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The Influence of Industrial Waste on the Magnetic Properties of Salt-Affected Soils from Two Soda Ash Manufacturing Sites

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Abstract: The aim of this study was to characterize the impact of soda ash manufacturing on the magnetic properties of soils located in the agricultural landscape in north-central Poland. Two study sites were chosen: Mątwy (SM) and Janikowo (SJ). Highly saline soils with halophyte communities were selected in order to develop an understanding of the relationship between salinization of water–soil interface and the potential contamination risk of the environment. Basic chemical and physicochemical properties of topsoil (0–25 cm) and water (surface and groundwater) samples from five locations were characterized. The characteristics of soil contamination were based on the content of selected metals, magnetic properties and salinity indices. Potential routes of contaminant migration (air and water fluxes) were analyzed. High magnetic anomalies of technogenic origin were revealed in the studied soils. A statistically confirmed relationship between high magnetic susceptibility and the content of selected metals (Co, Ni, Cu, Zn, Ba, Pb and Mn) showed the high utility of magnetometric techniques in soil research (diagnosis of soil transformation and contamination during technogenic impact). Three potential factors influencing contaminant migration were revealed: highly saline ground and surface water, eolian transport of fine-grained mineral fractions from waste ponds and atmospheric deposition of coal combustion products.

Keywords: agricultural soils; heavy metals; human impact; magnetic susceptibility; soil salinity; SUITMAs

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1. Introduction

In recent years, measurements of magnetic susceptibility (MS) have been commonly used in the assessment of soil pollution level [1–3]. They have also been used in the diagnosis of geogenic, pedogenic and technogenic sources of magnetic signal in soils [1,4,5]. The MS values are much higher in polluted areas compared to the natural values. Hence, magnetic susceptibility measurements can be used to distinguish technogenic soil horizons in profiles. The presence of heavy metals in transformed horizons can be confirmed relatively quickly using this technique. It helps to understand the soil genesis as well as the rates and directions of pedogenic processes [1,6,7].

The magnetic properties of soils are directly influenced by the type and concentration of ferromagnetic iron oxides, mainly those of geogenic (weathering of igneous and metamorphic rocks) and anthropogenic origin (deposition of industrial and urban dusts, as well as the presence of artifacts in soils) [8–10]. As revealed by many authors [11,12], magnetic susceptibility shows a linear relationship with the content of potentially toxic

elements (PTEs) such as cadmium, lead, zinc, copper and chromium. While the MS measurement does not show the metal content in the sample itself, it provides information about the presence of magnetic particles with accompanying metals. The MS values can be also controlled by texture, especially clay content and organic matter, which are the main binding agents in the soil [13,14]. Organic horizons are highly vulnerable to contaminant accumulation in soil profiles. This is due to the process of bioaccumulation caused by the uptake of contaminants by plants [15,16]. The presence of magnetic particles in soil organic horizons is strictly related to the deposition of industrial dusts, which contain iron oxides and FeO-associated PTEs. High-temperature manufacturing processes are believed to be the main source of these pollutants [1].

Soils of urban agricultural areas are typically found to be contaminated by various toxic substances, including those released by industry, which pose a potential threat to waterbodies, human health and ecosystems [17]. According to European Environment Agency data [18], toxic trace metals are one of the most frequent (37.3%) soil contaminants. Some branches of the chemical industry produce a huge amount of waste—for example, the soda industry can sometimes cause strong soil salinization and sodification [19,20]. These processes can also significantly influence the content and behavior of PTEs. It is known that under salinity conditions, metals such as Cu, Cd, Pb and Zn can form complex compounds with chlorides or sulfates, and salinity itself usually increases the bioavailability of PTEs as a result of an ion exchange reaction, most often with sodium [21,22]. However, in the literature, there are still a limited number of studies on behavior of toxic metals in the industrial salt-affected soils [23,24], especially in relation to soil magnetic properties. Therefore, the aim of this research was to evaluate the technogenic influence on magnetic susceptibility in soils contaminated by soda ash industry waste. We selected two industrial sites in Inowrocław and Janikowo in north-central Poland. Our results also allowed for the identification of magnetic anomalies in the studied soils under very strong technogenic salinity.

2. Materials and Methods

2.1. Study Area

These studies were carried out in the vicinity of the Ciech Soda Poland S.A. plants in Inowrocław-Mątwy (established in 1879) and Janikowo (established in 1957) in north-central Poland (Figure 1). This manufacturer produces both soda ash (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$), calcium chloride ($CaCl_2$) and sodium chloride (NaCl). In the past, post-production waste was stored in ponds (over 100 ha at each site). The solid waste of the soda ash produced by Solvay's process is alkaline (pH 10–12) and contains mostly $CaCO_3$ (70–80% of dry mass), $CaSO_4$, $Ca(OH)_2$, $Fe(OH)_3$, silicates, aluminosilicates and water-soluble salts such as $CaCl_2$ and NaCl [25]. Despite ongoing land reclamation and other pro-ecological activities, several dozen years of soda industry waste accumulation caused the high salinization of waterbodies and soils in the nearby agricultural area. The infiltration of saline waters into the soils resulted from bad construction of industrial ponds [26,27]. Eolian transport of mineral dusts from the surface of unreclaimed ponds seems to be a second crucial factor causing salinization and pollution of the adjacent area [20]. The long-term impact of contaminants on the nearby arable land significantly decreased the productivity of soils. Moreover, a part of the agricultural land was totally excluded from crop production and pasture. Highly saline soils are covered by unique halophyte communities [28].

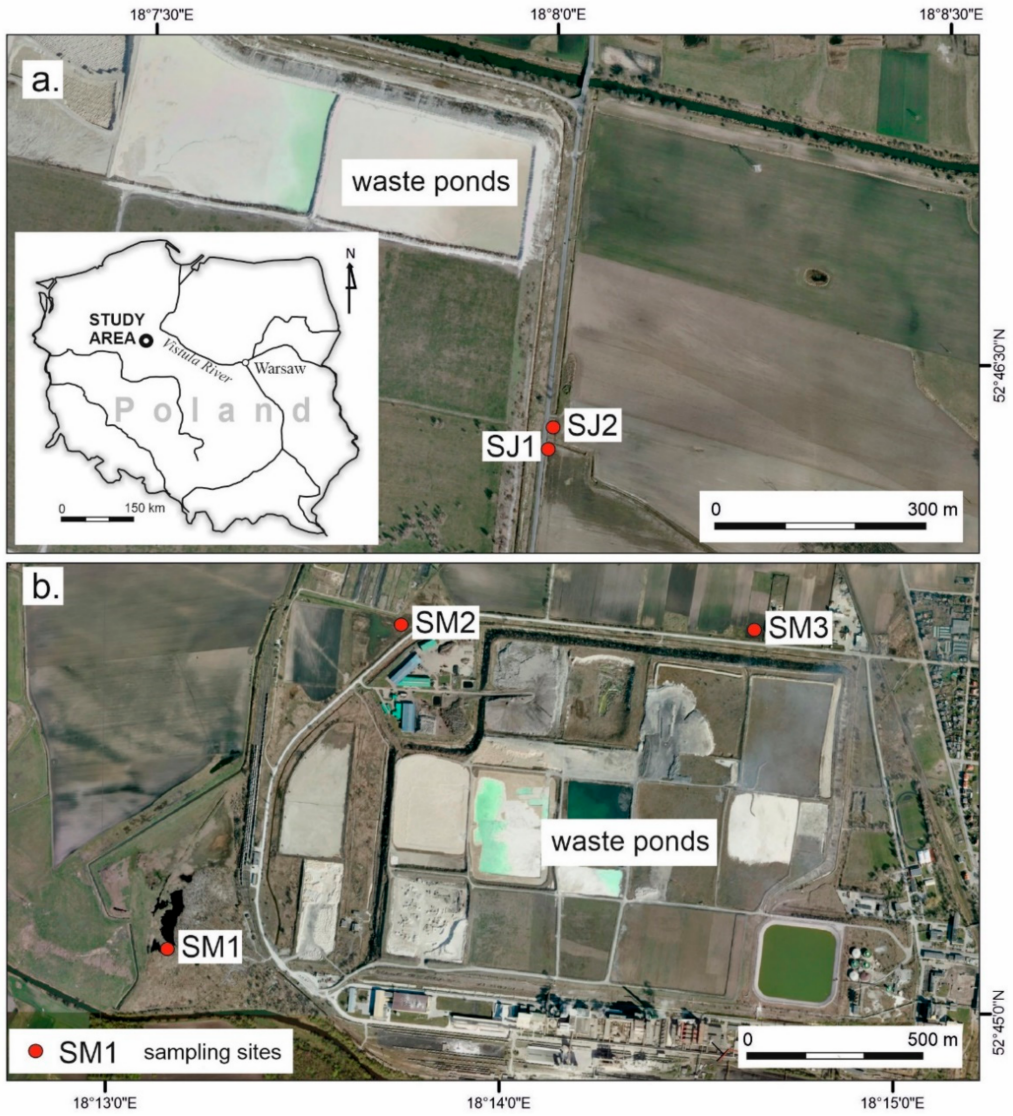


Figure 1. Location of the study area and sampling sites: (**a**)—Janikowo (SJ1 and SJ2) and (**b**)—Inowrocław (SM1–SM3).

2.2. Field Work

The research was carried out in 2017 in two rural areas contaminated by soda post-production waste: Inowrocław (SM) and Janikowo (SJ). Five sampling sites (SM1–SM3 in Inowrocław; SJ1 and SJ2 in Janikowo) were located in patches of *Salicornia europaea* (Figure 1). As reported by Piernik [28], this halophyte is an indicator of a high soil salinity. Soil samples were taken from topsoils, with three repetitions at a depth of 0–25 cm. In some places (SM2 and SJ2), more samples were taken from the topsoil due to the presence of thin layers of various technogenic materials. In total, 26 soil samples were submitted for analysis. A detailed description of the sampling sites is shown in Table 1. Additionally, in each sampling site, three soil cores were obtained with a Humax sampler for MS measurements (in total, 15 cores). Soils were described and classified based on auger drillings up to a depth of 1 m. The significant impact of water conditions on soil salinity, surface and ground water samples was also taken into account.

Table 1. Characteristics of the sampling sites.

Site	Coordinates	Location
SM1	52°45′5.671″ N 18°13′9.433″ E	edge of the old peat excavation pond
SM2	52°45′37.732″ N 18°13′50.672″ E	saline wetland
SM3	52°45′35.972″ N 18°14′36.626″ E	arable field
SJ1	52°46′25.490″ N 18°7′59.445″ E	arable field
SJ2	52°46′26.883″ N 18°7′59.576″ E	edge of the drainage ditch

2.3. Laboratory Analysis

The soil samples were air dried and passed through a 2 mm mesh screen. The total organic carbon content (TOC) was determined using the Analyzer Multi N/C 3100 (Analytik Jena GmbH, Germany) with a furnace for combustion of solid samples (HT 1300). The calcium carbonate content was determined by Scheibler's method. The pH was measured potentiometrically in soil-water suspension 1:2.5. Saturated paste extracts were prepared to evaluate soil salinity level. Electrical conductivity (EC_e), saturation percentage (SP) and content of chlorides (Cl^-) were also determined [29].

Selected metals (Mn, Zn, Cu, Cd, Fe, Co, Ni, Pb, Cr and Ba) were determined by inductively coupled plasma mass spectrometry (Agilent ICP-MS 7700, Agilent Technologies Inc., Santa Clara, USA) after digestion with a mixture of HCl and HNO_3 (3:1). The specific (mass) magnetic susceptibility (χ) was calculated on the basis of measurements using the MS2 "Bartington" laboratory magnetic susceptibility meter (Bartington Instruments Limited, Witney, United Kingdom) with a dual-frequency MS2B sensor (0.47 and 4.7 kHz). Measurements of the vertical distribution of the low-field magnetic susceptibility κ were performed in the soil cores using the MS2C sensor.

In addition, reference measurements were taken in samples of surface and ground waters [30]. The pH was determined using potentiometric method. The EC was determined by conductometric method and the content of macro and microelements by ICP-MS.

2.4. Data Analysis

Based on the obtained results, the following calculations were made:

i. Salt percentage in soil (P_{ss}) [29]:

$$P_{ss} = 0.064 \times EC_e \times (SP/100), \quad (1)$$

where EC_e is the electrical conductivity of the saturation paste extract and SP is the saturation percentage.

ii. Frequency-dependent magnetic susceptibility χ_{fd} calculated as a relative and absolute change of magnetic susceptibility obtained for low and high frequencies [31]:

$$\chi_{fd}\ (\%) = ((\chi lf - \chi hf)/\chi lf) \times 100, \quad (2)$$

where χlf is the MS measured at low frequency (0.46 kHz) and χhf is the MS measured at high frequency (4.6 kHz).

iii. Contamination factor (CF):

$$CF = C_{metal}/C_{background\ value}, \quad (3)$$

where C_{metal} is the metal concentration in the soil sample and $C_{background\ value}$ is the background value of that metal. As a geochemical background, the following values were adopted (in $mg \cdot kg^{-1}$): Cd = 0.18, Co = 4.0, Cr = 27.0, Cu = 7.1, Fe = 12900, Mn = 289, Ni = 10.2, Pb = 9.8, Zn = 30.0 [32] and Ba = 350 [33]. The contamination level (pollution) can be classified based on the following scale: 0–none, 1–none to moderate, 2–moderate, 3–moderate to strong, 4–strong, 5–strong to very strong, 6–very strong [34].

iv. Pollution Load Index (PLI):

$$PLI = n\sqrt{(CF1 \cdot CF2 \cdot CF3 \cdot \ldots \cdot CFn)}, \quad (4)$$

where CF is the contamination factor and n is the number of metals.

A PLI value > 1 indicates soil pollution, whereas PLI < 1 indicates no pollution [35].

Datasets were analyzed using Statistica 9 software (StatSoft Europe GmbH, Hamburg, Germany). Basic statistical characteristics (arithmetic mean, standard deviation, coefficient of variation) and Spearman's rank correlation coefficients (rs) were calculated. A nonparametric Mann–Whitney U test was used to test the significance of differences between mean values. Differences at $p < 0.05$ were considered statistically significant. Moreover, principal component analysis (PCA) was used. The first two principal components (PC1 and PC2) were selected to identify potential sources of metals in the studied soils.

3. Results and Discussion

Heterogeneity of soil cover was a specific feature of the study sites. Based on the results of our field works, the soils from the Inowrocław (SM) site were characterized as Mollic Gleysols and Murshic Histosols, while Albic Luvisols dominated in the Janikowo (SJ) site [36]. Primary soil properties were transformed due to both the influence of highly saline groundwater (Table 2) and technogenic materials. These materials were deposited on the soil surface or mixed with primary soils [20,37]. The presence of some features in topsoils suggested that they were formed during human-induced pedogenesis and technopedogenesis [38]. The main features were: the presence of thin, artificial soil horizons enriched with coarse-grained fractions—diameter > 2 mm (maximally 11% in SM, maximally 56% in SJ); accumulation of $CaCO_3$ (2.4–26.6% in SM, 3.6–54.5% in SJ); high pH level (pH–H_2O 7.4–10.4 in SM, pH–H_2O 7.3–7.8 in SJ); very strong salinity (EC_e 9.05–64.5 dS·m^{-1} in SM, 20.5–110 dS·m^{-1} in SJ) and accumulation of iron (maximally, 15.2 g·kg^{-1} in SM and 36.7 g·kg^{-1} in SJ) (Tables 3 and 4). There were statistically significant differences between the two industrial sites in percentage of fraction > 2 mm, calcium carbonate content, salinity (expressed by chloride content in saturation paste extract and salt content in soils) and saturation percentage (SP). Values of the last parameter relate to the texture and organic matter content. As estimated on the basis of the US Salinity Laboratory Staff study [39], the SP ranges in both sites were typical for mineral soil horizons, with a range of texture from sandy loam (27–40%) to silt loam (>40%) (Table 3).

Mass magnetic susceptibility (χ) is a parameter proportional to the concentration of magnetic particles in soil [8,12]. High magnetic enhancement of soils was detected at the Mątwy site (SM), where the mean value of χ was equal to 78.9 $\times$ 10^{-8} m^3·kg^{-1} (Table 4). At the Janikowo site (SJ), the mean value of χ reached 52.2 $\times$ 10^{-8} m^3·kg^{-1}. The results of a nonparametric Mann–Whitney U test, for a 5% significance level ($\alpha = 0.05$), showed that there were no statistically significant differences between mean values of χ for both sites. High χ values indicate the magnetic enhancement caused by the presence of magnetics and their accompanying metals. In comparison, the lime and cement industry emits dust rich in Pb, Mn, Cd and Zn with average magnetic susceptibility values of 98 $\times$ 10^{-8} m^3·kg^{-1} [10], while in dust from the coke industry, containing Cu, Zn, As, Pb and Cr, χ values can reach as much as 287 $\times$ 10^{-8} m^3·kg^{-1} [3,12].

The frequency-dependent magnetic susceptibility (χ_{fd}) is used as a proxy parameter for identifying anthropogenic (technogenic) influence [40]. The χ_{fd} is calculated as the percentage of magnetic susceptibility loss measured at low and high frequencies of the applied magnetic field. If the value of χ_{fd} is greater than 4%, it indicates the presence of superparamagnetic particles of natural origin in the soil. A value below 4% indicates magnetic particles from anthropogenic sources [40]. The χ_{fd} values in the studied soils showed high variability (0.3–8.1% SM, 0.0–4.3% in SJ) (Table 4) and were generally lower than 4%. Hay et al. [41] stated a significant accumulation of anthropogenic magnetic particles in soils based on high values of mass magnetic susceptibility ($\chi > 37 \times 10^{-8}$ m^3·kg^{-1}) together

with low values of frequency-dependent magnetic susceptibility (χ_{fd} < 3%). These criteria were met for soils from the SM1, SM2, SJ1 and SJ2 sites.

Table 2. Surface and groundwater properties in the study sites: Inowrocław (SM1-SM3) and Janikowo (SJ1 and SJ2).

	SM1	SM2	SM3	SJ1	SJ2
	Cutover Peatland (Pond)	Drainage Ditch	Arable Field (Ground Water)	Drainage Ditch	Drainage Ditch
pH	10.2	7.9	6.6	7.4	7.5
EC ($dS \cdot m^{-1}$)	31.0	32.2	58.0	111	123
Cl^- ($g \cdot dm^{-3}$)	8.1	13.2	28.9	54.2	62.0
Na^+ ($g \cdot dm^{-3}$)	6.1	3.0	5.9	11.0	22.0
K^+ ($g \cdot dm^{-3}$)	0.3	0.1	0.2	0.2	0.8
Ca^{2+} ($g \cdot dm^{-3}$)	0.1	5.9	11.9	20.3	14.8
Mg^{2+} ($g \cdot dm^{-3}$)	22.8	18.5	24.2	88.4	0.1
Mn ($mg \cdot dm^{-3}$)	0.1	0.1	1.0	6.8	<0.1
Fe ($mg \cdot dm^{-3}$)	2.1	0.4	0.2	0.2	0.2
Co ($mg \cdot dm^{-3}$)	0.2	<0.1	<0.1	<0.1	0.0
Ni ($mg \cdot dm^{-3}$)	0.2	<0.1	<0.1	<0.1	0.1
Cu ($mg \cdot dm^{-3}$)	0.1	<0.1	<0.1	0.1	0.1
Zn ($mg \cdot dm^{-3}$)	0.2	<0.1	<0.1	0.2	0.1
Cd ($mg \cdot dm^{-3}$)	<0.1	<0.1	<0.1	<0.1	<0.1
Ba ($mg \cdot dm^{-3}$)	0.8	2.2	5.8	3.6	1.1
Pb ($mg \cdot dm^{-3}$)	<0.1	<0.1	<0.1	<0.1	<0.1
Cr ($mg \cdot dm^{-3}$)	<0.1	<0.1	<0.1	<0.1	<0.1

Table 3. Summary of descriptive statistics of basic soil properties and salinity indices: minimum (min), maximum (max), mean, standard deviation (SD) and coefficient of variation (CV). The significant differences between two study sites with $p < 0.05$ are marked by small letters (nonparametric Mann–Whitney U test).

Study Site	Parameter	ϕ > 2 mm (%)	TOC (%)	$CaCO_3$ (%)	pH-H_2O	EC_e ($dS \cdot m^{-1}$)	Cl_e^- ($g \cdot dm^{-3}$)	SP (%)	P_{ss} (%)
SM (n = 11)	Min	0	1.5	2.4	7.4	9.05	3.3	27.2	0.2
	Max	11	15.6	26.6	10.4	64.5	32.9	41.0	1.3
	Mean	2 [a]	6.8 [a]	10.7 [a]	8.3 [a]	33.7 [a]	16.0 [a]	33.3 [a]	0.7 [a]
	SD	3	5.5	8.2	1.3	19.1	9.7	4.9	0.4
	CV (%)	138	81	76	16	57	61	15	60
SJ (n = 15)	Min	0	0.4	3.6	7.3	20.5	16.1	31.6	0.5
	Max	56	8.7	54.5	7.8	110	69.0	57.0	3.6
	Mean	17 [b]	3.9 [a]	27.0 [b]	7.6 [a]	55.6 [a]	40.0 [b]	47.6 [b]	1.7 [b]
	SD	21	2.4	16.9	0.2	30	16.7	7.5	1.0
	CV (%)	123	61	63	3	54	42	16	57

Symbol explanations: ϕ > 2 mm—content of coarse-grained fractions (including artefacts), TOC—total organic carbon, pH-H_2O—pH measurement in soil-water suspension 1:2.5, EC_e—electrical conductivity of the saturation extract paste, Cl_e^-—concentration of chlorides in the saturation extract, SP—saturation percentage, P_{ss}—salt percentage in soil calculated from EC_e [29].

Table 4. Summary of descriptive statistics of soil magnetic properties and content of trace elements: minimum (min), maximum (max), mean, standard deviation (SD) and coefficient of variation (CV). The significant differences between two study sites with $p < 0.05$ are marked by small letters (nonparametric Mann–Whitney U test).

Study Site	Parameter	χ ($\times 10^{-8}$ $m^3 \cdot kg^{-1}$)	χ_{fd} (%)	Mn	Fe	Co	Ni	Cu	Zn	Cd	Ba	Pb	Cr
				($mg \cdot kg^{-1}$)									
SM (n = 11)	Min	9.0	0.3	55.8	3900	1.5	3.2	6.4	13.2	0.1	66.5	11.7	6.1
	Max	205	8.1	213	15240	4.3	8.2	22.8	114	0.8	292	104	10.6
	Mean	78.9 [a]	2.8 [a]	130[a]	6900 [a]	2.4 [a]	5.4 [a]	11.9 [b]	44.0 [a]	0.3 [b]	135 [a]	38.8 [b]	7.5 [a]
	SD	71.4	2.4	54.1	3970	1.0	1.9	4.9	34.4	0.3	77.8	29.3	1.4
	CV (%)	91	85	42	58	42	35	41	78	76	60	76	19
SJ (n = 15)	Min	24.7	0.0	158	4210	1.5	2.5	4.7	4.6	0.03	29.6	2.5	2.5
	Max	86.6	4.3	1150	36740	6.1	9.5	15.9	33.6	0.27	282	31.9	21.8
	Mean	52.2 [a]	2.2 [a]	594 [b]	12,810 [b]	3.1 [a]	5.5 [a]	9.2 [a]	16.7 [a]	0.1 [a]	97.4 [a]	14.9 [a]	8.7 [a]
	SD	19.8	1.1	385	9050	1.4	2.6	3.5	10.1	0.1	59.8	9.1	4.9
	CV (%)	38	53	65	71	45	47	38	61	48	60	61	56

Symbol explanations: χ—specific (mass) magnetic susceptibility, χ_{fd}—frequency-dependent magnetic susceptibility.

The high magnetic enhancement of soils from the SM site was most likely due to the content of metals such as Co (1.5–4.3 mg·kg^{-1}), Ni (3.2–8.2 mg·kg^{-1}), Cu (6.4–22.8 mg·kg^{-1}), Zn (13.2–114 mg·kg^{-1}), Ba (66.5–292 mg·kg^{-1}) and Pb (11.7–104 mg·kg^{-1}) (Table 4). Moreover, Spearman's correlation analysis revealed that there were significant strong and positive correlations between χ and metals mentioned (rs 0.85, 0.90, 0.82, 0.64, 0.75 and 0.64, respectively) (Table 5.) Other relationships were found for the Janikowo site (SJ), where magnetic susceptibility was influenced only by Mn (158–1150 mg·kg^{-1}), Ni (2.5–9.5 mg·kg^{-1}) and Cu (4.7–15.9 mg·kg^{-1}). In the analyzed dataset, it is surprising that there is no significant correlation between magnetic susceptibility and iron. This may be explained by the presence of iron associated with non-magnetic forms such as pyrite [1]. It is a common component of the limestone rocks used in the soda ash production process [25]. The non-parametric Mann–Whitney U test revealed that soils in the Mątwy site had significantly higher Cu, Cd and Pb content and significantly lower Fe and Mn content than soils from the Janikowo site. It can be assumed that these differences were most likely due to the local specificity of pollutant deposition and emission.

Table 5. Spearman's rank correlation (rs) between mass magnetic susceptibility and content of trace elements.

	χ	Mn	Fe	Co	Ni	Cu	Zn	Cd	Ba	Pb	Cr
SM (n = 11)											
χ	1.00										
Mn	−0.03	1.00									
Fe	0.55	−0.01	1.00								
Co	0.85 *	0.18	0.79 *	1.00							
Ni	0.90 *	0.10	0.75 *	0.92 *	1.00						
Cu	0.82 *	0.26	0.76 *	0.87 *	0.94 *	1.00					
Zn	0.64 *	0.00	0.90 *	0.82 *	0.76 *	0.76 *	1.00				
Cd	0.41	−0.06	0.90 *	0.70 *	0.55	0.55	0.91 *	1.00			
Ba	0.75 *	0.12	0.88 *	0.88 *	0.79 *	0.82 *	0.95 *	0.84 *	1.00		
Pb	0.64 *	−0.03	0.93 *	0.81 *	0.74 *	0.77 *	0.96 *	0.89 *	0.95 *	1.00	
Cr	0.04	0.08	0.78 *	0.37	0.31	0.37	0.61 *	0.79 *	0.52	0.67 *	1.00
SJ (n = 15)											
χ	1.00										
Mn	0.62 *	1.00									
Fe	0.33	0.55	1.00								
Co	0.59	0.82 *	0.60	1.00							
Ni	0.78 *	0.79 *	0.22	0.57	1.00						
Cu	0.68 *	0.94 *	0.50	0.79 *	0.89 *	1.00					
Zn	0.46	0.49	0.02	0.06	0.80 *	0.62 *	1.00				
Cd	−0.07	−0.02	−0.50	−0.26	0.32	0.10	0.60	1.00			
Ba	0.39	0.56	0.77 *	0.56	0.20	0.51	−0.05	−0.44	1.00		
Pb	0.52	0.48	0.13	0.08	0.81 *	0.61 *	0.93 *	0.44	−0.01	1.00	
Cr	0.50	0.48	0.12	0.17	0.84 *	0.62 *	0.90 *	0.55	−0.09	0.94 *	1.00

* Statistically significant results at $p < 0.05$.

According to the Regulation of the Polish Minister of Environment on assessment procedures for the land surface pollution (dated 1 September 2016) [42], the admissible contents of Zn, Cu, Cd, Co, Ni, Pb, Cr and Ba were not exceeded in the studied soils (Table 4). However, compared to the geochemical background values [32,33], some enrichment of metals such as Mn (SJ), Cu (SM, SJ), Zn (SM), Cd (SM) and Pb (SM, SJ) was recorded, which was confirmed by the relatively high values of the contamination factor (CF) and Pollution Load Index (PLI) (Figure 2). As shown in the study of Sutkowska et al. [43] carried out in the historical Solvay soda ash plant area in Jaworzno (southern Poland), the solid post-production waste can be a potential source of Cd, Cr, Ni, Pb and Zn. However, the concentrations of these metals rarely exceeded Polish quality standards. Similar conclusions were formulated by Wiatrowska et al. [44].

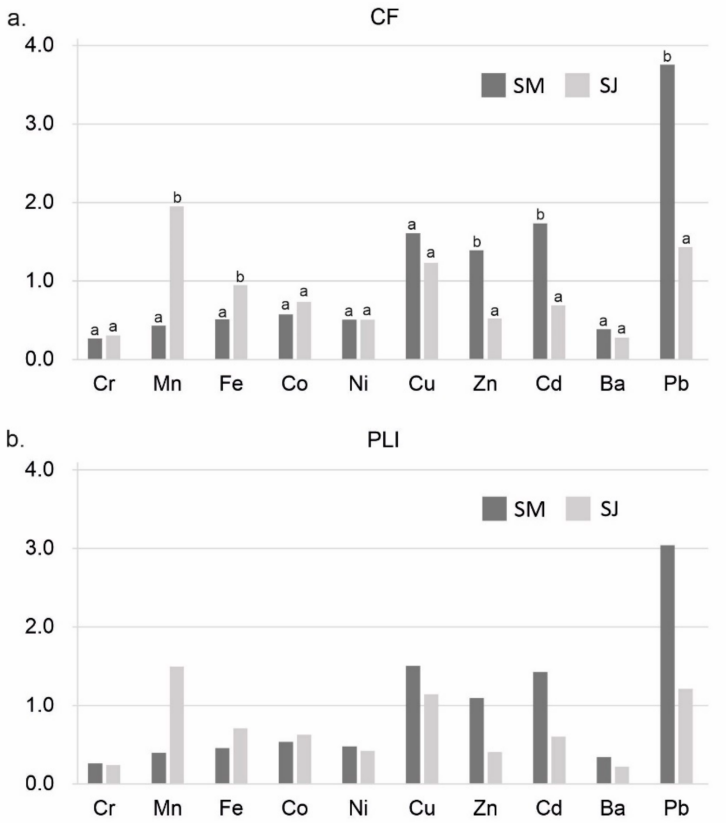


Figure 2. The pollution indices calculated for soil samples from the SM and SJ study sites (mean values): (**a**)—contamination factor (CF), (**b**)—Pollution Load Index (PLI). The significant CF differences between two study sites with $p < 0.05$ are marked by small letters (nonparametric Mann–Whitney U test).

The results of the principal component analysis (PCA) suggested two sources of soil contamination by metals (Figure 3). The first group was related to the impact of soda industry waste resulting in high salinity and accumulation of carbonates in topsoils [20]. The effect of these processes was also the enrichment of soils with metals such as Fe, Mn, Co and Cr. A strong relationship between metals and magnetic susceptibility was observed in the second group. It is highly probable that the source of metals such as Ba, Cd, Cu, Ni, Pb and Zn was coal combustion in the production process and emissions from nearby households.

In the soils from the SM site, a surface deposition of dust containing significant amounts of calcium carbonate and a relatively high content of metals such as Cu, Cd, Pb and Zn was observed, which was related to high values of EF and PLI indices (Figure 2). These observations were consistent with the results of measurements of magnetic susceptibility carried out in the soil cores. In the SM1 profile at a depth of 6 cm, a very high value of low-field magnetic susceptibility (κ) equal to 521×10^{-5} SI was recorded, which proved a very high environmental risk (Figure 4). As reported by Strzyszcz [45], the κ value at a level higher than 30×10^{-5} SI indicated the technogenic contamination of soils. Investigations conducted by Wiatrowska et al. [44] also confirmed that the main source of metals in this area was atmospheric deposition. Similarly, Hulisz et al. [20] described the formation of several centimeter-thick mineral layers on highly saline organic soils due to the eolian transport of mineral material from waste ponds in the SM area. The cause of the magnetic enhancement of soils may also be the supply of metals, especially iron, cobalt, nickel and barium, during high water levels in ditches (Table 2). The values of the low-field magnetic susceptibility (κ) at the SJ site can confirm the deposition of technogenic dusts. It was particularly visible in the SJ2 profile, where at a depth of 3–4 cm the value of κ

exceeded 80 × 10^{-5} SI (Figure 2). Attention should also be paid to the high magnetic enhancement at a depth of 10–15 cm in the SJ1 profile (Figure 4). The relatively high manganese content of 6.8 mg·dm^{-3} in the water sample taken from the ditch (Table 2) and the statistically significant positive correlation between χ and Mn (Table 4) suggested the impact of groundwater.

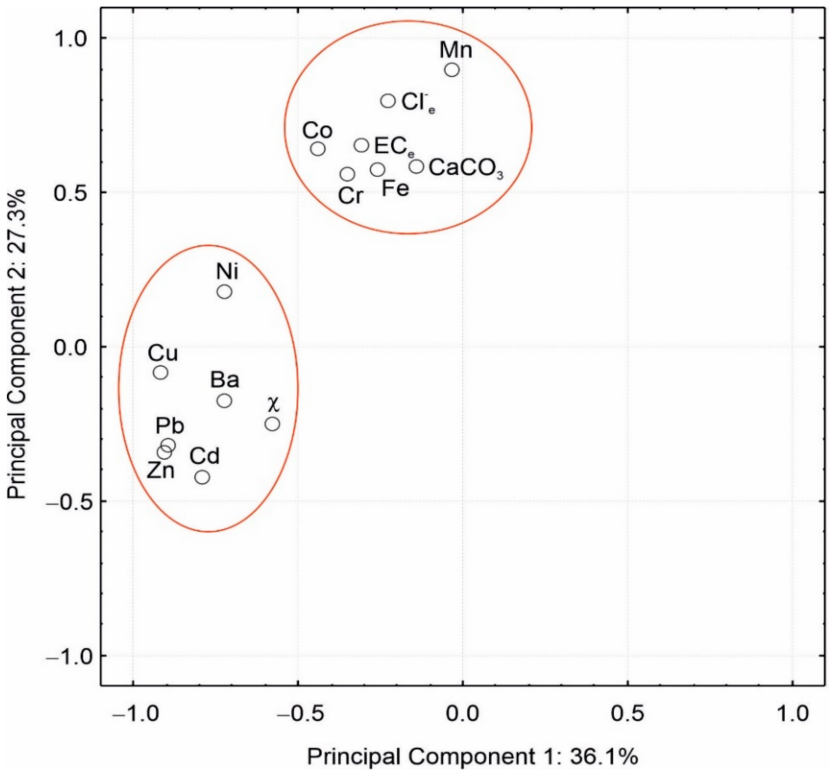


Figure 3. Principal component analysis (PCA) loading plot for selected soil properties (n = 26).

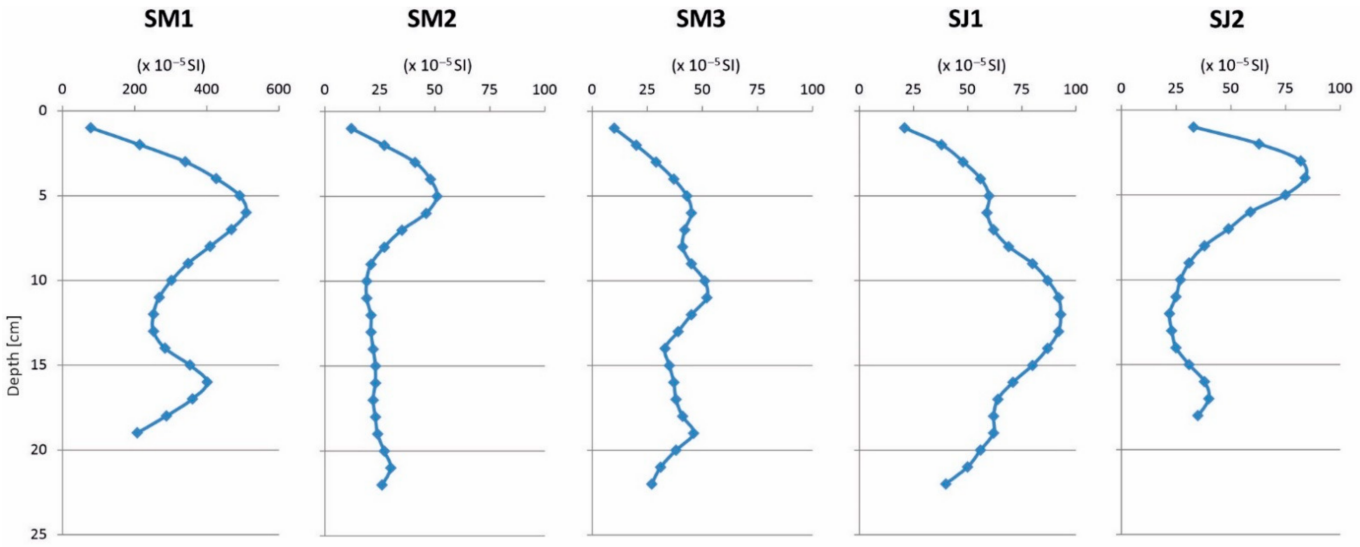


Figure 4. Distribution of volume magnetic susceptibility (κ) in topsoils (0–25 cm) from the study sites: Inowrocław (SM1–SM3) and Janikowo (SJ1–SJ2).

The behavior of metals in highly saline environments is complex. Due to the high pH of the soil material, the mobility of metals is limited [46,47]. On the other hand, studies including those by Sherene [48] and Kadkhodaie et al. [49] have shown that the solubility of

some heavy metals in saline soils, especially Cd and Cu, increases due to the formation of chloride complexes and a decrease in the surface charge density of soil colloids. In addition, there are other mechanisms that control the mobility of Pb, Zn or Cu. These metals and calcium may compete for common absorption sites and form complexes with sulfates [50]. Therefore, it is important to monitor the state of the saline environment, with particular emphasis on the content of heavy metals. As shown in this study, fast and relatively cheap techniques like magnetic susceptibility measurements gain not only valuable data on metal contamination, but they can also provide information about soil development under the strong human impact.

The potential uptake of metals by halophilic plants, reducing their content in the soil, cannot be excluded. Numerous studies indicate the accumulation of heavy metals such as Mn, Cd and Zn, primarily in the roots but also in small amounts in the stems and leaves of halophytes [51,52]. These include *Salicornia europaea* L. and *Tripolium pannonicum* (Jacq.) Dobrocz., which can be used for phytoremediation [22].

4. Conclusions

In the studied soils, the high magnetic enhancement of technogenic origin linked to metals such as Co, Ni, Cu, Zn, Ba, Pb and Mn was observed. The metal content did not exceed the Polish quality standards. It was revealed that the magnetic susceptibility of soils was controlled by direct eolian transport of dust from waste ponds, as well as the influence of highly saline ground and surface waters. Moreover, the effect of atmospheric deposition of coal combustion products is also possible. Statistically significant differences in the content of Cu, Cd, Pb, Fe and Mn were found between the two study sites. This can be explained by the heterogeneity of soil properties associated with strong human impact.

Interpretation of the magnetic parameter measurements in technogenic salt-affected soils can be difficult, e.g., due to their alkalization (high pH values), very high content of calcium carbonate (mainly allochthonous) and an extremely high concentration of easily soluble salts. However, this study shows the high utility of magnetometric techniques in soil research in the context of the diagnosis of soil transformation and contamination during technopedogenesis.

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