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ORIGINAL PAPER

MAGNESIUM STATUS IN SOILS UNDER THE IMPACT OF THE SODA INDUSTRY*

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Abstract

Soda production (Na_2CO_3) in the plant Janiko-Soda SA, in the region Kujawy, generates large amounts of waste deposited in sedimentation tanks near the factory. The impact of soil salinization caused by the waste on the magnesium status in nearby soils, classified to Gleyic Phaeozems, was studied. Soil samples were collected from 9 representative sites from two depths: 0-20 cm and 20-40 cm. Samples differed in soil salinity, expressed by electrical conductivity, which was in the range of 0.75-43.91 dS m^{-1}. Exchangeable, plant available and total magnesium as well as exchangeable cations: Ca^{2+}, K^+, Na^+ were determined. Moreover, the concentration of Cl^- ions was also determined. For the characterization of the properties of soil material, the organic matter content and pH in H_2O and 1M KCl were evaluated. The content of chlorides varied in a wide range: from 18.0 mg kg^{-1} up to 19 570.0 mg kg^{-1}. It was observed that available and total magnesium content was comparable to the content of this element in soils beyond the impact of soda waste. Negative changes were mainly extended to exchangeable forms of magnesium. Calcium was the dominant cation and an extremely low proportion of Mg was present in exchangeable sites in the studied soils. The concentration of Ca^{2+} exceeded the Mg^{2+} concentration by one to two orders of magnitiude. The exchangeable magnesium content decreased with an increasing soil salinity level, measured by electrical conductivity. Excess of exchangeable sodium ions was also observed in soil samples taken from the vicinity of sedimentation tanks filled with soda waste. Calcium, sodium and chloride content was statistically correlated with electrical conductivity of the soil extract ($r = 0.933$, $r = 0.961$, $r = 0.984$, respectively).

Keywords: magnesium availability, soil degradation, waste, landfill.

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INTRODUCTION

Industrial activity results in increasing amounts of waste, often deposited in landfills. Alkaline residues of the soda production in the plant Janiko-Soda S.A. accumulated in so-called “white seas” (earth tanks) bear influence on the adjacent soils, causing their degradation. The major component of waste deposited are soluble salts, mainly $CaCl_2$ and NaCl. These components infiltrate to the ground and change the ionic balance in groundwater and soils.

Natural or induced soil salinity reduces plant growth and the activity of microorganisms as a result of low water availability (due to high osmotic potential of the soil solution) and ion toxicity (Pathak, Rao 1998). Furthermore, dispersion of clay particles, slaking and poor soil structure are observed. This can affect water and air movement in soil (Crescimanno et al. 1995).

Several papers on the direction of changes and consequences for the soil environment as well as plant condition affected by the soda production waste have been published (Cieśla et al. 1981, Gonet, Hermann 1995). However, there is no data on the magnesium status in these potentially very productive soils classified to black earths (Gleyic Phaeozems).

The excess of calcium and sodium salts might change the magnesium availability in these soils. Mg deficiency causes physiological perturbations in plants, like a decrease in the photosynthetic rate and appearance of chloroses (Shaul 2002, Przybysz et al. 2016). Magnesium is critical to energy storage by making adenosine triphosphate (ATP) biologically active (Likens et al. 1998, Gerendas, Fuehrs 2013).

The major objective of this work was to estimate the pool of magnesium available to plants, and to characterize forms of this nutrient in the soils in the vicinity of landfills which receive waste deposits from the plant Janiko-Soda S.A.

MATERIALS AND METHODS

The study area is located in the region Kujawy, close to the town Inowrocław. Here, the soda producing plant Janiko-Soda S.A. has been depositing alkaline slurry consisting mainly of $Ca(OH)_2$, CaO, $CaCO_3$ and NaCl for over sixty years. The studied sites are almost free of plant cover, with occasionally encountered halophytic vegetation.

Soils for the study were sampled in May 2015, in the direct vicinity of deposition tanks: sites A – G were located 5 to 8 m from the base of the tanks. Nine representative sites had been chosen and soil samples were taken from two depths: 0-20 cm and 20-40 cm for the study.

Samples were air dried, passed through a 2-mm sieve, and analyzed using the standardized methods. The pH was measured potentiometrically in deionized water (pH_{H_2O}) and 1 M KCl (pH_{KCl}) with a combined electrode using a pH meter. Electrical conductivity was determined in a 1:5 soil: water extract. Total carbon was determined with a TOC FORMACTSTM analyzer Primacs (provided by Skalar). Organic carbon was calculated according to Santi et al. (2006). The concentration of Cl^- ions was determined using the potentiometric method.

Total magnesium was determined after mineralization of soil samples in concentrated HNO_3 and $HClO_4$. Available magnesium was extracted according to the Schatschabel method. Exchangeable ions were analyzed after the extraction with 0.01 M $BaCl_2$. Total, exchangeable and available Mg as well as exchangeable Ca were measured by flame atomic absorption spectrometry (AAS) and exchangeable K and Na by flame emission spectrometry (AES) on a Philips PU-2100 spectrometer. All analytical measurements were performed with three replications. Arithmetic mean values are shown in tables. Precision and accuracy of the analyses were determined using certified reference material (Till-3).

Statistical evaluation of the results was accomplished using Statistica 6.0 software.

RESULTS AND DISCUSSION

Selected soil properties are presented in Table 1. Soils are characterized by slightly alkaline pH (pH in H_2O 7.10-8.15 and in 1 M KCl 7.20-7.98). The clay fraction contentranged from 4.20 to 14.80%. The organic carbon content varied from 0.0 to 96.07 g kg^{-1}, with the mean value as low as 23.67 g kg^{-1}. According to other authors (Muhammad et al. 2008, Ondrasek, Rengel 2012), a low level of soil organic matter may exacerbate negative effects of salinization.

Salinity measured by electrical conductivity differed between 0.75 dS m^{-1} and 43.91 dS m^{-1}. Generally, salinity increased with depth in 5 sites (A,B, D, E and I) and was higher in deeper layers than in the surface. Such a salt distribution pattern was due to the leaching of easily soluble compounds, mainly in the form of chlorides. The highest value of this parameter was detected for sample H, which had three sources of salinity: from the sedimentation tanks, sewage treatment plant and municipal waste dumping. According to quantitative criteria for the diagnosis of soil salinity, a saline soil has been defined as having an EC of more 4 dS m^{-1}. This value generally corresponds to approximately 40 mmol salt l^{-1}.

The content of chloride in the studied soils ranged from 18.0 to 19570.0 mg kg^{-1} of soil. The content of Cl^- was highly correlated with electrical

Table 1

Selected physicochemical properties of soils

Site	No of sample	Depth (cm)	Fraction <0.002 mm	C_{org}	pH		S	EC	Cl^-
			(%)	(g kg^{-1})	H_2O	KCl	(cmol(+) kg^{-1})	(dS m^{-1})	(mg kg^{-1})
A	1	0-20	14.8	88.21	7.93	7.98	21.9	1.59	365.0
	2	20-40	12.0	0.00	7.58	7.78	27.0	10.10	660.0
B	3	0-20	4.2	6.66	7.93	7.80	9.0	0.75	44.0
	4	20-40	4.2	5.38	8.15	7.81	9.0	5.17	39.0
C	5	0-20	7.9	57.97	7.67	7.59	13.3	1.52	113.0
	6	20-40	7.9	96.07	7.89	7.82	10.2	1.19	84.0
D	7	0-20	7.9	10.47	7.74	7.67	15.2	0.75	65.0
	8	20-40	7.2	7.65	7.69	7.69	12.9	0.80	100.0
E	9	0-20	5.6	8.13	7.63	7.66	11.3	0.78	58.0
	10	20-40	5.6	8.64	7.41	7.75	13.9	2.86	113.0
F	11	0-20	7.3	47.66	7.90	7.90	11.3	1.58	286.0
	12	20-40	5.9	18.82	7.96	7.95	8.3	1.55	338.0
G	13	0-20	4.8	4.66	7.46	7.70	17.4	2.67	432.0
	14	20-40	4.8	3.57	7.58	7.73	15.6	2.50	493.0
H	15	0-20	6.6	30.17	7.10	7.35	70.1	43.91	19570.0
	16	20-40	6.6	27.23	7.24	7.38	44.9	38.18	17275.0
I	17	0-20	8.2	2.22	7.95	7.27	15.8	2.68	73.0
	18	20-40	9.8	2.50	7.66	7.20	16.3	6.68	18.0
	min		4.20	0.00	7.10	7.20	8.3	0.75	18.0
	max		14.80	96.07	8.15	7.98	70.1	43.91	19570.0
	mean		7.30	23.67	-	-	19.1	6.96	2229.0
	SD		2.72	29.70	0.27	0.23	15.3	12.67	590.72
	CV		37.27	125.48	3.53	2.98	80.4	182.11	265.0

conductivity EC ($r = 0.984$), exchangeable Ca^{2+} ($r = 0.922$) and exchangeable Na^+ ($r = 0.935$) – Table 2.

The Mg fractions in soils may be divided into non-exchangeable, exchangeable and water soluble forms. These three forms are in an equilibrium. The largest fraction of soil Mg is in the non-exchangeable form, which includes all the Mg in the primary minerals, where it is mainly present as a cation in octahedral units, and most of the Mg in the secondary clay minerals. Exchangeable Mg^{2+} is usually in the order of 5% of the total content and this fraction, along with the water soluble Mg^{2+}, is of the greatest importance in the supply to plants (Chu, Johnson 1985). In well-buffered soils, calcium

Table 2

Correlation coefficients between determined parameters ($P < 0.05$)

Specification	Exchangeable				Total
	Na^+	K^+	Ca^{2+}	Cl^-	Mg^{2+}
Fraction <0.002 mm	-	0.691	-	-	0.690
S	0.955	-	0.997	0.933	-
EC	0.961	-	0.933	0.984	-
Cl^-	0.935	-	0.922	-	-
Na^+	-	-	0.930	-	-

ions occupy the majority of exchangeable sites in soil colloids. But the share of exchangeable magnesium is considerably large, while monovalent cations occupy a few per cent of the sites (GERENDAS, FUEHRS 2013).

The sum of base exchangeable cations (S) in the soils varied from 8.3 to 70.1 cmol(+) kg^{-1} (Table 1). Exchangeable potassium ranged from 0.14 to 1.03 cmol(+) kg^{-1} with the mean value of 0.54 cmol(+) kg^{-1} (Table 3). All soils had a very high exchangeable calcium concentration. The percentage of calcium ions in the exchangeable complex ranged from 76.75 to 94.36 % of the total cation exchange capacity (Table 4). Thus, the calcium ion was the dominant exchangeable cation in all of the samples and an extremely low proportion of Mg was present on the exchange sites. The fraction of Mg^{2+} occupying exchangeable sites of soil colloids ranged from 0.01 to 0.40 cmol(+) kg^{-1} (i.e. 0.07 to 2.87% – Table 4), while exchangeable calcium was in the range 6.91-59.03 cmol(+) kg^{-1}. In general, exchangeable magnesium decreases with an increasing salinity level, expressed by electrical conductivity (Tables 1, 3). However, there was no statistical correlation between these two parameters. A high level of a single cationic species (e.g. calcium) can induce plant deficiencies of other cations.

For an evaluation of the exchangeable complex quality in soils, the ratio of Ca^{2+}/Mg^{2+} was calculated. The ratio of Ca to Mg ions in exchangeable forms was very high, ranging from 31.0 to 655.9. The concentration of Ca^{2+} exceeded Na^+, K^+, Mg^{2+} concentrations by one or two orders of magnitude and even more in several samples . Thus, the analyzed soils demonstrated depressed nutrient-ion activities and extreme ratios of Na^+/Ca^{2+}, Na^+/K^+, Mg^{2+}/Ca^{2+}.

It was shown in the nutrient solution experiments that a high concentration of Ca^{2+} can lead to a severe decreas in the Mg uptake by plants (GRANSEE, FUEHRS 2013). Other reports showed that the ratio of Ca^{2+} to Mg^{2+} in exchangeable forms in soils with proper amounts of these cations is 5:1 to 9:1 (MAGUIRE, COWAN 2002).

According to SUMNER (1993), a high concentration of exchangeable Ca^{2+} changes the cation exchange capacity of soil. Excess of calcium ions is

Table 3

Exchangeable ions, the ratio of Ca^{+2}/Mg^{2+} and available and total magnesium in soils

Site	No of sample	Exchangeable					Available Mg	Total Mg
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Ca^{2+}/Mg^{2+}		
		cmol(+) kg^{-1}					(mg kg^{-1})	(g kg^{-1})
A	1	1.30	0.96	19.52	0.12	162.7	255.5	18.33
	2	5.27	0.86	20.70	0.14	147.8	284.7	25.37
B	3	0.28	0.30	8.35	0.06	139.2	190.2	7.36
	4	0.47	0.32	8.22	0.03	274.0	406.8	7.26
C	5	0.44	0.43	12.23	0.16	76.4	87.8	8.20
	6	0.36	0.66	8.94	0.20	44.7	76.2	8.56
D	7	0.62	0.35	14.20	0.03	473.3	160.9	6.55
	8	0.58	0.14	12.21	0.01	111.0	196.9	6.86
E	9	0.41	0.28	10.59	0.06	176.5	228.1	8.12
	10	0.82	0.28	12.41	0.40	31.0	641.0	8.66
F	11	0.65	0.87	9.65	0.10	96.5	117.1	6.80
	12	0.71	0.55	6.91	0.14	49.4	103.6	4.97
G	13	1.38	0.47	15.43	0.15	102.9	94.0	1.81
	14	1.70	0.43	13.33	0.16	83.3	74.9	1.64
H	15	10.43	0.53	59.03	0.09	655.9	96.7	3.54
	16	8.86	0.52	35.37	0.13	272.1	81.3	3.26
I	17	0.41	1.03	14.36	0.05	287.0	139.1	2.98
	18	0.36	1.02	14.88	0.08	186.0	138.1	3.50
	min	0.28	0.14	6.91	0.01	31.0	74.9	1.64
	max	10.43	1.03	59.03	0.40	655.9	641.0	25.37
	mean	1.95	0.54	16.46	0.11	187.2	187.0	7.43
	SD	3.04	0.29	12.45	0.09	160.64	14.4	5.87
	CV	155.98	53.09	75.62	75.98	85.81	76.6	78.93

responsible for the formation of so-called quasicrystals or clay domains. When Ca^{2+} cations are adsorbed on montmorillonite surfaces, individual clay platelets form aggregates. Each quasicrystal consists of four to nine clay platelets with an interplatelet distance of 0.9 nm. The Ca^{2+}- clay behaves like a system having a much smaller surface area and lower concentration of exchangeable ions (Shainberg, Letey 1984).

The difference in exchangeable bases between “normal” soils and saline soils are mainly in cation ratios. The normal sequence is: $Ca^{2+}>Mg^{2+}>K^{+}>Na^{+}$ (Jaworska et al. 2008). In the majority of the soils studied, affected by soda waste, the order of abundance is: $Ca^{2+}>Na^{+}>K^{+}>Mg^{2+}$. Exchangeable sodium

Table 4

Percentage share of exchangeable cations in the exchange complex of soils

Site	N$_o$ of sample	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}
A	1	5.94	4.38	89.13	0.55
	2	19.54	3.19	76.75	0.52
B	3	3.11	3.34	92.88	0.67
	4	5.20	3.54	90.93	0.33
C	5	3.32	3.24	92.23	1.21
	6	3.54	6.50	87.99	1.97
D	7	4.08	2.30	93.42	0.20
	8	4.48	1.08	94.36	0.08
E	9	3.62	2.47	93.39	0.53
	10	5.90	2.01	89.22	2.88
F	11	5.77	7.72	85.63	0.89
	12	8.54	6.62	83.15	1.68
G	13	7.92	2.70	88.53	0.86
	14	10.88	2.75	85.34	1.02
H	15	14.88	0.76	84.23	0.13
	16	19.74	1.16	78.81	0.29
I	17	2.59	6.50	90.60	0.32
	18	2.20	6.24	91.06	0.49
	min	2.20	0.75	76.75	0.07
	max	19.74	7.71	94.36	2.87
	mean	7.29	3.69	88.20	0.81
	SD	5.5	2.14	5.02	0.73
	CV	75.49	58.01	5.69	90.00

was in the range 0.28-10.43 cmol(+) kg^{-1}. High exchangeable Na$^+$ and Ca^{2+} were related to elevated electric conductivity. It was proved by statistical correlation coefficients between the Ca^{2+} concentration and EC (r = 0.933, $P < 0.05$) and between Na$^+$ content and EC (r = 0.961, $P < 0.05$). Moreover, statistical correlation was observed between exchangeable Na and Ca in the studied soils (r = 0.930, $P < 0.05$) – Table 2; such a relationship indicates that both components originate from the same source .

High calcium content is related to the infiltration of water rich in CaCl$_2$ from sedimentation tanks. Furthermore, magnesium ions adsorb less strongly to soil colloids than other cations due to the high radius of hydrated ions, and are therefore easily leached (Mayland, Witkinson 1989, Maguire, Cowan

2002). A magnesium ion is unique among biological cations because it has the largest hydrated radius (0.428 nm), the smallest ionic radius (0.072 nm) and the highest charge density (Bose et al. 2011).

The lack of plant cover also causes the loss of magnesium due to erosion processes (Chowaniak et al. 2015). Additionally, Mg^{2+} is not particularly bound to clay minerals, unlike K^{+}, which is adsorbed in the interlayers of 2:1 clay minerals.

Magnesium is an essential element involved in numerous plant methabolic processes, many enzyme activities and in the structural stabilization of tissues; its deficiency may cause disruption of photoassimilation and other important physiological processes. As a result, magnesium deficiency causes delayed plant growth and late maturation (Guo et al. 2016). Magnesium is also necessary to lower aluminium toxicity in plant tissue (Bose et al. 2011).

Sodium does not have a metabolic role in plants but is important in soils, where – together with the other base cations – it buffers acidity changes through an exchange reaction.

In plants, calcium ion plays an important physiological role in the cell structure and cellular division (McLaughlin, Wimmer 1999).

Negative changes in the magnesium status in the soils exposed to the impact of soda waste concern only exchangeable forms of the element. The content of available and total magnesium was comparable to the content of this nutrient in soils beyond the impact of the soda industry. Available magnesium was in the wide range 74.9 - 641.0 mg kg^{-1} and total Mg varied from 1.64 g kg^{-1} to 25.37 g kg^{-1} (Table 3). Total Mg was correlated with the content of the clay fraction ($r = 0.690$, $P < 0.05$). According to other studies (Maguire, Cowan 2002), the total content of Mg in soils varies considerably between 0.05% and 0.6%.

The study showed that magnesium deficiency is not only a problem inherent to acid soils due to the high saturation of the soil complex with H^{+} ions and Mg leaching from the soil. The deficit of Mg in easily available forms, i.e. exchangeable ones, is caused by the excess of calcium and sodium ions from an anthropogenic source in soils exposed to the impact of the soda industry.

CONCLUSIONS

The results of the research lead to the conclusion that soil salinization is of great concern in the vicinity of soda waste sedimentation tanks. Cations responsible for salinity measured by electrical conductivity are calcium and, to a lesser extent, sodium. A high concentration of chloride ions was also detected.

The negative changes of the ion equilibrium in the sorptive complex were observed in the studied soils. The dominant base cation is Ca^{2+}, its content ranged from 6.91 to 59.03 cmol(+) kg^{-1}, while the Mg content was in the range 0.01 - 0.40 cmol(+) kg^{-1}. An elevated content of exchangeable sodium was also detected (up to 10.43 cmol(+) kg^{-1}).

Undesirable changes in the magnesium status did not concern the content of available and total forms of this nutrient.

An excessively high concentration of calcium and an unfavorable calcium/ /magnesium ratio in the soil exchange system may lead to magnesium deficiency in plants growing in the studied soils.

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