from the aspect of exceeding standard contents, which can be considered to be tolerable and not endangering the growth of a tree (Table 5; classes: EC1 – background, EC2 – common, EC3 – excessive) [11].

Calculated weight ratios of macroelements were compared with limit values (Table 6; classes: IC1 – lower value of harmonic value, IC2 – harmonic value, IC3 – upper value of harmonic value; comp. [19, 28]).

The results obtained were evaluated as a multivariate data using factor analysis [20]. All 12 variables (content of the elements) were included in the analysis. Standardized data were used. Extraction of factors: principal components, rotation: Varimax simple.

Table 3. Mean content of microelements and non-nutrient elements ($mg \cdot kg^{-1}$) in soil layer (2-3 cm depth) of control sites (2000).

Site	pH	Mn	Zn	Cu	Pb	Cd
Pakuska	4.79	40	65^{I}	2.9^{O}	68^{I}	1.14^{II}
Bolesław – I	6.79	57	933^{IV}	5.5^{O}	286^{III}	6.65^{V}
Bolesław – II	6.78	157	$1,450^{IV}$	8.9^{O}	644^{IV}	13.50^{V}
Bolesław – III	5.65	42	592^{III}	8.0^{O}	345^{III}	7.42^{V}
Klucze	6.61	48	63^{I}	3.6^{O}	59^{I}	1.21^{II}
Bukowno	6.30	230	527^{III}	6.2^{O}	241^{III}	5.07^{V}
Niepołomice	4.65	1,035	57^{I}	8.5^{O}	43^{I}	0.53^{I}

Letters indicate Polish contamination standards: O – natural (background content), I – slightly elevated content, II – weak pollution, III – medium heavy pollution, IV – heavy pollution, V – very heavy pollution [6].

Results

Soil Analysis

Soil analysis (Table 3) shows low to moderate (in PA and NI only) acidity [21], and large variation in selected metal content. The content of Cu corresponded to natural background at all locations. The contents of Zn, Pb, and Cd were slightly elevated at NI [6], and the content of Mn was elevated. Low contents of metals were also determined at PA and KL (slightly elevated to weak pollution; [6]). At BU and BO locations the contents of Zn and Pb corresponded from medium heavy pollution to heavy pollution, the content of Cd to very heavy pollution [6].

Macroelements

During the monitored period the content of sulphur in birch leaves reached 0.71-2.75 $mg \cdot g^{-1}$. The lowest contents, significantly different from locations of sub-region Bolesław, were found at the Niepołomice location throughout the period. At Bolesław II the contents were highest and significantly differed from the other locations (Table 4). In the period 1995-2001, values of the sulphur content in leaves were within classes CC2 and CC3 and then a trend of the general decline of values occurred. Generally, half the determined values ranked the stands among the class of a sufficient content, remaining values were equally distributed into CC1 and CC3 classes (Table 5).

With respect to the content of nitrogen (15.50-30.36 $mg \cdot g^{-1}$), particular values occurred mainly in class CC1 (Table 5). The amount of nitrogen <20 $mg \cdot g^{-1}$ (36% of values) corresponded in the area of Olkusz in 2004 and 2007. Particular stands showed the similar content of nitrogen in leaves with the exception of the Niepołomice plot, where the content did not decrease under 20 $mg \cdot g^{-1}$ and was significantly different from most other locations (Table 4).

Although the content of phosphorus in birch leaves (1.02-3.75 $mg \cdot g^{-1}$) includes mainly values of sufficient content (Table 5), differences were noted between particular locations (Table 4). In stand NI, values of the content of P corresponded to class CC2, in stands PA, BI, and BU to classes CC2 and CC3, and plot BIII ranked by its half to the class of the lowest content CC1.

Values of the content of calcium at particular plots fluctuated but were sufficient (Table 5) 6.54-16.22 $mg \cdot g^{-1}$. The lowest content of Ca (mean±confidence interval <10 $mg \cdot g^{-1}$) characterizes markedly the Pakuska and Niepołomice sites (Table 4).

The content of magnesium (1.56-4.96 $mg \cdot g^{-1}$) was almost evenly distributed in the class of a sufficient and optimum/increased content (Table 5). Generally, the lowest content of Mg occurred at Niepołomice plot (significant difference from the other locations), the highest content at plots Bolesław II and III (Table 4). Within the period of monitoring, the variability of values was only a common fluctuation within particular growing seasons. Only at Pakuska plot did a fall occurre after 2001.

The content of potassium (3.27-10.59 $mg \cdot g^{-1}$) was insufficient (Table 5). The highest level of potassium occurred at Niepołomice (different from the other locations), the lowest one at Bolesław II (Table 4).

Microelements

The determined level of manganese in birch leaves (25-3,692 $\mu g \cdot g^{-1}$), mostly at a level of optimum/increased content (Table 5), and the mean (3,454 $\mu g \cdot g^{-1}$) achieved at the Niepołomice plot (2007) (Table 4) is related to the high content of Mn in soil (Table 3). Such an amount of Mn in leaves can be considered to be excessive. High contents of the microelements at NI and PA locations were significantly different from contents at other locations (Table 4). In all monitored stands, the content of Mn slightly increased in birch leaves (1995-2007).

The amount of zinc in birch leaves (191-2,070 $\mu g \cdot g^{-1}$) occurred exclusively in class CC3 (Table 5). All stands, with the exception of the Niepołomice locations (significantly lower contents compared to other locations), showed excessive values (>400 $\mu g \cdot g^{-1}$) (Table 4), which fully corresponded with the content of Zn in soil (Table 3).

Table 4. The mean and confidence interval (α=0.05) of the content of macro-, micro-, non-nutrient elements according to sites (pooled for the time of sampling).

Sites	Macroelements (mg·g^{-1})					
	Sulphur	Nitrogen	Phosphorus	Calcium	Magnesium	Potassium
PA	1.50^{B2,B3}	21.61^{N}	2.60^{B1,B3,K,N}	8.67^{B2,K,B}	2.70^{B2,B3,B,N}	5.72^{B2,B3,N}
	1.26-1.75	20.47-22.76	2.40-2.81	8.00-9.33	2.42-2.99	5.23-6.22
BI	1.68^{B2,N}	21.91	2.00^{P,B2,B3,B}	9.84^{B,N}	2.99^{B2,B3,N}	5.90^{B2,B3,N}
	1.51-1.86	20.73-23.08	1.80-2.20	9.02-10.67	2.75-3.23	5.42-6.38
BII	1.99^{P,B1,K,B,N}	20.00^{N}	2.53^{B1,B3,K}	11.38^{P,N}	3.96^{P,B1,K,B,N}	4.33^{P,B1,B,N}
	1.79-2.18	18.90-21.11	2.31-2.75	10.02-12.73	3.76-4.19	4.01-4.65
BIII	1.78^{P,K,N}	21.19^{N}	1.52^{P,B1,B2,B,N}	10.31^{N}	3.63^{P,B1,K,N}	4.53^{P,B1,N}
	1.49-2.07	19.60-22.77	1.34-1.70	9.31-11.30	3.23-4.03	3.94-5.12
KL	1.55^{B2,B3}	21.21^{N}	1.92^{P,B2,B}	10.74^{P,N}	3.05^{B2,B3,N}	5.11^{N}
	1.41-1.69	19.73-22.70	1.70-2.15	9.68-11.79	2.90-3.20	4.45-5.76
BU	1.65^{B2,N}	20.04^{N}	2.55^{B1,B3,K,N}	11.66^{P,B1,N}	3.34^{P,B2,N}	5.44^{B2,N}
	1.54-1.77	18.66-21.41	2.35-2.75	11.02-12.31	3.19-3.48	5.14-5.74
NI	1.43^{B1,B2,B3,B}	24.42^{P,B2,B3,K,B}	2.13^{P,B3,B}	7.99^{B1,B2,B3,K,B}	1.69*	7.89*
	1.33-1.52	23.36-25.47	1.94-2.32	7.65-8.33	1.61-1.77	7.26-8.52
Sites	Microelements (μg·g^{-1})			Non-nutrient elements (μg·g^{-1})		
	Manganese	Zinc	Copper	Lead	Cadmium	Aluminium
PA	630*	695^{B1,B2,B3,B,N}	4.99^{B2,B}	10.69^{B1,B2,B3,K}	1.65^{B2,B3,B,N}	72^{B1,B2,K}
	519-742	633-758	4.75-5.22	9.65-11.72	1.40-1.91	66-78
BI	64^{P,B2,K,N}	918^{P,B2,B3,B,N}	4.82^{B2,N}	23.32^{P,B2,B3,K,N}	1.45^{B2,B3,B,N}	57^{P,B2,B3,N}
	51-78	835-1,000	4.55-5.09	20.69-25.96	1.02-1.88	51-64
BII	254^{P,B1,B3,N}	1,234^{P,B1,B3,K,N}	7.52*	262*	5.76*	99*
	187-322	1,107-1,361	6.10-8.94	199-324	5.18-6.35	95-104
BIII	131^{P,B2,K,N}	1,471^{P,B1,B2,K,N}	5.02^{B2}	44.50*	2.56^{P,B1,B2,K,N}	68^{B1,B2}
	100-162	1,302-1,640	4.64-5.39	37.46-51.54	1.81-3.30	63-74
KL	314^{P,B1,B3,B,N}	732^{B2,B3,B,N}	4.81^{B2,N}	7.89^{B1,B2,B3,B}	1.24^{B2,B3,B}	61^{P,B2,N}
	224-404	610-853	4.57-5.05	6.90-8.89	0.84-1.64	56-66
BU	157^{P,K,N}	1,305^{P,B1,K,N}	4.49^{P,B2,N}	28.05^{P,B2,B3,K,N}	2.62^{P,B1,B2,K,N}	65^{B2,N}
	120-194	1,186-1,425	4.24-4.74	25.01-31.09	2.28-2.97	55-74
NI	2,692*	300*	5.49^{B1,B2,K,B}	3.17^{B1,B2,B3,B}	0.50^{P,B1,B2,B3,B}	78^{B1,B2,K,B}
	2,392-2,991	281-319	5.13-5.84	2.68-3.66	0.42-0.58	69-87

Letters indicate significant differences between marked sites - only the first character, * indicated differences to all sites.

The content of copper in leaves fluctuated (3.5-11.7 μg·g^{-1}), being mainly insufficient (Table 5). Maximum values of Cu determined in leaves (Table 4) and soil (Table 3) occurred at Bolesław II (significant difference from the other locations), where in 2007 the content of Cu in leaves increased twice (11.7 μg·g^{-1}). The high content of copper in soil (Table 3) did not show adequate response in birch leaves at Bolesław III and Niepołomice (Table 4).

Non-Nutrient Elements

The amount of lead in birch leaves (2.2-429.0 μg·g^{-1}) was mostly in the class of excessive content (Table 5). The limit of phytotoxicity (30 μg·g^{-1}; [22]) exceeded 30% values. The lowest level of Pb in leaves occurred at Niepołomice (Table 4), where decreased contamination of soil was also found (Table 3). Sites Klucze and Pakuska can

Table 5. Classes of element content in birch leaves and their distribution.

Element	CC2 value	CC1 – class	CC2 – class	CC3 – class
S	1.3-2.0	26	50	24
N	25-40	84	16	-
P	1.5-3.0	11	80	9
Ca	3-15	-	96	4
Mg	1.5-3.0	-	43	57
K	10-15	98	2	-
Mn	30-100	1	30	69
Zn	15-50	-	-	100
Cu	6-12	90	10	-
	EC2 value	EC1 – rate	EC2 – rate	EC3 – rate
Pb	2-10	-	33	67
Cd	0.1-0.2	-	2	98
Al	103-120	94	6	-

Value for S, N, P, Ca, Mg, K in $mg \cdot g^{-1}$, for Mn, Zn, Cu, Pb, Cd, Al in $\mu g \cdot g^{-1}$. Distribution (class) in % (related to all values of content).

be characterized similarly. The increased content of Pb in soil (240-644 $mg \cdot kg^{-1}$) affected also its level in leaves at the Bukowno, Bolesław I, II*, and III* plots (*significant difference from the other locations; Table 4). At Bolesław II, the mean content of Pb increased linearly in 2001-07.

The level of cadmium in birch leaves (0.19-7.42 $\mu g \cdot g^{-1}$) corresponds to the class of excessive content (Table 5). The content of Cd in soil corresponds with the content of Pb in the area (Table 3). The decreased (Niepołomice) and increased (Bolesław II, significant difference from the other locations) amounts of Cd in soil corresponds to the low or high level of Cd in leaves (Tables 2 and 3). With the exception of the Bolesław II site, the content of Cd has slightly decreased since 2001.

The content of aluminum (29-111 $\mu g \cdot g^{-1}$) was at the background level class (Table 5), the occurrence of values of a common content being sporadic (Bolesław II – significant difference from the other locations, Niepołomice). In 2007 the aluminum content decreased at all sites.

Element Ratios

Element ratios were assessed collectively for the whole monitored period and each of the plots according to criteria given in Table 6. N/P and N/Ca ratios were largely harmonic. Values of the IC1 class of both ratios were not found at Niepołomice. At other plots, they occurred only sporadically. Also, S/N ratios were mostly harmonic, part of the values corresponding to class IC3 (Table 6).

Values of the N/K ratio were evenly distributed between classes IC2 and IC3. At plots Bolesław II/Klucze and Bolesław III, the values were exclusively/mostly IC3; at the Niepołomice/Bolesław I plot, the values were all/mostly harmonic (Table 6).

The N/Mg ratio (Table 6) has indicated the larger disturbance of harmonic values; only values of Niepołomice have ranked among the IC2 class; since 2001 also Pakuska plots.

As of other evaluated ratios, the Ca/Mg ratio was quite harmonic. In the case of K/Ca and K/Mg, values of IC1 predominated. Harmonic values were found at the Niepołomice plot (both ratios) and at the Pakuska plot (only K/Ca) (Table 6). Values of the P/Al ratio were evenly distributed between classes IC2 and IC3 (Table 6). This indicates that the content of Al was low in leaves and did not have negative effects on tree growth.

Factor Analysis

Factor analysis involving all 12 variables (S, N, P, Ca, Mg, K, Mn, Zn, Cu, Pb, Cd, and Al) found four factors whose eigenvalues were greater than 1 (4.86, 2.60, 1.47,

Table 6. Classes of element weight ratio in birch leaves and their distribution.

Ratio	Range	IC2 value	IC1 – class	IC2 – class	IC3 – class
S/N	0.026-0.140	0.035-0.080	-	60	40
N/P	5.4-19.3	8.3-26.7	27	73	-
N/Ca	1.2-4.4	1.7-13.3	27	73	-
N/Mg	3.7-16.0	8.3-26.7	65	35	-
N/K	2.4-5.8	1.7-4.0	-	52	48
K/Ca	0.25-1.22	0.7-5.0	70	30	-
K/Mg	0.76-6.66	3.3-10.0	85	15	-
Ca/Mg	2.01-5.57	3.3-10.0	-	95	5
P/Al	16-104	12.5-29.1	-	47	53

Ratio and range dimensionless. Distribution (class) in % (related to all values of ratio).

and 1.03). These factors together explained 82.99% of the variability found. The found commonalities ranged from 0.6001 (Ca) to 0.9242 (Pb). The structure factors were simplified with Varimax simple rotation. Factor loadings greater than 0.6 were considered significant. Each variable has now occurred only in the factor that enabled us to identify the factors. The first factor can be described as S_N, because S and N variables were highly correlated. The second factor has been identified as heavy metals Cu, Pb, and Cd variables that were highly correlated. The third factor corresponding to nutrients included highly correlated variables Ca, Mg, Zn (positive correlation), K, and Mn (negative correlation). Finally, the fourth factor was identified as P_Al, highly correlating with variables P and Al.

Discussion

Emissions Situation

Locations west of Olkusz are so far significantly stressed by pollutants from ore mining and processing nonferrous metals. The area of Niepołomice is affected by sources related to the production of iron. The level of air pollution stress on monitored plots can be accessed on the basis of data of measuring stations Olkusz and Niepołomice [17], and the set of stations situated in Kraków [3].

Since 2001, air pollution concentrations of SO_2 (Table 2) in the region of Olkusz and Niepołomice only sporadically exceeds a limit value (20 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$) for forest stands [17], showing no negative effects on the stands. In 1970-71, SO_2 emissions reached 99 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$ (maximum 151 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$) related to the *Pinus sylvestris* L. [23] reducing population in the region of Bolesław. The long-term decline of air pollution load is also characterized by Kraków because a continuous fall occurred from 120 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$ (1970) to a level of almost 50 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$ (1995) and 20 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$ (2006) [3]. In 2003, increasing NO_x concentrations in the region of Olkusz exceeded limit values (30 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$), [17, 24] endangering forest stands. The area of Niepołomice did not note excess values of NO_x (Table 2). The slight increase of NO_x concentrations is also proved by the measurements carried out in the region of Kraków [3].

PM10 concentrations in the region of Olkusz (Table 2) are above a limit value determined for forest stands on a long-term basis (40 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$) [17]. In the surroundings of Kraków, the PM10 concentration after decline from values >100 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$ (1970) to <50 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$ (2000), increased to 80 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$ [3]. Particles are the cause of the uptake of Pb, Zn, Cd, and Mn to forest soils (Table 3). Values of the content of Pb and Zn in 2-year-old needles of pine in 1970 (Pb 113 $\mu g{\cdot}g^{-1}$, Zn 1,458 $\mu g{\cdot}g^{-1}$; [23]) and 1994 (Pb 76 $\mu g{\cdot}g^{-1}$, Zn 312 $\mu g{\cdot}g^{-1}$; [8]) show the decline of dust emissions in the area of Olkusz. Nevertheless, the actual inputs of these metals remain high.

Thus, acidification of the soil environment by sulphur oxides is always intensively neutralized by dust emissions. The pH value 6.78 in Ah horizon (Table 3) determined in the vicinity of "Bolesław" (locality BII) in 2000 is higher than the value mentioned by [23], viz. pH 6.

Soil Conditions

Soil in the sites of interest is very slightly acidic (Table 3). This phenomenon relates to the fact that pollutant fallout in the vicinity of Bolesław contains a lot of basic substances. This leads to increasing soil pH. Thus, also soils of coniferous forests, which are commonly acid, show pH (H_2O) values exceeding a value of 7. This results in the altering of biochemical processes in soil. The total content of Zn, Pb and Cd accumulated in forest litter and in the humus horizon of forest soils in this region is many times higher than in areas free of air pollution [2, 25, 26]. This state still persists (Table 3).

Macroelements

The content of total sulphur in stands corresponded to their air pollution load by sulphur dioxide. Thus, the subregion of Bolesław (BI, BII, BIII, BU) and particular locations of Klucze, Pakuska, and Niepołomice are differentiated. Based on the analogy of the results from the air-polluted area of the Krušné hory Mts. [9], values of the sulphur content found in the region of Bolesław (>2.0 $mg{\cdot}g^{-1}$) correspond to the air pollution load at a level of 30-40 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$ or values determined after 2001 (1.3-2.0 $mg{\cdot}g^{-1}$) to the air pollution load at a level of 20-30 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$. The air pollution flux of SO_2 in the surroundings of Olkusz after 2001 was uneven, which reflected in the insufficient content of sulphur in birch leaves <1.3 $mg{\cdot}g^{-1}$ (2007 – 0.76 $mg{\cdot}g^{-1}$) at Klucze and Pakuska locations corresponding to an SO_2 air pollution load markedly less than 15 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$. In spite of the substantial decline of air pollution load [8], there are significant differences in the amount of sulphur in pine needles at locations situated in a transect from the Bolesław metallurgical complex. The Niepołomice plot shows the content of sulphur in birch leaves at the lower limit of sufficient content – 1.3 $mg{\cdot}g^{-1}$. Thus, it is possible to derive air pollution load <15 $\mu g{\cdot}m^{-3}{\cdot}year^{-1}$. The content of sulphur in leaves is consistent with determined concentrations of air pollution load (Table 2). This fact confirms conclusions [9] on the existing relationship between the mean annual concentration of SO_2 and the content of total sulphur in birch leaves.

The content of nitrogen in birch leaves was mostly insufficient in spite of the increased pollution load by NO_x in the region of Olkusz in the second half of the monitored period. In the Krušné hory Mts., at a comparable lower air pollution load, the higher content of nitrogen in birch leaves was determined [11]. This means that inputs of nitrogen from soil are low with respect to requirements of a tree (birch). All of it demonstrates that the stands were not overloaded by excessive air pollution by nitrogen compounds [27]. At the same time, the content of nitrogen in leaves does not correspond to the maximum growth of the trees [28].

The sufficient content of phosphorus mostly corresponds with conclusions coming from the eastern part of the Krušné hory Mts. Similarly, the content of basic elements in birch leaves was the same (sufficient) for calcium and higher for magnesium (sufficient to optimum) in the Krušné hory Mts. The dynamics of changes in the content of elements is dependent on the character of the growing season [11].

Mostly the insufficient content of potassium as a result of its low supply in soil confirms conditions of the eastern Krušné hory Mts. For birch stands, the lower supply of potassium is typical [11].

Element Ratios

The predominance of harmonic values of N/P and N/Ca ratios indicates that trees receive P and Ca only in such an amount from soil that they can use in relation to the content of nitrogen (insufficient content). Thus, the content of P (with the exception on 2007) and Ca was sufficient. Göransson [29] mentions harmonic values of N/P and N/Ca (13.7 and 16.7, respectively) in young birch trees. Also, in the eastern Krušné hory Mts. values of both ratios were mostly harmonic in mature trees, although the content of N was at the lower limit of sufficient content and the content of P and Ca corresponded to conditions of monitored stands in Poland [30].

Exceeding the upper limit of a harmonic class at values of the S/N ratio is related to the higher content of sulphur in birch leaves (with the exception of Niepołomice), whereas the content of nitrogen did not change markedly. The same conclusions result from the area of the eastern Krušné hory Mts. [11]. The deficit of nitrogen does not affect the uptake of sulphur. Trees also can absorb its compounds (particularly SO_2 and H_2S) by leaves [31-35]. The uptake of sulphur from soil in the form of sulphates can be inhibited (at the sufficiency of nitrogen) by the surplus of cysteine or glutathione [36].

Determined values of the N/K ratio were half in class IC2 and IC3. Using results from the area of the Krušné hory Mts. [11], it appears that values of the N/K ratio corresponding to the IC3 class are the result of low contents of potassium. Göransson [29] mentions values at a level of 1.92 (i.e. at the lower limit of a harmonic ratio) for young birch trees. Actually, monitored mature trees require relatively less potassium and more nitrogen.

IC1 values of the N/Mg ratio are affected by the insufficient content of nitrogen and a sufficient-to-optimum content of magnesium. The input of nitrogen into stands was insufficient at Polish locations as compared with the region of the Krušné hory Mts. where harmonic ratios were mostly determined [11].

Harmonic values of the Ca/Mg ratio show that monitored birch stands are supplied by both elements according to requirements of trees. Lower harmonic values of K/Ca and K/Mg ratios demonstrate the deficit of potassium in stands. Harmonic and upper-harmonic values of the P/Al ratio do not show a negative influence of Al on utilizing P in leaves, therefore content of phosphorous-compounds decreases only slightly [37].

Microelements

The content of manganese in birch leaves is related to its amount in soil and to the pH value of the soil environment. At the Niepołomice plot, the pH value reached 4.65 and the content of manganese in soil 1,035 $mg \cdot kg^{-1}$ (Table 3) and in birch leaves up to 3,500 $\mu g \cdot g^{-1}$. The higher content of Mn in leaves at the Pakuska plot (Table 4) shows that low pH values affect the content of Mn in leaves more than its soil supply. It corresponds to findings on the intensity of the Mn uptake by roots from soil depending on pH of the soil environment [7]. In the region of the Krušné hory Mts. [11], up to 3,250 $mg \cdot kg^{-1}$ were on the markedly acid soil (pH 2.8-3.4), which became evident in the amount of manganese in leaves of birch exceeding the level of 10,000 $\mu g \cdot g^{-1}$. In both cases, it was necessary to classify the content as excessive. Present findings show that even the content of Mn in birch leaves at a level of 10,000 $\mu g \cdot g^{-1}$ does not mean unambiguous mortality, but necrotic damage appears on leaves and the premature fall of leaves occurs and the assimilatory function decreases [11, 38]. Plants with Mn content exceeding 10,000 $\mu g \cdot g^{-1}$ are considered to be hyperaccumulators [39].

High values of the content of zinc in birch leaves indicate the unnatural input of Zn compounds from soil through roots. With the exception of the Niepołomice location, the amount of zinc in soil was above the reference value (60 $mg \cdot kg^{-1}$; [21]). The amount of zinc in leaves is affected by the soil supply and dispersion of the root system. Kaźmierczakowa [4] mentions different contents in the aboveground and underground biomass of some herbs, and these differences relate to the root system character and changing pH values in the soil profile. Effects of the soil pH environment in birch at monitored plots were low because the intensity of the Zn uptake was constant within determined values (Table 3) [7]. The content of zinc in birch leaves was considerable, and 65% values exceeded the limit of phytotoxicity (400 $\mu g \cdot g^{-1}$; [10]). At the Bolesław II location (1,450 $mg \cdot kg^{-1}$ Zn in soil), toxicity became evident in the past at the broad spectrum of experimentally used shrubs and trees to test possibilities of their use for the afforestation of stressed localities. It resulted in open stands of birch.

The insufficient content of copper in birch leaves is not surprising. It is an usual situation known from the eastern part of the Krušné hory Mts. [11]. Copper is not accumulated in leaves, because leaves contain only such amounts of this metal as are inevitable for the growth of trees [10, 40]. Young growing parts contain the largest content of Cu and then its amount decreases [41].

Non-Nutrient Elements

It is evident that, similar to Zn there is excessive content of lead in birch leaves (Tables 3 and 4) due to environmental pollution by emissions coming from the metallurgical industry in the region. This is indicated by the content of lead in soil when the reference value of 8 $mg \cdot kg^{-1}$ is largely exceeded [21], e.g. at the Bolesław II plot (644 $mg \cdot kg^{-1}$)

(Table 3). In the area of the Krušné hory Mts. with a different structure of industry in the region, the content of Pb in birch leaves did not exceed the background level (<2 $\mu g \cdot g^{-1}$) and gradually decreased. In 2007, it fell back to 65% of the 1995 level [11].

The content of cadmium in birch leaves was excessive (Tables 3 and 4). Eighty-three percent of values were above the limit of standard content (0.05-0.5 $\mu g \cdot g^{-1}$; [10]). Both evaluations clearly show significant air pollutant inputs of Cd to soil in the region of Olkusz (Table 3), where the reference value of 0.2 $mg \cdot kg^{-1}$ is markedly exceeded [21]. The importance of inputs from soils is also demonstrated by results obtained from the region of the Krušné hory Mts., where the low content of Cd in soil (at a level of 0.1 $mg \cdot kg^{-1}$) reflected the lower content of Cd in birch leaves (max. 0.9 $\mu g \cdot g^{-1}$; [11]).

The content of Al in birch leaves was in the background class further decreasing in 2007. It is proved by a reaction to the alkaline environment conditioned by the air pollution impact from smelting works, because significant inputs of Al through roots into trees are possible only at the very low pH value of the soil environment. Reduction of the Al content in 2004/07 can be related to a further pH increase and immobilization of Al ions in soil [11].

Degradation of the environment in the region of Olkusz is also confirmed by monitoring the content of metals in rodents. In these rodents, significant amounts of Zn, Pb, and Cd were accumulated in teeth. After 1996 the content of Pb and Cd in rodents decreased [42-43]. The rate of cover of vegetation and the concentration of Cd and Pb in soil affected the species structure and spatial distribution of Carabidae. Mn showed significant effects on the number of individuals. It has been found that there are species of Carabidae that actively colonize or tolerate sites with high Mn content (Niepołomice). In the extremely stressed location Bolesław III, *Calathus erratus* (Sahl.) appears to be a highly tolerant species [44].

Interdependence of Variables

For this purpose, factor analysis was used. The first factor, labelled as nutrient (NU), shows the interrelationship of important macro-and micronutrients. Except for K^+, elements occurring in plants with oxidation number II belong to this group. These elements are important activators of enzymes, and counterions of important coenzymes [7]. In a plant, these elements compete for binding sites, which shows the negative value of factor loadings for Mn and K. The negative correlation of K and Mn results in negative effect on uptake, for contents of positively correlated elements such as Ca, Mg, and Zn.

The second factor, labelled heavy metals (HM), relates to the uptake of two highly toxic elements (Pb and Cd), and copper microelements. Their inclusion into one group can be derived from the same oxidation number (ions M^{2+}), a high affinity to sulphur, and low mobility in plants. Cu is different from Pb and Cd, because Cu is susceptible to redox reactions and forms easily complex compounds. These properties of Cu results in its biological function (part of the redox systems [45]). The HM factor also reflects the existence of significant air pollution load profile by these metals.

The third factor, labelled S_N, relates to the essential role of nitrogen and sulphur, the elements involved in the formation of amino acids and proteins [46]. A generic point of the assimilation of both elements is the formation of cysteine, which in addition to sulphur requires O-acetyl-L-serine, amino acid produced in the nitrogen assimilation [47]. The existence of the factor suggests that the forests do not have disturbed uptake of nitrogen and sulphur.

The fourth factor, P_Al, shows the relationship of these elements in the case of birch leaves. The interaction of these elements is based on the mutual affinities of the two elements that are reiterated in the leaves (or other plant parts, [37]).

Conclusions

The areas of Olkusz and Niepołomice are regions with permanently existing air pollution loads. Although emission concentrations of SO_2 significantly decreased at the turn of the last millennium (under the limit level of 20 $\mu g \cdot m^{-3} \cdot year^{-1}$), NO_x and PM10 concentrations (with a significant proportion of heavy metals) increased during this period, fluctuating above the limit for forest ecosystems (30 $\mu g \cdot m^{-3} \cdot year^{-1}$ NO_x, 40 $\mu g \cdot m^{-3} \cdot year^{-1}$ PM10). This condition was affected by the content of select macro-, micro- and non-nutrient elements in birch leaves.

The content of total sulphur in birch leaves is sufficient, showing the trend of fall. The amount of nitrogen in birch leaves was largely insufficient in spite of the increase in air pollution concentrations of NO_x. The content of P, Ca, and Mg was sufficient or their changes corresponded to fluctuations in the growing season. The content of potassium was insufficient due to the low soil supply. The content of macroelements also corresponds with values of their weight ratios. Mainly harmonic ratios of N/P, N/Ca, and Ca/Mg occurred. Considerably disturbed harmonic values were at N/Mg, K/Ca, and K/Mg ratios. Values of N/K ratios were harmonic to supraharmonic.

The amount of microelements and non-nutrient elements in birch leaves was related to their amount in soil. At the Niepołomice plot with the high content of Mn in soil, the content of the element in leaves was 2,200-3,500 $\mu g \cdot g^{-1}$. The amount of Zn in soil exceeded a reference value (60 $mg \cdot kg^{-1}$). In leaves, 65% values were below the limit of phytotoxicity (400 $\mu g \cdot g^{-1}$). On the Bolesław II plot, only birch tolerates a high degree of toxicity. The content of copper was insufficient, being sufficient on the Bolesław II plot. Soil was the source of Cu. The content of lead in soil was markedly above a reference value (8 $mg \cdot kg^{-1}$), being largely excessive in leaves. Thirty percent of the values exceeded the limit of phytotoxicity (30 $\mu g \cdot g^{-1}$). The content of Cd in soil was above a reference value (0.2 $mg \cdot kg^{-1}$). In leaves, the content of Cd was excessive, and 83% of values exceeded 0.5 $\mu g \cdot g^{-1}$. The content of aluminum was largely at the background level, on some plots being below 50 $\mu g \cdot g^{-1}$.

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