

Original Research

Chemical Transformations in to Podzolic soils Induced by Alkaline and Acidic Emissions in the Świętokrzyski Region of Poland

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Abstract

The present study compares properties of podzolic soils developed from sandy materials overgrown by forests, affected either by alkalizing or acidifying emissions. The study entailed sampling 4 pedons in the vicinity of the Ożarów Cement Plant S.A. and 4 pedons near Rudniki village (within the impact zone of "Osiek" Sulphur Mine and Połaniec Power Plant). Soil samples were analyzed for basic chemical properties. The study showed significant changes in physicochemical properties of the alkalized podzolic soils: an increase in pH value, in base saturation of the exchange complex, contents of plant available potassium and magnesium, CaCO₃ content in organic and humic horizons and in salinity, and a decrease in organic carbon content and hydrolytic acidity, podzolic soils occurring in areas affected by anthropogenic acidification were characterized by decreased pH value, increased total sulphur and sulfate (S-SO₄) contents, increased hydrolytic and exchangeable acidity, and lowered base saturation of the exchange complex.

Keywords: alkalization, acidification, podzolic soils, degraded soils, south-central Poland

Introduction

Disadvantageous and multidirectional changes in the environment of the Świętokrzyski region (south-central Poland) are due to its industrial development based on the richness of mineral resources. On the one hand, large areas are affected by alkalization, which is particularly advanced in the Kielce Carbonate Mining District (1032 km²), and on the other, by global acidification caused by local household sources and remote industrial emission [1]. Forest ecosystems easily react to direct and indirect natural and anthropogenic influences changing its structure, function and interrelationships

between its components [2-5]. Forest ecosystems of the Świętokrzyski region are particularly at risk due to exposure to two-thousand-year long pressure of the local mining and smelting industry [6].

The aim of the present studies was to compare properties of *Haplic Podzols* and *Albic Arenosols* developed from sandy materials under forest vegetation, affected either by alkalizing or acidifying emissions.

Experimental Procedures

Four soil profiles were sampled in the vicinity of the Ożarów Cement Plant S.A. and 4 profiles were exposed near Rudniki village (within an impact zone of "Osiek" Sulphur Mine and Połaniec Power Plant) in 2002 and

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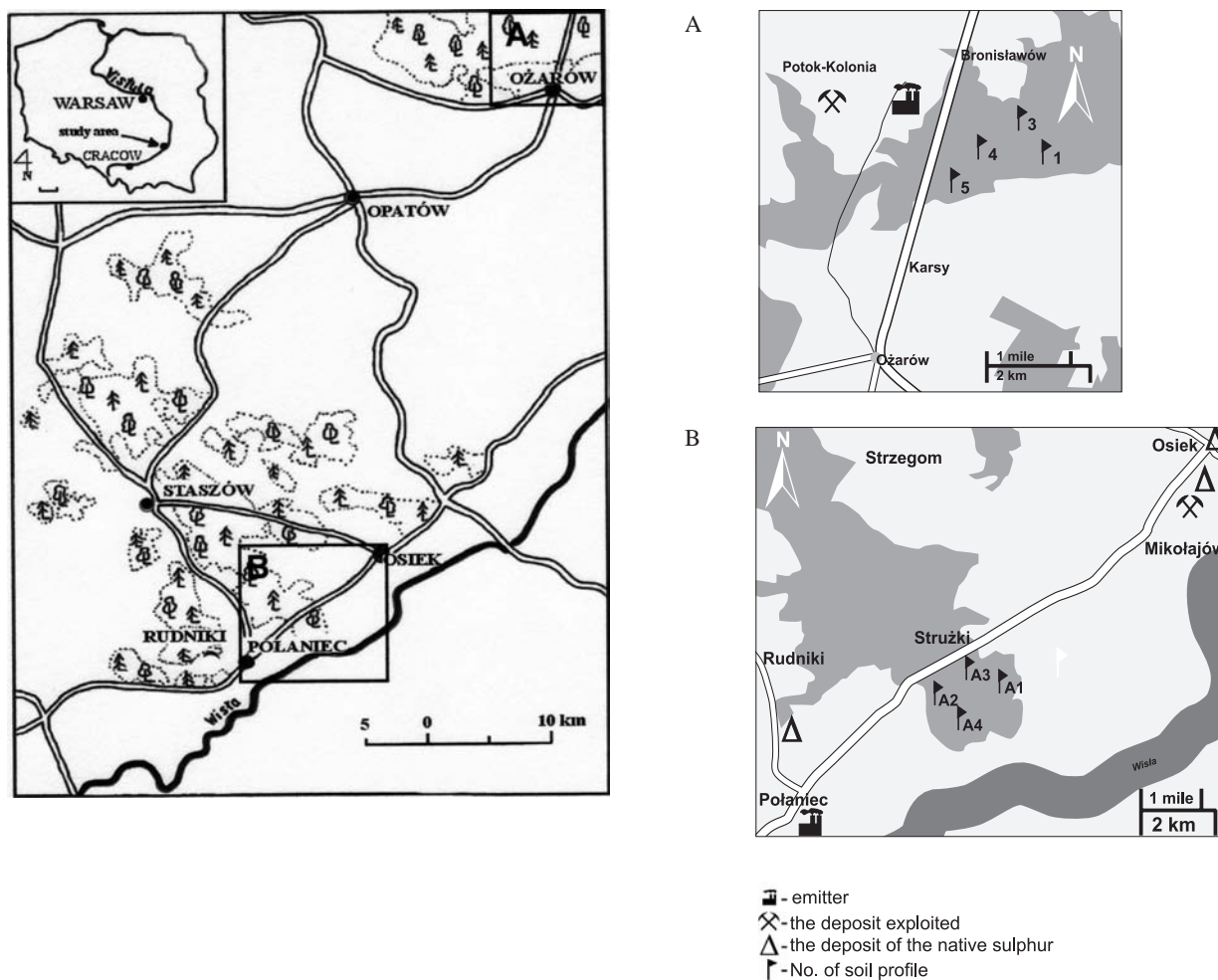


Fig. 1. Location of examined sites, A–Ożarów site, B–Rudniki site.

2003. Air-dried samples were used for determination of particle size distribution in the >0.1 mm fraction (using a sieve with a 10, 5.0 and 1.0 mm mesh) and the <0.1 mm fraction according to Casagrande's method modified by Prószyński, and the following chemical properties: pH of soil suspension in distilled water and 1M KCl by potentiometric method, hydrolytic acidity (Hh) by Kappen's method, exchangeable acidity (Hw) and exchangeable aluminum (Al^{3+}) by Sokolow's method, organic carbon (C_{TOT}) by Tiurin's method in mineral samples and by Altman's method in organic samples, total nitrogen (N_{TOT}) by a modified Kjel Dahl's method in Kieltec Auto 1030 autoanalyzer, $CaCO_3$ by Scheibler's method, soil salinity based on measurement of electro-

lytic conductivity PEW_{25} of soil extracts using a 1:5 proportion (Polish standard ISO-PN 11265), exchangeable cations in 1M CH_3COONH_4 , pH_{H_2O} 7.0 for non-carbonate samples and in 1M CH_3COONH_4 , pH_{H_2O} 8.2 for carbonate samples [7], sum of exchangeable base cations S, actual cation-exchange capacity PWK_r (ISO-PN 11260), potential base saturation of the exchange complex $V_{pot} = S/PWK_{8.2} \times 100\%$, where $PWK_{8.2} = S + Hh$, total sulphur (S_{TOT}) content according, while $S-SO_4$ was determined in 1% HCl. Heavy metals Cd, Cu, Cr, Mn, Pb, Sr, Zn were assayed after incineration in an electrical oven at about $480^\circ C$ and dissolution in HCl- HNO_3 (3:1) using ICP-AES with Jobin-Yvon spectrometer: JY 70 PLUS.

Table 1. Emission of pollution in the examined sites in 2002.

Site	Dust emission Mg/year	SO ₂ Mg/year	NO ₂ Mg/year	Dust sus- pension μg/m ³	SO ₂ μg/m ³	NO ₂ μg/m ³	H ₂ S μg/m ³	CS ₂ μg/m ³	Dustfall g/m ² /year
Rudniki	308	1103	345	18.4	13.9	30.1	1.7	2.4	32.1
Ożarów	453	1006	209	36.4	7.2	19.6	-	-	91.0

Study Area

The Rudniki site was located in a forest stand growing on fluvio-glacial sands. The Rudniki site (named by the nearest village) was situated 2 km away from Osiek town, where sulphur has been mined by a borehole method since 1993. The site was located 4 km from Połaniec, where there is a power plant whose emission additionally acidifies the environment under study (Fig. 1, 1A, 1B). The Połaniec Power Plant has affected surrounding ecosystems since 1979, while sulfur extraction from the deposits of the Tarnobrzeg Basin (Osiek, Baranów, Machów, Jeziórko, Basznia, Rudniki deposits) dates back to the 1960s. Over 30% of world sulfur resources, i.e. 560 million Mg, occurs in the Tarnobrzeg Sulfur Basin [8].

The second site was located in a forest stand growing on dune sand in Karsy village 300–800 m away from the Ożarów Cement Plant. The Ożarów Cement Plant S.A., which has operated since 1978, manufactures cement by a dry method and supplies more than 15% of the Polish cement market. Many processes of cement manufacture are hazardous to the environment: mining of raw material, its transport, crushing, burn-out, packing and storage [6, 9, 10]. Any of these processes is a source of systematic or incidental particulate and gaseous emission.

Both the Ożarów Cement Plant and “Osiek” Sulphur Mine have implemented monitoring of gaseous and particulate pollution. Pollution in direct neighborhood of these plants does not exceed allowable limits (Table 1).

Emission from the above-described sources in past years (until 1990) had been much higher and often exceeded allowable limits. Modification of the present physicochemical properties of soils is a result of long-term anthropogenic pressure.

Results

Based on soil profile, all soils were classified as *Haplic Podzols* (profile No. 3 Ożarów site and 2A Rudniki site) with the horizon sequence Ol-Ofh-AEes-Bfe-B-C and *Albic Arenosols* with horizon sequence Ol-Ofh-AEes-Bv-(BvC)-C (profile No. 1, 4, 5 Ożarów site and A1, A3, A4 Rudniki site [Fig. 1]). Analysis of particle size distribution of these soils showed dominance of loose and fine-clayey sands with 9% content of floatable particulate matter. These soils constituted an oligotrophic habitat of coniferous forest with scots pine (*Pinus sylvestris*) prevailing among trees. They are *Dicrano-Pinion* alliances of different degrees of degeneration. The alliances are composed of 40–90 year-old pinewoods. In the Ożarów and Rudniki area, transformations of species composition and health status of trees were observed (e.g. at the Rudniki site: impoverishment of herbaceous species, loosening of tree cover, pine tree defoliation, and at the Ożarów site: increase in the number of forest floor species, including dry-ground forest and synanthropic species, increased abundance of branches, increased shrub layer). In the study area, westerly (28%

annually) and southwesterly (16.7% annually) winds with an average speed 3.3 m/s [1].

Soils at the Ożarów site have markedly changed their natural properties, becoming more alkaline. The soils under study had variable pH values. Organic and organic-mineral horizons had pH_{KCl} ranging between 5.75 and 8.11, while pH of mineral horizons occurring below 7–10 cm was lowered to pH_{KCl} 4.35 (Table 2).

These pH values (in organic horizon) are much higher than those reported earlier for oligotrophic podzol soils [3, 12, 13] and most probably result from cement and limestone dust deposition (Table 2). The CaCO_3 content in soils detected to a depth of 100 cm is another consequence of the elevated soil alkalinity. The largest amounts of carbonates (7.15–19.11%) occurred in Ofh horizon and in litter horizon (2.25–7.59%), that hampered development of forest ground vegetation and caused elimination of species of the class *Vaccinio-Piccetetea* [6, 14].

Exchangeable acidity was measured only in a few mineral horizons occurring below 50–60 cm. Hydrolytic acidity was also very low in comparison with values reported for organic horizon *Haplic Podzols* and *Albic Arenosols* [4, 15, 16]. It ranged from 0.32 to 17.71 cmol/kg, with the highest values observed in Ol horizon. Hydrolytic acidity considerably declined with depth to 50–60 cm and then slightly rose in parent rock horizon. Calcium was the dominating element among exchangeable base cations on the exchange complex of the soils under study. Ca^{2+} content ranged from 37.0 to 91.2 cmol/kg in organic horizons and dropped to 0.31–0.65 cmol/kg in C horizons. Mg^{2+} content also was elevated (3.17–8.13 cmol/kg in Ol and Ofh levels). The sum of exchangeable base cations was the highest in surface horizons (10.54–99.97 cmol/kg), decreasing to 0.39–0.74 cmol/kg in C horizons.

Natural soil salinity is rare in Poland, and usually does not exceed 50 mg KCl/100 g on arable land [6]. Excessive salinity caused *inter alia* by alkalization can be a measure of anthropogenic soil degradation. Ionic balance is under such conditions displaced and soil solution is superfluously concentrated, which lowers availability of water and nutrients for plants. This process is particularly aggravated in dry soils. Due to its hygroscopicity, cement and limestone dust accumulate in surface horizons and increase water deficit, particularly in summer [9, 14].

High salinity of surface horizons (111.0–270.3 mg KCl/100 g) causes the majority to not be absorbed by the exchange complex. Therefore, exchangeable cations occur in soil as soluble salts. For this reason, the exchange complex is characterized well by actual cation-exchange capacity PWK_r. In acidic samples, PKW_r was much lower than potential cation-exchange capacity PKW_r, whereas in alkaline samples both values were similar. The soils under study had high cation-exchange capacity PWK_r ranging between 43.27–100.05 cmol/kg in organic horizons and 1.86–2.09 cmol/kg in C horizons. In surface horizons, these values are manifold higher than those reported for emission-free podzolic soils, while in the C horizon the values were comparable and indicated a slight impact of pollution on horizons below 70–80 cm (Table 2).

Table 2. Selected chemical properties of the examined soils. S* (sum of exchangeable base cations).

Profile No	Horizons	Depth (cm)	pH _{H₂O}	pH _{KCl}	C _{TOT}		N _{TOT}	Al ³⁺	Hw	Hh	S* (cmol/kg)					V (%)	
					CaCO ₃	(%)					Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	S*		PWKr
Alkalinized soils at the Ożarów site																	
1	Ol	0-2	6.05	5.89	5.98	48.17	1.22	0.01	0.02	10.19	38.99	3.19	2.57	0.17	44.92	44.95	81.51
	Ofh	2-5	8.10	7.96	19.11	20.98	0.89	0	0	1.21	87.12	8.13	1.41	0.21	96.87	96.87	98.77
	AEes	5-14	7.98	7.24	4.63	1.12	0.05	0	0	0.32	25.12	1.04	0.32	0.10	26.58	26.58	98.81
	Bv	14-65	5.61	5.41	0.51	0.23	0.04	0.15	0.17	1.15	6.12	0.24	0.09	0.03	6.48	6.8	84.93
	C	65-120	4.51	4.47	0.0			0.69	0.77	2.11	0.55	0.06	0.02	0.00	0.63	2.09	22.99
3	Ol	0-2	6.11	6.10	2.35	48.34	0.96	0	0	16.10	38.12	4.11	2.23	0.15	44.61	44.61	73.48
	Ofh	2-4	8.24	8.11	7.15	29.32	0.85	0	0	2.15	86.23	4.98	1.53	0.17	92.91	92.91	97.74
	AEes	4-15	7.66	7.54	2.23	1.11	0.09	0	0	1.23	12.05	0.72	0.25	0.05	13.07	13.07	91.40
	Bfe	15-28	5.71	5.63	1.30	0.78	0.09	0.07	0.12	2.45	6.54	0.09	0.07	0.02	6.72	6.91	73.28
	B	28-59	5.69	5.59	0.41	0.28	0.05	0.25	0.33	2.87	2.12	0.08	0.03	0.02	2.25	2.83	43.95
4	C	59-110	4.78	4.62	0.00			0.49	0.59	3.01	0.41	0.04	0.03	0.01	0.49	2.04	15.05
	Ol	0-2	6.87	6.33	7.59	43.97	1.31	0.03	0.05	14.72	91.20	6.52	2.09	0.16	99.97	100.05	87.17
	Ofh	2-8	8.32	8.12	18.93	31.81	1.06	0	0	5.39	45.91	3.52	1.56	0.14	51.13	51.13	90.46
	AEes	8-12	8.22	8.00	7.11	0.99	0.11	0	0	0.33	9.98	0.27	0.23	0.06	10.54	10.54	95.91
	Bv	12-65	5.49	5.21	1.11	0.21	0.02	0.13	0.15	1.78	1.71	0.09	0.06	0.03	1.89	2.17	51.50
5	C	65-100	4.21	4.10	0.21			0.61	0.65	1.99	0.51	0.05	0.03	0.01	0.60	1.86	23.17
	Ol	0-2	6.10	6.05	6.43	49.23	0.92	0.05	0.08	17.71	37.00	3.98	2.00	0.16	43.14	43.27	70.90
	Ofh	2-4	7.99	7.78	7.15	21.13	0.75	0	0	2.98	84.50	3.17	1.43	0.21	89.31	89.31	96.77
	AEes	4-19	7.51	7.20	5.10	1.07	0.09	0	0	1.12	25.97	1.23	0.77	0.09	28.06	28.06	96.16
	Bv	19-60	5.55	5.13	0.22	0.40	0.08	0.12	0.19	2.45	2.75	0.24	0.07	0.02	3.08	3.39	55.70
C	60-130	4.55	4.35	0.0			0.51	0.71	2.99	0.65	0.06	0.03	0.00	0.74	1.96	19.84	

Table 2. continued

Acidified soils at the Rudniki site																	
A1	Ol	0-2	4.21	4.11	absent	45.24	1.30	4.73	7.33	121.1	10.97	0.79	0.13	0.31	12.2	24.26	9.15
	Ofh	2-5	4.00	3.99		40.62	1.28	4.56	8.45	116.3	9.74	0.41	0.09	0.17	10.41	23.42	8.22
	AEes	5-14	3.98	3.72		1.57	0.05	1.89	1.99	8.81	0.07	0.08	0.05	0.03	0.23	4.11	2.54
	Bv	14-65	3.65	3.59		0.19	0.03	0.32	0.43	1.72	0.01	0.05	0.04	0.02	0.12	0.87	6.52
	C	65-120	4.09	4.00				0.22	0.28	1.17	0.04	0.02	0.02	0.01	0.09	0.59	7.14
A2	Ol	0-2	4.00	3.95		39.21	1.25	3.89	6.99	99.5	10.21	0.68	0.14	0.29	11.32	22.20	10.21
	Ofh	2-4	3.51	3.29		36.23	1.09	2.98	5.90	92.7	7.72	0.33	0.1	0.19	8.34	17.22	8.25
	AEes	4-15	4.02	3.34		1.45	0.06	1.55	2.09	10.11	0.57	0.12	0.06	0.03	0.78	4.42	7.16
	Bfe	15-28	4.33	4.12		0.31	0.06	1.32	1.77	2.76	0.39	0.1	0.04	0.04	0.55	3.64	16.62
	B	28-59	5.00	4.55		0.13	0.03	0.99	1.06	2.34	0.35	0.09	0.03	0.03	0.49	2.54	17.31
A3	C	59-110	4.17	4.07				0.34	0.61	1.55	0.05	0.03	0.03	0.01	0.12	1.07	7.19
	Ol	0-2	3.53	3.34		43.19	1.35	9.12	10.11	109.7	8.75	0.71	0.11	0.21	9.78	29.01	8.19
	Ofh	2-8	3.23	3.57		41.99	1.12	3.89	7.99	97.6	6.65	0.31	0.09	0.18	7.23	19.11	6.90
	AEes	8-12	3.67	3.33		1.19	0.07	1.99	2.11	11.4	0.04	0.05	0.02	0.01	0.12	4.22	1.04
	Bv	12-65	4.07	3.92		0.20	0.03	0.98	1.12	3.13	0.03	0.03	0.02	0.01	0.09	2.19	2.80
A4	C	65-100	4.33	4.23				0.43	0.98	2.09	0.04	0.03	0.01	0.01	0.09	1.50	4.13
	Ol	0-2	4.12	4.00		45.34	1.28	6.32	8.67	103.11	10.66	0.81	0.12	0.19	11.78	26.77	10.25
	Ofh	2-4	4.08	3.78		42.11	1.11	5.12	6.99	98.6	8.78	0.29	0.11	0.16	9.34	21.45	8.65
	AEes	4-19	3.97	3.81		1.46	0.08	3.43	5.02	9.88	0.09	0.11	0.07	0.04	0.31	8.76	3.04
	Bv	19-60	4.21	4.10		0.20	0.03	2.19	3.12	2.96	0.09	0.07	0.04	0.02	0.22	5.53	6.92
0	C	60-130	4.13	4.08				1.67	2.14	1.89	0.06	0.03	0.01	0.01	0.11	3.92	5.50
	Unpolluted soil by cited data [3, 12, 14] mean values																
	Ol		4.60	4.41	absent	45.34	1.55	6.32	3.10	79.22	14.78	0.94	0.15	0.24	16.11	25.53	16.90
	Ofh		4.20	4.09		40.11	1.09	4.12	2.52	67.41	11.94	0.33	0.16	0.28	12.71	19.35	15.86
	AEes		4.27	4.18		1.16	0.05	1.43	1.06	3.97	1.19	0.22	0.11	0.10	1.62	4.11	28.98
Bv		4.73	4.65		0.30	0.02	0.72	1.15	2.11	1.15	0.12	0.09	0.08	0.62	2.49	22.71	
C		4.15	4.09				0.32	0.18	0.85	0.13	0.06	0.05	0.07	0.25	0.75	22.73	

Table 3. Salinity, sulphur and heavy metals of the examined soils.

Profile No	Horizons	Depth (cm)	Soil salinity	S _{TOT}	S-SO ₄	Cr	Cu	Mn	Pb	Sr	Zn
			(mg KCl/100g)	(mg/kg d. w. of soil)							
Alkalized soils at the Ożarów site											
1	Ol	0-2	260.7	4.13	0.97	10.2	12.0	620.5	87.0	16.0	134.3
	Ofh	2-5	151.8	3.09	1.12	28.1	21.0	811.0	107.0	74.0	189.0
	AEes	5-14	27.7	0.89	0.13	20.5	17.0	431.0	89.0	55.0	67.0
	Bv	14-65	14.4	0.11	0.05	7.0	10.0	351.0	55.0	12.0	34.0
	C	65-120	36.2	-	-	3.0	5.0	54.0	9.0	6.0	11.0
3	Ol	0-2	270.3	3.96	0.87	15.0	8.0	556.0	51.0	15.0	100.0
	Ofh	2-4	136.2	2.78	0.97	25.0	16.0	1196.0	91.0	65.0	239.3
	AEes	4-15	26.5	0.76	0.12	19.0	14.0	440.5	29.0	17.0	48.0
	Bfe	15-28	7.3	0.63	0.10	6.0	4.0	334.0	7.0	6.0	19.0
	B	28-59	17.2	0.09	0.06	5.0	3.0	95.0	3.0	5.0	10.0
	C	59-110	24.2	0.09	0.02	2.0	1.0	64.0	2.0	3.0	12.0
4	Ol	0-2	255.6	3.99	0.96	13.0	11.0	621.0	85.0	17.0	131.0
	Ofh	2-8	128.0	3.12	1.11	28.0	20.0	810.5	112.0	73.0	181.0
	AEes	8-12	25.7	0.77	0.14	20.0	17.0	421.0	78.0	59.0	62.0
	Bv	12-65	19.2	0.12	0.08	7.0	12.0	350.0	52.0	14.0	36.0
	C	65-100	21.1	-	-	3.0	4.0	52.0	11.0	6.0	10.0
5	Ol	0-2	220.3	4.23	1.06	10.0	13.0	779.5	39.0	26.0	134.0
	Ofh	2-4	111.0	3.67	1.14	22.5	21.0	1037.0	77.0	61.3	192.0
	AEes	4-19	27.8	0.98	0.21	5.0	3.0	389.0	12.0	6.0	19.0
	Bv	19-60	21.3	0.11	0.06	7.0	4.0	108.0	17.0	4.0	17.0
	C	60-130	30.2	0.09	0.03	4.0	3.0	77.0	6.0	2.0	13.0
Acidified soils at the Rudniki site											
A1	Ol	0-2	78.1	64.5	10.4	16.0	14.1	800.5	120.0	10.0	180.0
	Ofh	2-5	55.3	99.6	14.2	43.0	11.3	1010.6	210.6	55.0	210.3
	AEes	5-14	24.8	27.4	6.6	45.0	7.0	640.0	91.0	26.0	56.0
	Bv	14-65	18.4	11.8	3.1	31.4	5.4	576.0	41.6	6.0	37.5
	C	65-120	15.1	9.3	2.0	25.0	4.0	402.5	20.0	3.4	31.0
A2	Ol	0-2	77.3	78.5	11.5	18.5	16.0	901.0	119.0	12.0	185.0
	Ofh	2-4	56.3	89.5	15.1	44.0	15.0	1003.0	207.7	51.0	190.5
	AEes	4-15	20.9	65.4	10.2	29.0	9.2	530.0	51.2	22.0	54.0
	Bfe	15-28	17.6	50.3	6.1	42.3	7.0	420.0	22.0	14.0	44.0
	B	28-59	16.8	22.1	4.2	27.0	6.2	390.1	24.3	9.0	39.3
	C	59-110	15.9	20.9	2.4	24.0	6.0	223.3	12.0	6.0	21.0
A3	Ol	0-2	81.2	75.3	12.2	17.0	14.0	874.0	107.5	14.0	179.0
	Ofh	2-8	48.0	93.2	17.5	50.2	18.2	1113.0	159.0	46.0	198.0
	AEes	8-12	30.1	44.6	8.6	32.0	15.0	490.0	49.0	19.0	55.0
	Bv	12-65	12.7	37.4	4.2	41.0	8.0	280.2	43.4	11.0	43.0

Table 3. continued

A3	C	65-100	12.0	12.4	2.3	24.0	7.3	234.0	16.0	6.8	21.0
A4	Ol	0-2	69.6	70.8	11.3	18.0	19.0	956.0	100.0	15.0	156.0
	Ofh	2-4	50.2	98.1	15.9	46.0	20.6	1134.5	149.0	49.7	179.0
	AEes	4-19	24.7	49.4	6.6	33.0	13.0	508.4	56.2	23.0	59.4
	Bv	19-60	19.4	34.7	4.6	34.0	10.3	496.0	50.2	19.5	51.0
	C	60-130	16.2	16.5	2.3	22.0	7.0	210.0	13.0	9.1	18.0
Unpolluted soil by cited data [3, 12, 14] mean values											
0	Ol	0-3	65.6	4.10	0.87	10.5	12.5	310.2	72.3	10.0	90.5
	Ofh	3-6	42.2	2.79	1.02	6.5	20.2	160.1	12.2	30.2	10.5
	AEes	6-20	21.2	0.69	0.10	3.9	5.5	36.5	6.5	13.0	9.5
	B	20-60	17.9	0.10	0.05	9.5	3.5	50.2	3.8	10.2	6.5
	C	60-120	15.8	0.0	0.0	5.5	4.5	45.8	4.0	4.0	3.5

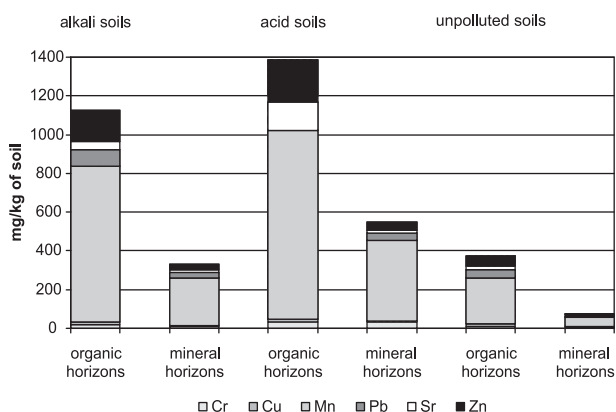


Fig. 2. Mean concentrations of trace elements in the organic and mineral soil horizons.

Total sulphur contents were low, fluctuating from 0.09 to 4.22 mg/100g while sulfate sulphur ($S-SO_4$) contents were between 0.05 and 1.14 mg/100g.

Organic carbon contents C_{TOT} averaged 49.3% in Ol horizon, 26.6% in Ofh horizon and 1.5% in AEes horizon. Total nitrogen contents N_{TOT} (1.31–0.49%) corresponded with carbon contents (Table 2). It is worth noting that organic carbon content in the Ofh horizon was lower than in similar unpolluted soils (Table 3), suggesting a higher decomposition rate. Properties of soils at the Rudniki site, exposed to long-term acidic emission, were in sharp contrast to the Ożarów site (Table 2 and 3). All soil horizons were strongly acidified with pH_{KCl} between 3.29–4.28 (pH_{KCl} unpolluted soils between 4.09–4.65, Table 3). Acidification declined with depth. Exchangeable acidity was high (0.51–10.00 cmol/kg) and was caused mostly by exchangeable aluminum. It is worth emphasizing that Al^{3+} concentrations were the highest in surface horizons, which suggests anthropogenic influences [15, 17, 18]. Hydrolytic acidity was between 1.17–121.1 cmol/kg in all soil horizons under study.

The sum of exchangeable base cations was very low (from 0.09 cmol/kg in C horizon to 12.2 cmol/kg in Ol horizon). Exchangeable aluminum and hydrogen were the dominating ions on the exchange complex, while only traces of exchangeable calcium were detected, particularly in mineral and organic-mineral horizons. The soils under study had low cation-exchange capacity, $PWKr$, which amounted to 19.24–29.01 cmol/kg in organic horizons. Alkali saturation V_{pot} ranges from 2.80 to 17.31%, while these values are a little higher in emission-free soils (Table 2).

In contrast to alkaline soils, salinity of acidic soils was low (12.0–81.2 mg KCl/100g). The S_{TOT} concentrations were high, the highest in organic horizons (70.8–99.6 mg/100 g), lower in mineral horizons (9.3–65.4 mg/100g). Sulfate sulphur $S-SO_4$ constituted 20% of total sulphur on the average and its contents ranged from 2.0 to 14.2 mg/100g.

Organic matter contents and total nitrogen concentrations were the highest in surface horizons (36.23–45.24% and 1.09–1.35%, respectively).

Contents of heavy metals in the soils under study also differed (Table 3). The highest concentrations of heavy metals were observed in surface horizons of acidic soils (Fig. 2), while the lowest amounts were found in mineral horizons of alkaline soils. Lead contents were increased, exceeding geochemical background for sandy soils [18, 19, 20], in surface horizons (variability ranges for alkaline, and acidic soils were: 39–112 mg/kg and 100–210 mg/kg respectively, at the mean content for unpolluted soils: 12.0 to 7.0 mg/kg, Table 3). Chromium contents were the highest in Ofh horizons of acidic soils 42–50 mg/kg (at the content for unpolluted soils below 10.0 mg/kg, Table 3). Zinc concentrations in organic horizons of acidic soils ranged between 100–236 mg/kg, manganese between 800–1134 mg/kg, copper between 11–15 mg/kg, and chromium between 16–50 mg/kg. The Zn and Mn contents were slightly higher than geochemical background [5, 19,

20], but their current contents in soil are not hazardous to the environment.

Discussion

Strong acidification of *Haplic Podzols* and *Albic Arenosols* at the Rudniki site has developed in causal relationship with properties of its sandy parent material, weak buffering capacity and acidifying influence of forest vegetation [4, 15, 21, 22]. These natural processes occurring in the ecosystem were strengthened by an intense long-term deposition of sulphur and nitrogen compounds. The Połaniec Power Plant and Osiek Sulphur Mine have added to the environmental stress of the area. Sulphur and its derivatives belong to the most controversial elements affecting the environment [14, 19, 23]. On the one hand, sulphur is an essential nutrient for plants (its content in plants is comparable to phosphorus), while on the other, deposition of SO_2 derivatives is a serious hazard to the environment, disrupting main soil functions [24, 25, 26]. The marked accumulation of total sulphur, observed in surface horizons of soils under study, is undoubtedly of anthropogenic origin. They may be classified as soils with high, though not degrading, sulphur content [19, 25]. Sulfate sulphur S-SO_4 is not only a major component of plant nutrient cycle, but is also an indicator of anthropogenic soil pollution. The S-SO_4 content in organic horizons of acidic soils oscillated around 13.5 mg/100 g of soil (i.e. the threshold value for organic soils indicating their heavy pollution (Table 3)). The soils under study markedly differed in total sulphur and S-SO_4 contents. Sulphur content was low in surface horizons of alkaline soils.

Total nitrogen content only slightly differed between soils at the study sites. A little higher N contents than in alkalized areas (by 10–20%) were observed in the Ol and Ofh horizons in soils of the Rudniki site, but did not exceed the range reported for forest podzolic soils having developed naturally (Table 2). Cement manufacturing process generates NO_x compounds, which, though at lower levels, are emitted to the environment [10]. Many reports demonstrated a beneficial trend towards lowering of NO_x content in the air [27].

After acidifying emissions cease, a transient improvement of acidity in forest ecosystems occurred, although their permanent regeneration to $\text{pH} > 4.4$ according to Becker 2003 [28] and Kowalkowski, Kopron 2005 [29] is possible only after liming. Full renaturalization of acidified soils, after stressor elimination, was emphasized by other authors [30, 31, 32].

Alkalization of forest soils is not a common process and usually occurs locally. Usually, changes in the environment of strongly acidified soils at the first stage of power plant operation should be considered to be positive with conspicuous shift from aluminum to silica buffering and exchangeable aluminum reduction [6, 33]. However, uncontrollable and long-lasting introduction of excessive CaO doses is disadvantageous. Field studies have shown

that the effects of liming of sandy soils (4–5 t/ha) persisted for more than 15–30 years [33, 34]. In the study area, airborne particulate matter deposition averaged from 360 $\text{g}\cdot\text{m}^{-2}/\text{year}$ (1990) 50 $\text{g}\cdot\text{m}^{-2}/\text{year}$ (2005 r.) CaO, which led to changes in their chemical properties.

Natural soils in Poland are not salinized, except for coastal zones [6, 19,]. The increased salinity of surface horizons of alkaline soils is of anthropogenic origin and is associated with a considerable increase in soil pH (by 3–4 units) and CaCO_3 content. The studied soils strikingly differed in these features and in the elevated Ca^{2+} content on the exchange complex. The rise in calcium ion content in the exchange complex can result in lowered absorption of manganese and zinc by plants [5, 18, 20].

Sorption complex saturation in alkalized soils is comparable to unpolluted soils, but in acidified soils it is markedly diminished.

Mobility heavy metals in acidified and strongly acidified environment markedly rises [19, 35]. The highest contents of heavy metals were observed in the organic horizon (Ofh) of soils at the Rudniki site and in the humic horizon (AEes). It is an alarming phenomenon since these horizons constitute a storage place for easily available elements crucial for forest growth [28, 29]. In forest soils, migration of heavy metals inward to the profile is limited by a filter of the Ofh horizon. Among elements under study, lead was characterized by weak migration in soil profile [18, 35].

The largest differences in heavy metal contents were observed in manganese, lead and zinc concentrations. Large quantities of these elements accumulated in all horizons of acidic soils. This phenomenon has often been reported in literature [2, 3, 21, 36].

Conclusions

The present study showed marked changes in chemical properties of *Haplic Podzols* and *Albic Arenosol* subjected to constant alkalization, which included: the increase in pH, in base cation saturation of exchange complex, plant available potassium and magnesium contents, CaCO_3 concentration in organic and humic horizons and in salinity, and the decrease in organic carbon and hydrolytic acidity. Soil alkalization increases trophy of habitats and facilitates humus formation. High saturation of soil sorption complex and the presence of carbonates in surface horizons do not accelerate podzolization and development of forest vegetation in this area.

Podzolic soils exposed to constant anthropogenic acidification showed the lowering of pH value and base cation saturation of exchange complex and the rise in total and sulfate sulphur S-SO_4 contents and in hydrolytic acidity. Many years' strong anthropogenic acidification of podzolic soils, having persisted till the present, enhances leaching of nutrients and can lead to destruction of soil substance. Aggressive and quick oxidation of sulfur compounds, resulting in strong acidification of soil environ-

ment, can also accelerate decomposition of organic matter [31, 34], but this relationship has not been unequivocally demonstrated in the study soils.

It was observed that surface horizons, the most active to a depth of 20 cm, underwent the strongest transformation, regardless of type of deposit reaching soil surface. Summarizing the study results, it can be stated that as well cement and lime industry as sulfur industry or power industry have strong impact on soil substance. Secondary alkalization of organic and mineral horizons is less destructive, since it is slowly reversible. Sulfur compound emission strongly acidifies podzolic soils under study, causing a pH shift from slightly to strongly acidic range and increase in heavy metal concentration. Since the stressor is still present, these changes are long-lasting and are stabilized by natural soil processes.

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