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INFLUENCE OF GRADUATION TOWERS ON AVERAGE ANNUAL CATIONS CONTENT IN BLACK EARTHS (MOLLIC GLEYSOLS) IN THE INOWROCLAW CITY

WPŁYW TĘŻNI NA WARTOŚCI ŚREDNIOROCZNE KATIONÓW W CZARNYCH ZIEMIACH W INOWROCŁAWIU

Abstract: The research concerns soils located in the Inowroclaw Spa Park, under continuous influence of graduation towers. Such a continuous impact of aerosols may modify chemical composition of soils, and may lead to transformation of black earths into salt-affected anthropogenic soils in the nearest future. This specific anthropogenic factor effected the increase of calcium and sodium cations content, significantly changing the composition of soil sorption complex of the analyzed soils. The results of separate cations content in sorption complex showed the domination of calcium cations (91.42–333.35 mmol $\cdot$ kg^{-1}), which in several soil profiles attained a two or even three times higher value than in Cuiavian black earths under no anthropogenic influence. Sodium came second in content series of cations (16.28–73.46 mmol $\cdot$ kg^{-1}). In most of the horizons of the investigated soils the content of these exchangeable cations was on average level. It means that the content of sodium cations was several times higher than in the black earths not affected by salt, yet lower than in soils under the influence of sodium industry. The rest of the analyzed cations (Mg^{2+}, K^+) were characterized by low concentration both in soil sorption complex and in the soil solution and did not show accumulation characteristics in any genetic horizons.

Keywords: black earth, physical and chemical properties, anthropopressure, graduation tower

Soils of the Spa Park in Inowroclaw, as most Inowroclaw Plain's soils, belong to one of the largest black earths (Mollic Gleysols) complex in Poland [1]. The black earths are characterised by high amount of organic matter and content of calcium carbonate. Their high cation exchange capacity is effected by high concentration of calcium and magnesium cations and lower potassium concentration. The black earths richness in alkaline cations influences these soils' reaction and low concentration of hydrogen cations in sorption complex. On account of its location and agricultural usefulness, the

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area of black earths in Kujawy is exposed to considerable human impact, the consequence of which are changes in physicochemical properties of the soil. The most spectacular phenomenon of those soils' degradation is the salinity process. Natural salinity in Poland has a low range, and because of that the human activity is thought to be the main cause of that phenomenon, especially the impact of the sodium and mining industry, soil irrigation with sewage, the usage of mineral fertilizers, and deicing agents on roads. The unique factor occurring in the Spa Park in Inowroclaw and affecting the soils' chemical composition are graduation towers. Graduation towers effect appearance of halophytic plants or dying off of trees and bushes poorly selected for the spa area. Moreover, the salinity process is not only the problem of spatial adaptation of the investigated area. The long-term influence of aerosols hanging over the graduation towers can modify the chemical composition of the soils, up to the point that in the nearest future, they might stop existing as black earths and become saline-sodic soils or anthropogenic saline soils.

The objective of this research was to define the impact of graduation towers on changeability of the composition of the sorption complex and soil solution of the Inowroclaw Spa Park's soils.

Material and methods of research

The area of the research covers almost 60 hectares of the Spa Park in Inowroclaw. In the Park's area, three times during the year (Spring, Summer, Autumn) soil profiles from seven research points were identified (Fig. 1). From each of the genetic horizons

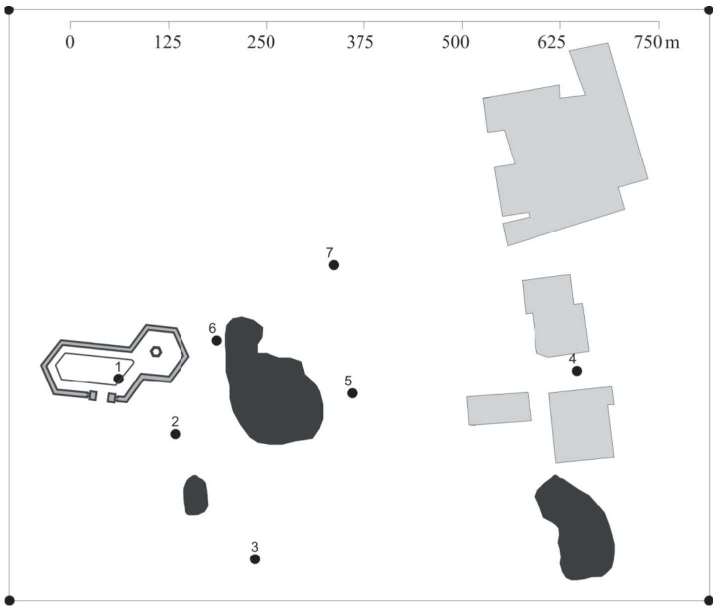

Fig. 1. Location of soil profiles

of soil profiles samples were taken to laboratory analyses. The following soil parameters were determined using widely applied methods in the soil science:

– exchangeable cations (Ca, Mg, Na, K) in 1M NH_4Cl of pH 8,2 using AAS method;

– water-soluble forms Ca, Mg, K, Na using AAS method;

– sorption capacity and a degree of a saturation of a sorption complex, which was determined mathematically.

Findings of the aspirated air quality measurements near the graduation towers collected in the development of the National Hygiene Institute in Poznan indicates that the dominating aerosol's compound produced by the graduation towers is sodium chloride 0.79–95.96 mg · m^{-3}. The content of the sodium chloride is diversified and depended on the distance from the graduated towers and the altitude above the ground level. The efficiency of brine pumps in graduation towers also have essential influence on aerosol concentration, technical condition of graduation towers, concentration and composition of brine (Table 1), and atmospheric factors – especially wind direction and speed. The highest concentration of NaCl was observed in the vicinity of fountain and pumping station, the lowest on graduation tower deck [2].

Table 1

Brine composition

Parameter	Brine pumped to graduation towers	Brine after distribution through the system
pH	7.8	7.5
Cations		
Na^+	18160.00 mg · dm^{-3}	21530.00 mg · dm^{-3}
Ca^{2+}	424.85 mg · dm^{-3}	464.93 mg · dm^{-3}
Mg^{2+}	228.47 mg · dm^{-3}	175.00 mg · dm^{-3}
Anions		
Cl^-	28000 mg · dm^{-3}	33200 mg · dm^{-3}
I^-	2.1 mg · dm^{-3}	2.3 mg · dm^{-3}
HCO_3^-	414.93 mg · dm^{-3}	463.74 mg · dm^{-3}
NO_2^-	0.38 mg · dm^{-3}	0.48 mg · dm^{-3}
NO_3^-	n.s.	n.s.
SO_4^{2-}	1341.49 mg · dm^{-3}	1316.80 mg · dm^{-3}
NaCl	46160 mg · dm^{-3}	54730 mg · dm^{-3}
Total	48572.20 mg · dm^{-3}	57152.22 mg · dm^{-3}

n.s. – non significant.
Results of National Institute of Hygiene in Poznan [2].

Results and discussion

On the basis of the results published earlier [3], soils of the Spa Park in Inowroclaw were classified as black earths (Mollic Gleysols). The analysis of separate cations in sorption complex showed the dominance of calcium cations 91.42–333.35 mmol · kg^{-1}, with specific differences in concentration of these cations in individual genetic horizons of investigated soil profiles (Table 2).

Table 2

The content of exchangeable and watersoluble cation forms in studied soils

Profile No.	PWK CEC	Ca^{2+} exch	Mg^{2+} exch	Na^{+} exch	K^{+} exch	H^{+} exch	Ca^{2+} wslb	Mg^{2+} wslb	Na^{+} wslb	K^{+} wslb
	mmol · kg^{-1}									
Profile 1										
0–20	277.06	220.29	10.85	41.64	4.28	0.00	1.04	1.17	14.51	0.69
20–40	248.00	190.18	10.57	43.93	3.32	0.00	0.26	1.12	17.52	0.73
40–60	197.21	130.13	7.52	56.31	3.25	0.00	0.12	1.43	26.22	1.10
110–130	172.06	91.54	4.85	72.79	2.88	0.00	0.09	1.63	30.00	1.19
130–150	249.60	168.45	4.66	73.46	3.03	0.00	0.20	2.04	31.64	1.78
Profile 2										
0–20	201.01	162.28	12.93	17.65	8.15	0.00	0.92	1.33	1.57	2.12
20–40	179.24	145.04	11.16	19.89	3.15	0.00	0.64	1.19	1.55	0.26
40–60	200.94	168.09	10.17	20.05	2.63	0.00	0.39	1.20	3.25	0.41
82–107	226.49	181.04	12.40	30.31	2.74	0.00	0.39	0.99	7.07	0.62
107–150	358.03	307.00	15.15	32.97	2.91	0.00	4.31	0.70	10.65	0.34
Profile 3										
0–20	192.08	130.41	10.22	24.79	4.76	21.90	0.36	0.91	0.85	1.45
20–40	199.71	154.66	9.38	18.94	3.30	13.43	0.07	0.94	1.24	0.44
40–55	255.49	207.49	11.94	21.16	3.07	11.83	0.04	1.00	0.99	0.55
55–92	203.88	156.70	16.83	18.00	3.88	8.47	0.38	1.27	1.03	0.69
92–150	329.57	292.56	12.18	19.15	2.91	2.77	5.31	0.98	1.19	0.28
Profile 4										
0–20	160.46	132.77	8.51	16.37	2.81	0.00	0.83	1.08	0.93	1.02
20–40	152.38	126.94	7.13	16.28	2.03	0.00	0.82	1.10	0.80	0.17
40–60	176.97	151.22	7.52	16.46	1.77	0.00	1.11	1.13	0.75	0.15
83–104	198.01	174.46	4.26	17.53	1.76	0.00	0.26	0.81	1.44	0.27
104–150	376.95	327.56	15.03	31.09	3.27	0.00	0.62	0.95	10.03	0.52
Profile 5										
0–20	332.40	268.34	30.01	30.78	3.27	0.00	5.12	2.52	10.00	0.49
20–40	345.20	278.66	25.83	37.72	2.99	0.00	8.91	3.44	15.08	0.31
40–60	332.36	267.01	23.43	37.29	4.63	0.00	5.66	3.21	15.65	1.23
104–110	371.78	298.82	28.97	37.18	6.81	0.00	5.17	1.63	14.50	0.92
110–150	378.49	321.71	13.98	39.29	3.51	0.00	5.33	1.23	15.99	0.56

Table 2 contd.

Profile No.	PWK CEC	Ca^{2+} exch	Mg^{2+} exch	Na^{+} exch	K^{+} exch	H^{+} exch	Ca^{2+} wslb	Mg^{2+} wslb	Na^{+} wslb	K^{+} wslb
	mmol · kg^{-1}									
Profile 6										
0–20	298.43	242.00	10.35	41.88	4.20	0.00	0.62	0.99	19.71	1.28
20–40	281.66	213.18	12.35	52.22	3.91	0.00	0.82	1.10	28.38	0.31
40–60	411.53	333.35	13.79	60.10	4.29	0.00	0.90	1.20	31.38	0.46
79–88	316.53	236.60	12.73	62.76	4.44	0.00	8.60	1.58	36.80	0.72
88–108	340.26	260.69	10.30	64.42	4.85	0.00	8.83	1.52	39.80	0.81
108–150	358.34	274.73	10.95	67.95	4.71	0.00	9.43	1.52	42.51	1.21
Profile 7										
0–20	217.43	153.17	10.60	26.75	2.54	24.37	0.68	0.86	1.32	0.21
20–40	237.63	188.90	5.86	20.61	2.13	20.13	0.17	0.66	0.96	0.37
40–60	183.19	139.33	6.81	17.63	2.22	17.20	0.14	0.66	0.80	0.43
84–128	148.32	109.59	6.07	17.76	2.23	12.67	0.07	0.75	0.69	0.95
128–150	132.86	91.42	7.79	17.96	2.72	12.97	0.05	0.87	0.94	0.96

exch – exchangeable, wslb – watersoluble.

In profiles No. 1 and 7 the quantitative predominance of Ca^{2+} cations in horizon of humus accumulation was determined, while in profiles 2, 3, 4 and 5 theses conditions were observed in horizons of parent material. In the research published by Ciesla [4] on not-salt-affected black earths of Kujawy region the content of calcium cations ranged from 61 to 120 mmol · kg^{-1}, whereas in soils investigated by Rytelewski et al [5, 6] and Czerwinski [7], effected by sodium industry this concentration was much higher than one hundred mmol · kg^{-1}. Sodium was the second cation in soil sorption complex

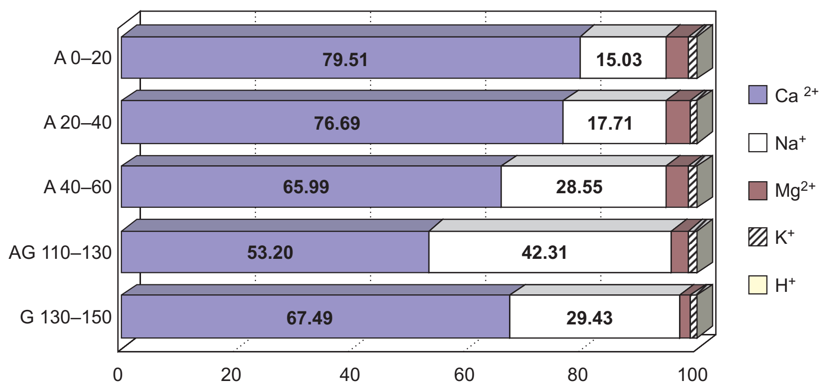

Fig. 2. The percentage of exchangeable cations in the sorption complex of the profile 1

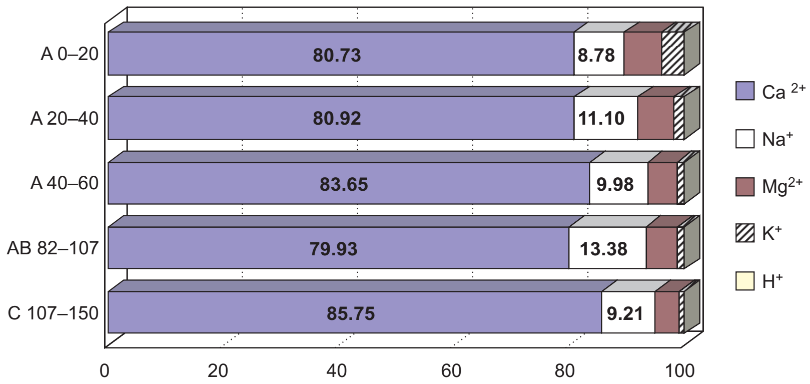

Fig. 3. The percentage of exchangeable cations in the sorption complex of the profile 2

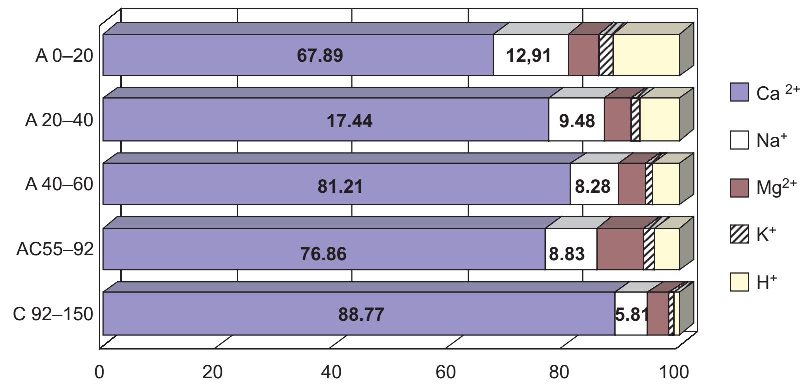

Fig. 4. The percentage of exchangeable cations in the sorption complex of the profile 3

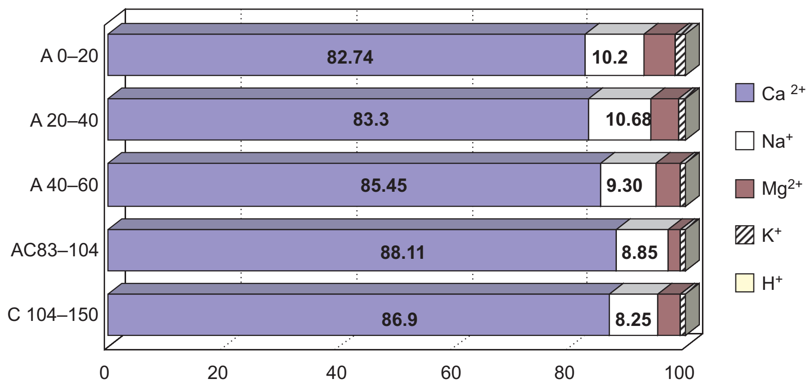

Fig. 5. The percentage of exchangeable cations in the sorption complex of the profile 4

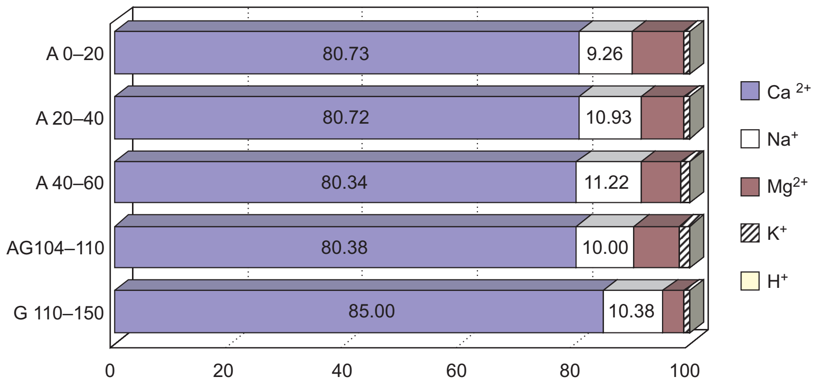

Fig. 6. The percentage of exchangeable cations in the sorption complex of the profile 5

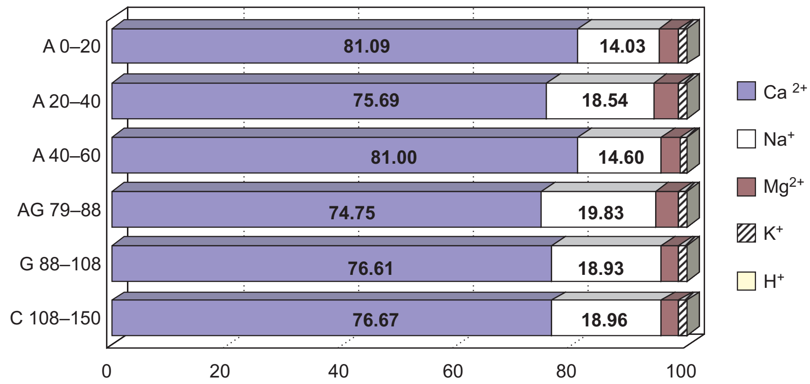

Fig. 7. The percentage of exchangeable cations in the sorption complex of the profile 6

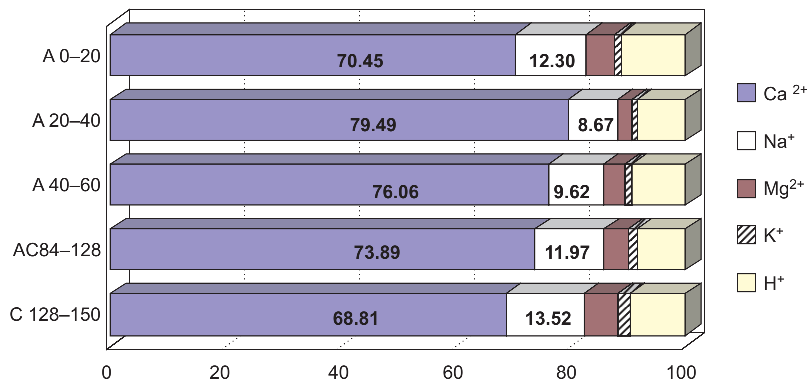

Fig. 8 The percentage of exchangeable cations in the sorption complex of the profile 7

16.28–73.46 mmol · kg^{-1}. In profiles No. 1, 2, 4, 5 and 6 accumulation of these cations was observed in horizons of parent material. In profiles No. 3 and 7 this accumulation was observed in surface horizons (Table 2). Sodium cation as one of the best water soluble cations is wash out with rainfall water into deeper horizons in soil profiles and its high concentration in surface horizons is possible only with continuous inflow of sodium compounds from outer sources (in this case from intensively use of graduation towers especially in the summer) [8]. The detailed research on chemical composition of black earths of Kujawy region conducted by Ciesla [4] in the 1960s confirmed that content of exchangeable sodium cations reached the level of 3–8 mmol · kg^{-1}. The content of Na cations determined in soils contaminated after brine pipeline failure or leakage from settling tank of sodium industry sewage, reached 120–130 mmol · kg^{-1} just after the inflow from contamination source [5, 6, 9]. Soils of investigated area in most horizons were characterized by intermediated values of sodium cations concentration – several times higher than in non-salt-affected black earths and much less than in soils under the influence of sodium industry. The content of exchangeable Mg cations ranged 4.26–30.01 mmol · kg^{-1} (Table 2) and it was the values 4 or 5 times lower than in black earths not under anthropopressure. Potassium exchangeable cations had the smallest content in sorption complex of analysed soils. It was between 1.76–8.15 mmol · kg^{-1} and showed no significant accumulation in any of the soil horizons. The predominance of calcium and sodium cations was confirmed by the results of percentage content of individual cations in sorption complex. In soil profiles No. 1, 2, 4, 5 and 6 analysed cations occurred in following order: Ca^{2+} 53.20–88.11 %; Na^{+} 8.25–42.31 %; Mg^{2+} 1.87–9.03 %; K^{+} 0.81–1.83 % (Fig. 2, 3, 5–7). In profiles No. 3 and 7, with acid reaction these values were as follows: Ca^{2+} 67.89–88.77 %; Na^{+} 5.81–13.52 %; Mg^{2+} 2.47–8.25 %; K^{+} 0.88–2.48 %; H^{+} 0.84–11.40 % (Fig. 4, 8).

The highest concentration in soil solution of the analysed profiles among detected cations were sodium cations 0.69–42.51 mmol · kg^{-1}. Moreover in profiles No. 1, 2, 4, 5 and 6 concentration of water-soluble sodium was increasing due to depth (Table 2). The obtained results of water-soluble Na^{+} were much higher than values for non--salt-affected black earths of Kujawy region, where it averaged at 7 mmol · kg^{-1} [8], but lower than values in soils under the influence of sodium industry reached even 65–100 mmol · kg^{-1} [5]. The concentration of water-soluble calcium cations was on the level between 0.05 mmol · kg^{-1} and 9.43 mmol · kg^{-1}. In soil profile No. 2, 3 and 6 the highest concentration of these cations was observed in horizons of parent material (Table 2). Water-soluble forms of other cations had much lower concentration ranging between 0.66 mmol · kg^{-1} – 3.44 mmol · kg^{-1} for Mg^{2+}, and 0.15 mmol · kg^{-1} – 2.12 mmol · kg^{-1} K^{+}, and did not show any tendency (regularity) in profile distribution of the analysed soils.

Conclusions

1. Dominating element in the sorption complex of the analysed soils, regardless of the soil profile's location, was calcium. Moreover in most endopedons the concentration

of the Ca^{2+} was two or even three times higher than in black earths (Mollic Gleysols) which were not subjected to anthropopression.

2. The soils of the Spa Park in Inowroclaw are black earths of the high content of sodium, which with a little amount of atmospheric precipitation and a constant inflow of sodium from the graduated towers may cause negative changes of their physical properties and composition of a sorption complex. This negative influence of sodium cations may be balanced by a high content of calcium ions.

3. The complex's deficiency in $Mg^{2+}$and K^{+} may be caused by the increased content of Na^{+} in a soil solution and a sorption complex or supplanting, especially magnesium from a complex by calcium ions.

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WPŁYW TĘŻNI NA WARTOŚCI ŚREDNIOROCZNE KATIONÓW W CZARNYCH ZIEMIACH W INOWROCŁAWIU

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Abstrakt: Badaniami objęto gleby zlokalizowane w Parku Zdrojowym w Inowrocławiu, będące pod stałym wpływem tężni. Stałe oddziaływanie aerozoli unoszących się z tężni może na tyle zmodyfikować skład chemiczny gleb, że przestaną one w niedalekiej przyszłości funkcjonować jako czarne ziemie, a staną się glebami słono-sodowymi czy glebami antropogennymi słonymi. Ten specyficzny czynnik antropogenny powoduje wzrost stężenia kationów wapniowych i sodowych, zmieniając tym samym istotnie skład kompleksu sorpcyjnego analizowanych gleb. Analizy zawartości poszczególnych kationów w kompleksie sorpcyjnym wykazały wyraźną dominację jonów wapnia (91.42–333.35 mmol · kg^{-1}), który w kilku profilach uzyskał często dwu- lub nawet trzykrotnie wyższe wartości stężenia niż w czarnych ziemiach kujawskich nie poddanych antropopresji. Kolejne miejsce w obsadzie kompleksu sorpcyjnego zajmował sód (16.28–73.46 mmol · kg^{-1}). Badane gleby przyjmowały w większości poziomów wartości pośrednie stężenia sodu wymiennego, to znaczy charakteryzowały się kilkukrotnie większym stężeniem kationów sodowych w stosunku do niezasolonych czarnych ziem, jednak mniejszymi wartościami stężenia Na^{+} niż w glebach poddanych silnej antropopresji przez przemysł sodowy. Pozostałe analizowane pierwiastki (Mg^{2+}, K^{+}) charakteryzowały się niskim stężeniem zarówno w kompleksie sorpcyjnym, jak i roztworze glebowym i nie wykazywały cech akumulacji w którymkolwiek z poziomów genetycznych.

Słowa kluczowe: czarne ziemie, właściwości fizykochemiczne, antropopresja, tężnie