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Technogenic Layers in Organic Soils as a Result of the Impact of the Soda Industry[1]

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Abstract—This study focused on characterization of salt-affected organic soils with thin surface mineral layers affected by waste of soda industry in the Inowrocław city area, Poland. The obtained results pointed out that the eolian supply of mineral material from waste ponds and locally, its transport by surface runoff can effect formation of layers contained up to 43% of carbonates. In addition, it was shown that these seemingly small transformations in the soil morphology can have a significant impact on functioning of the studied soils in the landscape. In this regard, the most important were deterioration of water properties and reduction of plant growth due to the salinization and sodification. Specific features of the studied soils could be well reflected in the WRB soil name as Eutric Murshic Histosols (Akromineralic, Salic, Sodic, Prototechnic). However, in the Author's opinion, the introduction of the new qualifier defining the artifact type in the name (i.e. Calcitechnic) would be advisable.

Keywords: Histosols, SUITMA, salt-affected soils, technogenic soils, WRB classification

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INTRODUCTION

Research on soils of urban, industrial, traffic, mining and military areas (SUITMAs) has become an important trend in soil science in the last three decades. Such soils have been presented in the past as white spots on maps but now with the rapidly growing interest, increased knowledge [19, 33, 35], substantial progress in their classification and mapping, these spots take on some colors. Various types of soil transformations in urban environments can be distinguished: (i) transport and deposition, (ii) long-term deposition, (iii) mixing, (iv) sealing [22]. Some of them are intentional and others unintentional. The process of their development could be defined as *technogenesis* [8] and, despite recent scientific advances, there is still a need for better understanding of the formation factors of technogenic soils.

Technogenic materials are commonly defined as constructed or strongly transformed by human activity [26, 34]. They are highly diverse in terms of the type of pedogenesis and the source of the material [24, 38]. As a result, the most characteristic feature of technogenic soils is their spatial and vertical heterogeneity [17]. Solid technogenic materials comprise building rubble deposited in residential areas [17, 22, 45], ashes from thermal power stations or refineries [47, 51], municipal and industrial waste [1, 3, 18, 24, 32, 52], asphalt, concrete or pavements geomembranes in ekranosols [7, 32]. A different group of technogenic materials are liquid waste (including salts, oil and gas), which strongly contribute to significant changes in physical and chemical properties of the soil and the formation of technogenic layers [16, 20, 39, 40]. Additionally, the transformation of soils can be caused by air pollutants (aerosols and dust), especially in big cities with a high-density transport system or in the neighborhood of industrial areas [11, 29, 53, 55].

Soils developed from technogenic material are a relatively new group in national and international soil classification systems [9, 13]. In the previous edition of the World Reference Base for Soil Resources [25], a separate soil unit with technic materials – Technosols – was created. However, only a specific group of soils forming on this type of material can be classified as a Technosols. For all other soils with less pronounced technogenic impact, the principal or supplementary qualifiers can be assigned: *Technic, Sodic, Salic, Toxic, Transportic* and others [26].

Inowrocław is an example of the multifunctional medium-sized city in north-central Poland (industrial

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Table 1. Characteristics of the sampling sites

Site	Altitude (m a.s.l.)	Distance from the waste ponds (m)	Thickness of the mineral layer (m)	Vegetation
M1	78.0	300	0	*Festuca arundinacea, Agropyron repens*
M2	77.8	280	0	*F. arundinacea, Atriplex prostrata* subsp. *prostrata* var. *salina, Aster tripolium, Puccinelia distans*
M3	77.9	255	0	*Spergularia salina, Triglochin maritimum, Salicornia europaea, P. distans, Aster tripolium*
M4	77.8	230	25*	*Phragmites australis*
M5	78.0	200	9	*A. tripolium, S. europaea, P. distans*
M6	77.9	190	8	*S. europaea, P. distans*
M7	78.0	140	4	unvegetated area

* Buried ditch.

and transport center, health resort, significant share of farmland). The soda factory CIECH Soda Polska S.A., founded in 1882, has had the biggest influence on environmental changes resulting in soil salinization. The soils affected by the soda post-production waste (Solvay's method) in the Inowrocław area were mostly studied for the purpose of classification [21] as well as to determine the salinity level [6, 20] and to analyze soil-plant relations in technogenic saline ecosystems [42, 43]. However, relatively little attention has been paid to the technogenic transformations of soil morphology. Therefore, the aim of this study was to explain the formation of mineral layers in Histosols located close to the soda plant in the Inowrocław city, in relation to their functioning within an urban landscape. The obtained results are also important in terms of the systematic description of soils with specific morphology, strongly affected by chemical degradation.

OBJECTS AND METHODS

The investigation was conducted on the saline meadow located in the Popowice village, west of the soda factory in Inowrocław, where 135 ha ponds filled with post-production waste are located; the waste is generated during the production of soda ash, using the "Solvay process" (Fig. 1). According to Abramski and Sobolewski [2], the sediments contain mainly $CaCO_3$, $CaSO_4$, $Ca(OH)_2$, $Fe(OH)_3$, silicates, aluminosilicates and supernatant liquid: solution of $CaCl_2$ and NaCl. Due to the leaks resulted from the long-term storage of waste in the poorly sealed ponds and unfavorable environmental conditions (primarily location in the Noteć River valley), surface and shallow ground waters were strongly contaminated. As a result, many hectares of Mollic Gleysols and Histosols located in the immediate vicinity have been transformed in recent decades into salt-affected soils [6, 42, 43]. Due to the technological process modernization, the waste ponds are currently not used and most of them have been reclaimed or turned into municipal landfills. Despite these undertakings, the salinity of waters and soils still remains relatively constant. This is confirmed by the occurrence of halophytes – plants resistant to salt stress [42, 43]. Halophilic plants found in the study area are represented by: *Salicornia europaea, Aster tripolium*, *Spergularia salina*, *Puccinelia distans* and *Atriplex prostrata* subsp. *prostrata* var. *salina* (Table 1).

According to Köppen-Geiger's climate classification, Inowrocław is located in the Cfb climate zone, which is generally described as warm temperate, fully humid with a warm summer [31]. However, the climate of this area is less humid than in most other regions in Poland, that does not contribute to the washing of soils from salts in the case of anthropogenic salinization. The mean annual precipitation is less than 500 mm and mean annual air temperature is about 8.0°C [36].

The research was carried out in 2016 in the area contaminated by soda post-production wastes (Fig. 1). The saline meadow is limited from the north and west by a drainage channel, from the east by a drainage ditch and railway embankment, and from the south by an old industrial dump. The terrain is flat (on average 78 m a.s.l.) with several local micro-depressions in the eastern part. A total of 11 samples were collected from individual soil layers up to a depth of 25 cm at 7 sites (M1–M7) along the selected transect (in W-SE direction; Fig. 1, Table 1). The distance between waste ponds and sampling sites was from 140 to 300 m. In the field, pH (in soil-water suspension 1 : 2.5 for mineral and 1 : 10 for organic samples) and redox potential (E_h) were measured against the reference electrode (Ag/AgCl), both by the potentiometric method. Additionally, in the same study sites, drillings were made to determine the thickness of organic sediments, as well as the ground water level.

Soil samples were sieved through a 2-mm mesh screen after air-drying for the following laboratory analyses: total organic carbon content (TOC) using

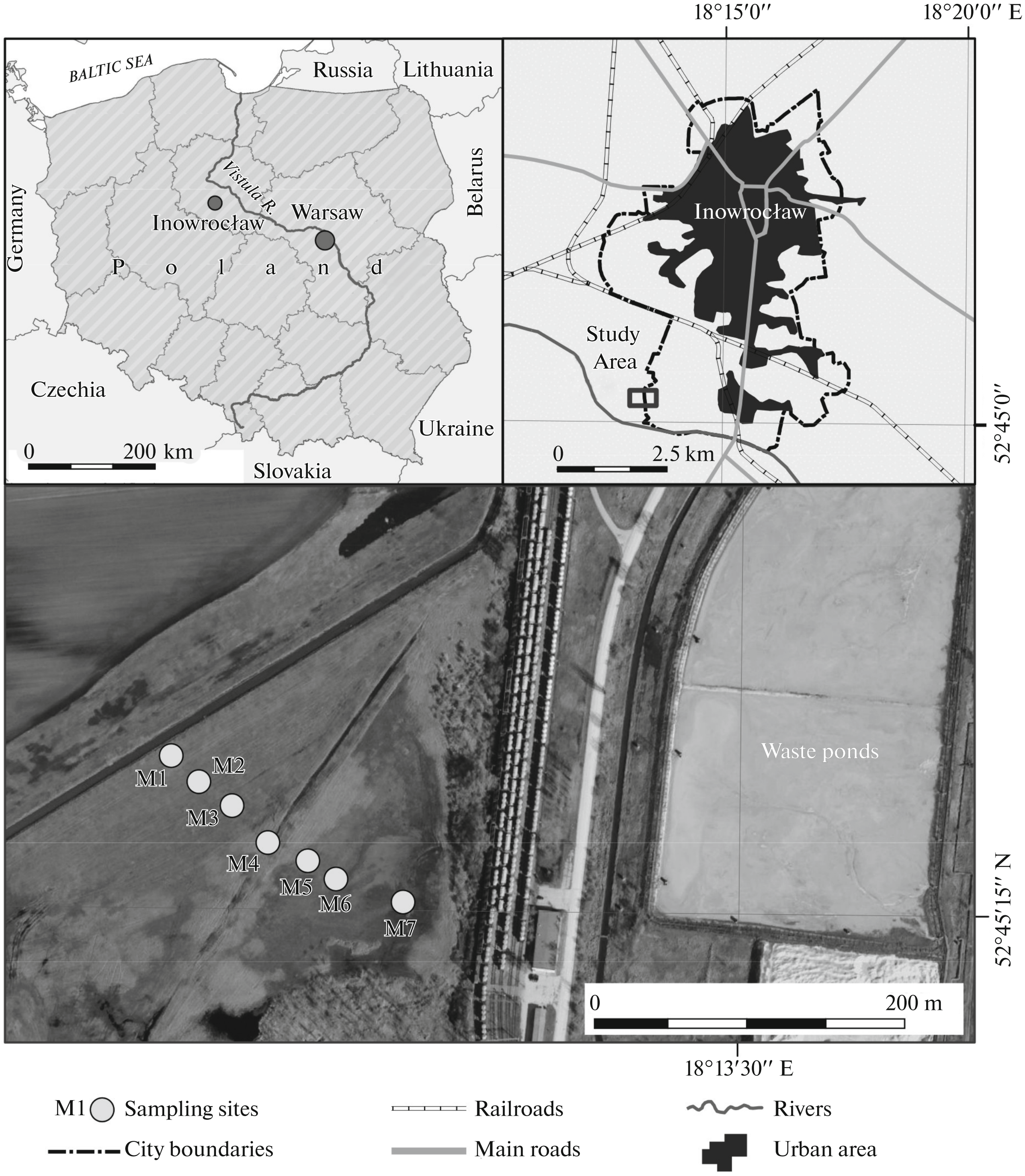

Fig. 1. Location of the studied area and sampling sites.

the VarioMax CN analyzer, calcium carbonate content by Scheibler's method, pH (in soil-water suspension 1 : 2.5 for mineral and 1 : 10 for organic samples) after oxidation of samples with 30% H_2O_2 [14]; specific (mass) magnetic susceptibility (χ) [49] was calculated on the basis of measurements using the MS2 "Bartington" laboratory magnetic susceptibility meter with a dual frequency MS2B sensor (0.47 and 4.7 kHz).

Salinity indices were determined in saturation soil paste extracts [46]: electrical conductivity (EC_e) by the conductometric method, Na^+ ion content by emission spectrometry (ES), Ca^{2+} and Mg^{2+} ions by atomic absorption spectrometry (ASA), Cl^- by argentometric titration.

In order to determine the origin of the technogenic material in mineral samples rich in $CaCO_3$ (M5a,

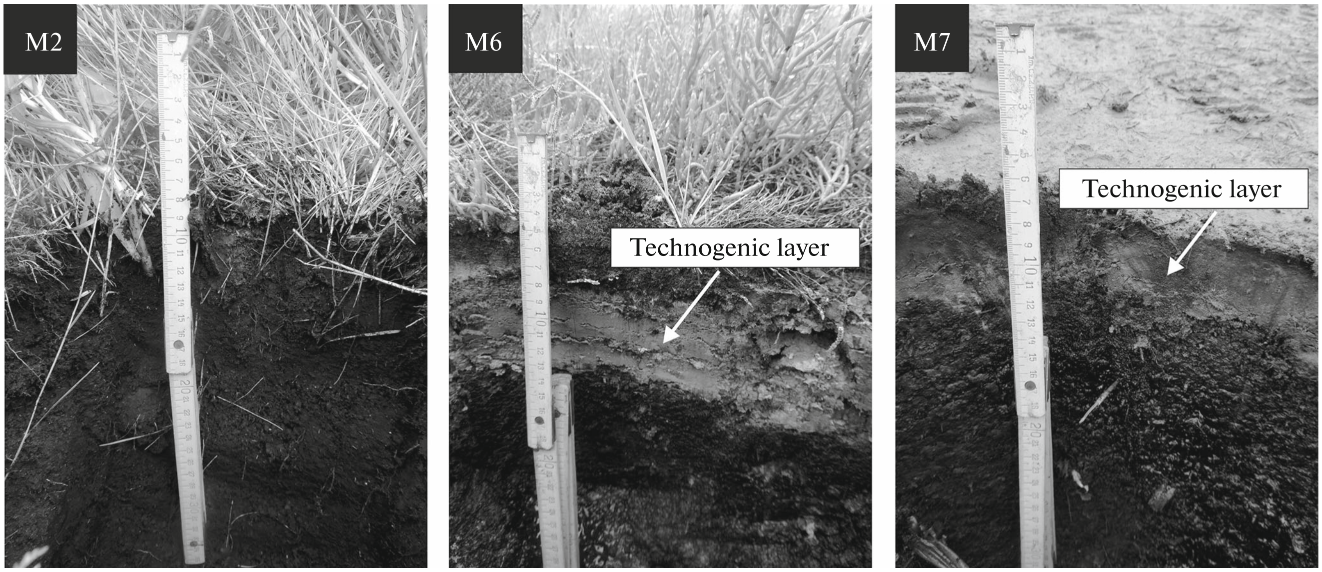

Fig. 2. Morphology of the studied topsoils.

M6a, M7a, M7b) and post-soda lime taken from waste ponds, the analysis of particle size distribution was performed using Mastersizer 2000 (Malvern Instrument). The mineralogical composition was analyzed using X-ray powder diffraction (XRD) in the same samples (XPERT-PRO diffractometer with the Empyrean XRD tube Cu LFF DK 303072; the X-celerator detector – type RTMS, and the goniometer PW 3050/60). Cu Kα radiation was used with an applied voltage of 40 kV and current of 30 mA. Powder samples were scanned from 10.0 to 60 2θ at a counting time of 30 s per 0.05 2θ step. The XRD patterns were processed using the ORIGIN software.

The redox conditions were described by the negative logarithm of hydrogen partial pressure (rH) calculated from pH (H_2O) and E_h values (FAO 2006) [14]. The sodicity hazard was estimated using the sodium adsorption ratio (SAR) and exchangeable sodium percentage, where ESP was calculated from SAR [46]. Granulometric indices, such as mean grain diameter (M_z) and sorting σ1, were calculated according to Folk and Ward [15] using the software GRADISTAT 5.11 PL beta [4]. The principal component analysis (PCA) was used to identify the variation of soil properties (MVSP software). The studied soils were classified according to the WRB classification system [26].

RESULTS AND DISCUSSION

Low peat deposits were found up to a depth of at least 150 cm along the studied transect. The ground water level was high – from 120 cm (M1) to 30 cm (M7). As evidenced by previous research conducted in this area by Hulisz et al. [21, 23], the analyzed soils are influenced by highly saline surface and ground waters (EC 6.8–80.8 dS m^{-1}). Their chemical composition was dominated by following ions: chloride (2.12–43.3 g dm^{-3}), sodium (0.46–11.0 g dm^{-3}) and calcium (0.74–13.5 g dm^{-3}). The highest values of these parameters were recorded in ground waters.

According to the World Reference Base for Soil Resources [26], the studied soils occur in the area where Murshic Histosols (Hypersalic, Sodic) dominate. Organic material (mucky or peaty) was present at most of the sampling sites within 25 cm from the surface. In the lowest-lying places located in the close proximity of a drainage ditch and waste ponds (sites M5–M7), the organic material was covered by mineral material (often stratified) with a thickness of 10 cm, silty loam texture (56–69% of silt) and light yellowish brown color (Table 2, Fig. 2). The exception was site M4, where another mineral technogenic material was found in an old drainage ditch (Table 1).

Some of the physicochemical and chemical properties of the studied soils are presented in Table 2. The range of the total organic carbon and carbonates content was very wide (TOC 1.36–48.8%, $CaCO_3$ 0.53–42.9%). Due to the salt influence (mainly NaCl and $CaCl_2$) and the presence of carbonates, the studied soils were from neutral to alkaline (7.1–7.9). Aerobic conditions prevailed in the analyzed soils (rH 30–32). The lowest rH values, indicating transitional conditions, were recorded at site M7 (rH 21–25), which together with a large difference between values of pH(H_2O) and pH(H_2O_2) may probably indicate the presence of iron sulfides [26]. Soils with such characteristics may be at risk of strong acidification [12]. It should be emphasized, however, that due to the high content of carbonates, alkaline cations and fine-grained composition, these soil materials are charac-

Table 2. Grain size distribution and granulometric indices in post-soda lime and technogenic soil layers

Sample no.	Percentage of fraction, mm								Textural class (USDA)	Granulometric indices (φ)	
	2.0–1.0	1.0–0.5	0.5–0.25	0.25–0.1	0.1–0.05	0.05–0.02	0.02–0.002	<0.002		M_z	σ1
Lime	0	0	0	0	9	37	48	6	Si	4.43	0.99
M5a	0	3	3	10	17	23	33	11	SL	3.84	1.89
M6a	0	1	3	8	20	24	34	10	SL	3.92	1.72
M7a	0	0	0	4	22	34	35	5	SL	3.99	1.17
M7b	0	2	3	7	18	31	32	7	SL	3.84	1.59

Symbol explanations: Si—silt, SL—silt loam, M_z—mean grain diameter, σ1—sorting.

Table 3. Properties of topsoils along the studied transect

Sample no.	Depth, cm	pH (H_2O)	pH (H_2O_2)	rH	TOC	$CaCO_3$	$\chi \times 10^{-8}$ m^3 kg^{-1}
					%		
M1	0–25	7.6	5.0	30	26.1	1.5	21.5
M2	0–25	7.1	4.5	32	48.8	0.5	9.5
M3	0–25	7.3	4.5	32	33.5	0.6	7.6
M4	0–25	7.9	5.9	30	1.43	1.4	0.0
M5a	0–9	7.9	5.7	32	2.80	33.5	7.9
M5b	9–25	7.8	4.9	32	20.1	5.1	4.7
M6a	0–8	7.9	5.8	32	2.92	35.1	4.6
M6b	8–25	7.6	5.3	32	38.2	4.5	3.1
M7a	0–2	7.9	5.4	25	6.61	42.9	22.9
M7b	2–4	7.8	5.3	24	1.36	32.9	11.9
M7c	4–25	7.2	4.4	21	17.2	0.5	3.4

Symbol explanations: pH (H_2O)—standard pH measurement in the field (in H_2O), pH (H_2O_2)—pH measurement after oxidation with 30% H_2O_2, rH—index of the reducing power of a redox system (calculated from Eh and pH), TOC—total organic carbon, χ—specific (mass) magnetic susceptibility.

terized by strong buffering capacity and respond slowly to changes in oxidation-reduction (redox) conditions [50]. The specific (mass) magnetic susceptibility (χ) ranged from 0.0 to 22.9 × 10^{-8} m^3 kg^{-1} (Table 3). This may indicate a very low content of ferromagnetics and the dominance of iron in the form of diamagnetic substances [44]. Therefore, the analyzed samples did not show magnetic properties induced by technogenic factors, and thus the soil contamination with heavy metals [48]. For comparison, magnetic susceptibility of cement dust may range from 66 to 806 × 10^{-8} m^3 kg^{-1}. Dusts from lime of the plant may be characterized by very low values of this parameter (1–5 × 10^{-8} m^3 kg^{-1}) [37].

According to Jackson's [27] classification, the studied soils are very strongly saline (EC_e > 16 dS m^{-1}). Values of electrical conductivity (EC_e) ranged from 15.3 up to 122 dS m^{-1} (Table 4), and their variability was generally correlated with the content of analyzed ions: Na^+ from 1.83 (M1) to 1.9 g dm^{-3} (M7 2–4 cm), Ca^{2+} from 2.15 (M5 9–25 cm) to 29.4 g dm^{-3} (M7 2–4 cm), Mg^{2+} from 0.01 (M5 9–25 cm) to 0.05 g dm^{-3} (M3) and Cl^- from 6.43 (M1) to 80.0 g dm^{-3} (M7 2–4 cm). The highest values of EC_e, SAR and ESP parameters, the content of Na^+, Cl^-, Ca^{2+} ions determined in the saturated extract were recorded at site M7, which was located in a small depression, in the closest vicinity of waste ponds (Table 4).

A complementary characteristics of the studied topsoils was provided by PCA analysis. The first principal component explains 47.2% of the total variation and the second one 23.7%; a two-component model thus accounts for 70.9% of the total variance. The following parameters were most strongly correlated with the PC1 axis: EC_e (positively), ESP (positively), $CaCO_3$ (positively) and TOC (negatively), while with the PC2 axis—pH (H_2O) and rH, both negatively. Figure 3 clearly showed that the samples are clustered into two different groups that correspond to the origin of the soil materials (I: M1–M4, M5b, M6b, M7c; II: M5a,

Table 4. Properties of the saturated extract paste

Sample no.	Depth, cm	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	EC_e, dS m^{-1}	SAR	ESP, %
		g dm^{-3}						
M1	0–25	1.83	2.24	0.02	6.43	15.3	11	13
M2	0–25	4.11	4.93	0.05	16.9	37.3	16	18
M3	0–25	5.90	6.66	0.05	22.1	49.1	20	22
M4	0–25	3.24	3.07	0.03	11.1	24.1	16	18
M5a	0–9	2.96	3.11	0.02	10.1	27.4	15	17
M5b	9–25	2.16	2.15	0.01	8.09	19.2	13	15
M6a	0–8	4.79	5.10	0.05	17.3	40.6	18	20
M6b	8–25	2.93	2.78	0.02	10.9	24.8	15	17
M7a	0–2	11.7	22.0	0.03	63.1	108	22	23
M7b	2–4	12.9	29.4	0.04	80.0	122	21	23
M7c	4–25	6.83	13.8	0.02	38.9	50.6	16	18

Symbol explanations: EC_e—electrical conductivity of the saturation extract paste, SAR—sodium adsorption ratio, ESP—exchangeable sodium percentage (calculated from SAR).

M6a, M7a, M7b). Parameters that differentiated natural and technogenic soil horizons/layers were total organic carbon and calcium carbonate content and electrical conductivity of the saturation paste extract.

As shown previously, the soil properties of the examined transect were strongly correlated with the distance from the source of their contamination, i.e. post-soda waste collected in waste ponds. In addition to ascension of saline ground waters, allochthonous accumulation of technogenic materials in topsoils plays an important role in this area. All analyzed mineral soil layers were characterized by similar mean grain size (M_z 3.84–3.99 φ) and poor sorting (σ1 1.17–1.89 φ). Furthermore, they are similar in terms of the analyzed granulometric parameters and mineralogical composition to the material collected from waste ponds (dominance of calcite, i.e. the main component of post-soda lime – Fig. 4) [2]. Soils developed from naturally weathered waste deposits of soda industry in Germany showed similar properties [18].

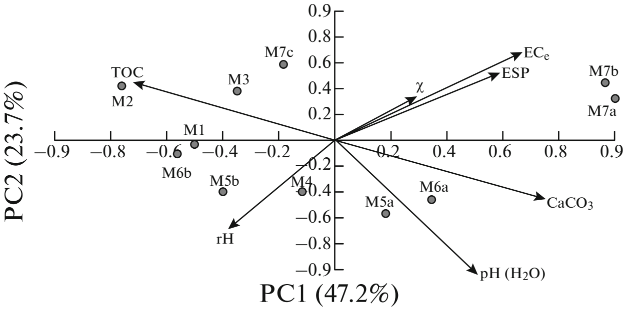

Fig. 3. Ordination plot of the principal component analysis (PCA) of selected topsoil properties (n = 11). The soil samples labelled as in Table 2. Symbol explanations: EC_e—electrical conductivity of the saturation extract paste, ESP—exchangeable sodium percentage, rH—index of the reducing power of a redox system, TOC—total organic carbon, χ—specific (mass) magnetic susceptibility.

In the light of the obtained results, it can be assumed that technogenic soil layers may result from short-distance eolian transport from waste ponds. In the past, the impact of lime dust was also intensified by heavy car traffic transporting post-soda lime used in agriculture [20]. The material could also be washed by surface runoff along the topographic gradient (i.e. M7 site) during rainfall and high water levels in the drainage ditch (surface-water floodings). As evidenced by the research of Piernik et al. [42], the main factor in the microrelief formation in the conditions of high exchangeable sodium content may be the dispersion and peptization of soil colloids and deterioration of the structure (Fig. 2; site M7). This phenomenon is commonly observed in typical sodic soils [54] and usually results in a small range of available moisture, high wilting percentage, swelling, cracking, a low infiltration rate, etc. As a result, the soil surface becomes more susceptible to water erosion, and in dry periods also to eolian erosion (e.g. transport by saltation). The microrelief may also affects the distribution of soluble salts in the topsoils. According to Kotenko and Zubkova [30], the total content of salts and the content of sodium, magnesium, chloride ions in the semi-arid zone is higher in the soils of microelevations. A similar phenomenon was observed in the studied soils primarily affected by shallow saline ground waters. Furthermore, this can be explained by the presence of highly saline allochthonous material as well as the periodic influence of stagnant surface waters on poorly permeable technogenic layers (sites M5–M7). The microrelief of salt meadows can also be of key importance to

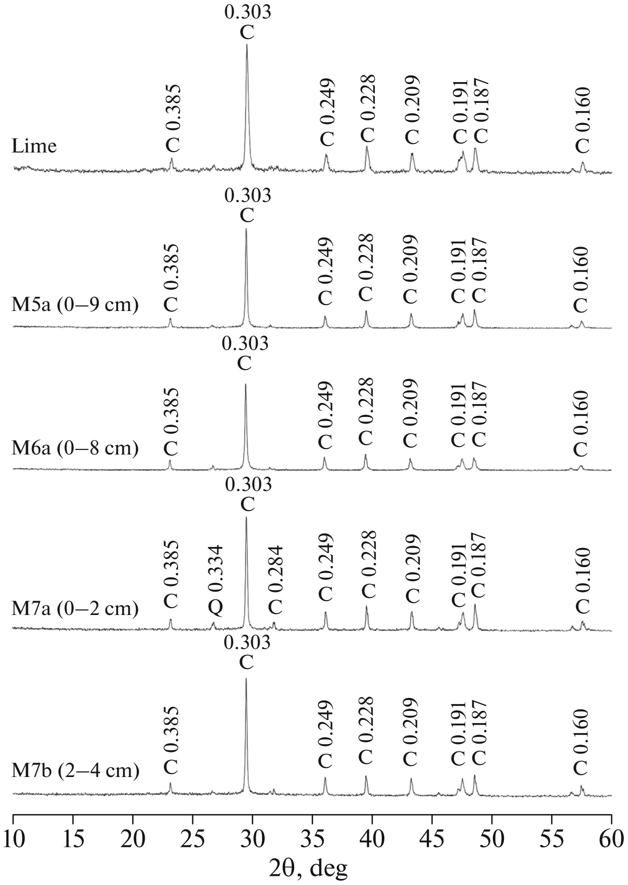

Fig. 4. X-ray powder diffraction patterns in post-soda lime and technogenic soil layers (C—calcite, Q—quartz).

the distribution of halophytes [42, 54]. Oxidative stress may occur in places of periodic water stagnation. It disturbs germination and early seedling growth. This applies even to halophytes—plants most resistant to salt stress, e.g. *Salicornia europaea* [5, 41]. Therefore, the last of the studied sites (M7) was unvegetated.

Given the degree of geomechanical transformation, the described changes can be considered minor as they only concern the topsoil. However, they are crucial for the functioning of soils in the landscape and the ecological functions they perform. Technogenic transformations usually concern thick layers, sometimes even the whole solum and are associated with intentional human activity related to construction. SUITMAs are frequently characterized by horizontal and vertical heterogeneity, often caused by multiple mixing and deposition [17, 24, 38]. This does not apply to the studied soils, where human impact is not so direct.

In the analyzed case, the technogenic material is displaced and deposited as a result of natural processes occurring in nature—eolian transport and rainwater runoff. The resulting soils can therefore be compared to another subtype of technogenic soils, edifisols, developing due to initial, relatively natural soil-forming processes occurring on technogenic substrates [10].

The analyzed mineral material meets the criteria for the artifacts in the WRB classification [26], i.e. it was brought to surface and substantially modified in the industrial processes, and its properties were only slightly changed by pedogenesis. It should be noted that specific features of the studied soils had a precise reflection in the name of the WRB soil unit thanks to a flexible system of specifiers such as Akro- and Proto-. However, it was impossible to emphasize the high amount of carbonates due to their technogenic origin. Therefore, it seems justified to create the possibility of defining the artifact type in the name of qualifiers (i.e. Calcitechnic) in the next edition of the WRB classification. The studied soils can be classified as Eutric Murshic Histosols (Akromineralic, Salic, Sodic, Prototechnic).

CONCLUSIONS

This research has shown the multidirectional impact of soda industry waste on soil properties with the participation of not only saline ground waters but also the eolian supply of mineral material from waste ponds and, in some cases, its transport by surface runoff. Due to these processes, soils with a complex genesis associated with the impact of natural (peat accumulation) as well as technogenic factors developed. The high soil salinity was recorded in all sampling sites. However, only the organic soils occurred within 200 m distance from the waste ponds were characterized by the presence of thin mineral surface layers, poor in organic carbon and rich in carbonates and easily soluble salts. As a result of sodification, these layers had unfavorable water properties that limited the plant growth. Despite the location in the industrial zone, the studied soils did not show magnetic properties induced by technogenic factors. Finally, it can be concluded that the described specific features of the studied soils could be well reflected using the WRB classification. However, in author's opinion, creation of the possibility of indication of artifact types in the form of subqualifiers would further improve this classification system.

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