



Enzymatic variation of soils exposed to the impact of the soda plant in terms of biochemical parameters

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Abstract

Salinity is the key global problem of the soil environment degradation. The paper demonstrates the results of research of the activity of selected soil enzymes (catalase, dehydrogenase, alkaline and acid phosphatase, rhodanase and arylsulphatase) as well as the content of macroelements (available phosphorus, potassium, magnesium and sulphates sulphur) in terms of the principal physicochemical properties. The soil was located in the vicinity of old sedimentation tanks within the impact of the plant of CIECH Soda Polska S.A (the soda plant) in Inowrocław (Central Poland). Pearson's correlation coefficients were applied to assess the interactions between some physicochemical properties, some macroelements and soil enzyme activities. The results have shown that the soil ECe, P, K, Mg and S contents were changing depending on the soil sampling locations. The soil enzymes did not change significantly with an increase in ECe. The activity of rhodanase differed from the other soil enzymes analysed; that one can be used as an indicator of environmental pollutants produced during chemical industry processes. The result of this study found inconsistent salt-affected soil effects on soil enzyme activity. It remains a challenge to thoroughly delineate effects of salt-affected soil on soil process in general and on biochemical processes in particular, and as a result, the selection of the adequate method of revegetating such soil.

Keywords Alkaline and acid phosphatase · Arylsulphatase · Catalase · Dehydrogenases · Macroelements · Rhodanase · Salt-affected soil

Introduction

Out of many soil-degrading factors, it is saline which is considered to have most impact. Salt-affected soils are a result of an excessive concentration of easily-soluble soils containing cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (Cl^- , NO_3^- , SO_4^{2-} and CO_3^{3-}) (Munns 2002; Rangasamy 2010). The reasons of soil saline can be broken down into natural (impact of salty waters in the coastal belt, migration of ions in the waters neighbouring with natural salt deposits) (Hulisz et al. 2016) and anthropogenic (mining industry, emissions of particulates containing sodium and potassium,

applying artificial fertilizers, waste, sewage) (Hulisz and Piernik 2013). The area of the salinate and sodic soils covers 932.2 Mha globally, in Europe about 30.7 Mha (Rangasamy 2006; Daliakopoulos et al. 2015). An approximate salinate soils area in Poland is about 0.00542 Mha. It changes, however, due to the disappearance of sources, precipitation, land development, changes in use, industrial plants closures, etc. (Hulisz 2007). According to Rangasamy (2006), a high concentration of salt in soil can have a detrimental impact on its physical, chemical and biochemical properties. Due to soil structure destruction, salinated and sodic soils get water- and wind-eroded much more easily. Saline has a negative effect on the health status of plants, inhibits the growth processes, decreases the photosynthesis efficiency, leads to physiological drought. Saline and sodication are abiotic soil factors which pose a serious threat to soil fertility and thus affect soil production (Bhaduri et al. 2016). To understand the soil system ecology, one must know the activity of soil microorganisms and soil enzymes which show a fast reaction to slight changes in soil environment. The parameters were considered to be the indicators potentially applicable

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to evaluate the intensity of land degradation and the spatial development management effectiveness (Singh 2016). The factor increasing the soil saline is a change in soil reaction to more alkaline, which makes mineral nutrients transform into insoluble salts which cannot be uptaken by plants. Limiting or monitoring the salinated soils is crucial for preventing a further soil degradation (Jesus et al. 2015). Garcia and Hernandez (1996), Rietz and Haynes (2003), Yan and Marschner (2012) report on an increase in soil saline having a significant effect on the enzymatic activity of soil and microbial activity. High saline in soils might be one of the two main factors limiting enzyme activities. The soil enzyme activities play an important role in P, and S cycling and are closely related to the biological and chemical properties of soil (Haddad et al. 2015, 2017).

The technogenic soils degraded by soda industry differ in physicochemical properties from natural saline soils. A long-term effect of non-production waste contributes to the formation of very saline soils, rich in chlorides (e.g., NaCl, CaCl₂) (Piernik et al. 2015). With the salt-affected soil sampled from different locations, in spring (May 2013), the primary objectives of the present study were to determine the level of catalase, dehydrogenases, rhodanase, alkaline and acid phosphatase, arylsulphatase activities and its vertical distribution in the impact zone of the Soda Plant and to compare a relative importance of soil saline, as well as available nutrients contents (phosphorus, potassium, magnesium and sulphur) in predicting enzymes activities.

Materials and methods

Description of the study area

The research was conducted in the Notec River Valley, in the area adjacent to the CIECH Soda Polska S.A (soda plant) in Inowrocław. Inowrocław is a town on the Inowrocław Plain in the kujawsko-pomorskie province (52° 40' N; 18° 16' E) (Central Poland), with the culmination of Cechsztyń salt dome. CIECH Soda Polska S.A. produces, e.g., light and heavy soda ash, sodium bicarbonate, calcium chloride, as well as silica gels, and fertilizer chalk. The production process for sodium carbonate uses the ammonia Solvay method, which is related to generating a high amount of waste dominated by CaCO₃ (40%), Ca(OH)₂, CaCl₂ and NaCl. The waste used to be stored in the so-called sedimentation tanks, without adequate safety measures, resulted in the penetration of salt to shallow-deposited ground waters and thus in the salinity of very fertile soils in the adjacent areas. The area shows lowland climate, with some marine climate features. The highest precipitation recorded during the year was noted in summer months, whereas the lowest in winter months, January through March. The area of the Inowrocław Plain

is located in the rain shadow of postlacustrine high grounds in the north-west and records Poland's lowest total annual precipitation, about 500 mm and less. The area is mostly covered with Phaeozems, mostly considered classes II and III of the soil valuation class and the second agricultural soil suitability complex: good wheat complex.

The soil was sampled in spring (May 2013) from four (I–IV) soil test pits in the vicinity of old sedimentation tanks (clarification units) within the plant impact zone (Fig. 1) and the control sample (Control). Soil was sampled from three mineral horizons: 0–20 cm, 20–40 cm and 40–60 cm in three independent replications.

Chemical analysis of soil samples

In the air-dried soil samples with a disturbed structure, sieved through \varnothing 2 mm, some physicochemical properties were determined: total exchangeable bases (TEB) with the Kappen method (Soil Survey Investigation 1996), pH in 1 M KCl measured potentiometrically (ISO 10390), electroconductivity (EC_{1:5}) with the conductometric method in the water–soil suspension at 1:5 (soil-to-water ratio), the property has been considered the measure of saline. The EC_{1:5} value (in water solution) has been converted into EC in soil paste (ECe) according to the formula by Rangasamy (2006): $EC_e = (14.0 - 0.13 * \text{clay}\%) * EC_{1:5}$. The granulometric composition was assayed with the laser diffraction method applying the Mastersizer MS 2000 analyser. The content of available phosphorus (P) was determined with the Egner-Riehm method—DL (PN-R-04023 1996), potassium (K) with the Egner–Riehm method (DL) (PN-R-04022 1996), the content of magnesium available to plants (Mg) following the Schachtschabel method (PN-R-04020 1994) and sulphate sulphur according to the Bardsley–Lancaster method (Bardsley and Lancaster 1960) modified by COMN-IUNG.

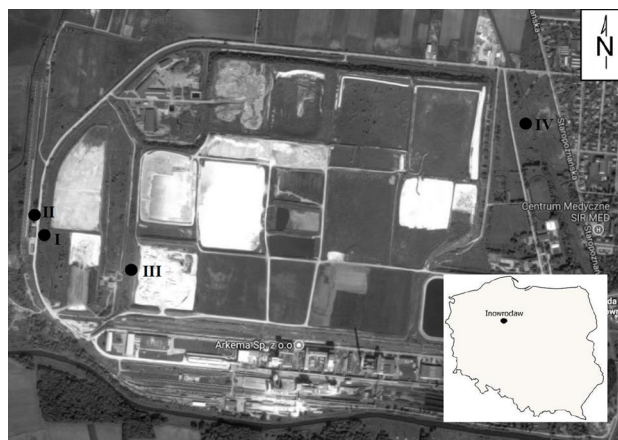


Fig. 1 Location of the study area

Biochemical analysis

Field-moist samples were sieved (2 mm mesh) and stored in a plastic box at 4 °C for not less than 2 days to stabilize the microbial activity and analysed for dehydrogenases, catalase, phosphomonoesterases, rhodanase and arylsulphatase activity within 1 week. The activity of selected redox and hydrolytic enzymes: the activity of dehydrogenases (DEH) [E.C. 1.1.1] in soil was assayed with the Thalmann method (1968), the activity of catalase (CAT) [E.C. 1.11.1.6] in soil with the Johnson and Temple method (1964), the activity of alkaline (AIP) [E.C. 3.1.3.1] and acid (AcP) [E.C. 3.1.3.2] phosphatase with the Tabatabai and Bremner method (1969), arylsulphatase (ARS) [EC 3.1.6.1] (Tabatabai and Bremner 1970) and the activity of alkaline (AcP) [E.C. 3.1.3.1] and acid phosphatases (AcP) [E.C. 3.1.3.2] in soil with the Tabatabai and Bremner method (1969), which facilitated the calculation of the (AIP/AcP) ratio defining the right soil reaction (Dick et al. 2000), based on the enzymatic activities of the samples.

Statistical analysis

The results were exposed to the analysis of variance, and the significance of differences between means was verified with the Tukey test at the significance level of <0.05. The calculations involved the use of one-way ANOVA based on Microsoft Excel. The descriptive statistical analysis, including Pearson's correlation coefficients, involved the use of STATISTICA 7.0 (StatSoft Inc, Tulsa, USA).

Results and discussion

The basic physicochemical properties of soil are given in Table 1, showing the soils alkaline reaction; the values expressed in pH KCl ranged from 7.59 to 8.47 (sampling location within the emitter impact zone), while in controls from 7.78 to 7.90. The study of the samples demonstrated the grain size composition of sand, and the content of clay fraction ranged from 0 to 8%, silt from 1 to 30%, and sand from 67 to 99% (Table 1). According to Corwin and Lesch (2005), the measurement of electrolytic conductivity ($EC_{1:5}$) is the reflection of physical and chemical processes which occur in soil, mostly the changes in the concentration of salts soluble in water. In the soil sampled from the 0–20-cm layer the highest ECe value was recorded in location I (22.89 dS m^{-1}). In the topsoil, there were identified no significant differences between soil saline from location II and the control (Table 2). The highest saline was found in the soil sampled from the 40–60 cm layer. Under moderate climate, where precipitation exceeds evaporation, the topsoil layers get naturally desalinated as a result of rainwater soaking-in with solved salts. The spatial distribution of soil saline resulted from comprehensive anthropogenic effects and some natural factors. The ECe value showed an increase in that parameter with depth in objects I, III and III. Saline in soils varies with depth and changes throughout the season in response to rainfall, surface evaporation, water use by vegetation and the leaching fraction (hydraulic conductivity) of the clay layer (Rangasamy 2010). However, the results reported by Yu et al. (2014) revealed that the saline in topsoil was higher, indicating that salt in subsoil moved

Table 1 Selected physicochemical properties

Sampling	Horizon (cm)	pH KCl	Fractions (%)			Symbol ^a
			Sand	Silt	Clay	
I	0–20	7.59	88	11	1	S
	20–40	8.47	99	1	0	S
	40–60	8.13	88	11	1	S
II	0–20	7.72	89	4	7	S
	20–40	7.82	94	4	2	S
	40–60	7.80	94	5	1	S
III	0–20	7.84	82	15	3	S
	20–40	7.86	81	16	3	S
	40–60	7.70	95	4	1	S
IV	0–20	7.75	68	29	3	SL
	20–40	8.05	67	30	3	SL
	40–60	8.34	88	8	4	S
Control	0–20	7.86	84	11	5	S
	20–40	7.90	78	12	8	S
	40–60	7.78	86	6	8	S

^aS sand, SL sandy loam (USDA 2006)

Table 2 Electrical conductivity (ECe) and total exchangeable bases (TEB)

Sampling	ECe (dS m ⁻¹)			TEB mmol(+) kg ⁻¹		
	0–20 cm	20–40 cm	40–60 cm	0–20 cm	20–40 cm	40–60 cm
I	22.89a±0.053	7.42d±0.078	66.30c±0.218	53.47a±0.028	51.24c±0.057	59.47b±0.565
II	9.42d±0.223	8.11d±0.257	8.88d±0.613	43.58b±1.413	41.44d±0.566	42.69c±2.835
III	21.78c±0.851	58.25a±0.595	122.2b±1.235	53.39a±2.546	58.47b±1.411	64.18a±1.407
IV	20.14b±0.592	54.03b±0.581	470.1a±1.027	53.18a±1.400	61.40a±1.640	66.93a±1.351
Control	8.94d±0.046	18.66c±0.281	3.63e±0.234	31.91c±1.322	30.61e±1.365	28.75d±2.793

Values followed by the same letter are not significantly different at $P < 0.05$

up and accumulated in topsoil as a function of evaporation. The highest TEB (the total exchangeable bases) value was noted in objects III and IV. The lowest TEB values (28.75–31.91 mmol(+) kg⁻¹) were reported in the control profile (Table 2). It was the location with the lowest saline. A positive significant coefficient of correlation between TEB and ECe ($r=0.561$, $P=0.0297$) suggests that the numbers of exchangeable cations in sorption complex depends on soil saline, which is due to an increase in the total sorption capacity of soils rich in easily-soluble salts (Ochman and Jezierski 2011).

With the ANOVA analysis, there was found a significant effect of the soil sampling location on the content of available phosphorus in soil. The significantly highest P content in the 0–20 layer was found in the control sample (79.48 mg kg⁻¹), whereas between locations III and IV no significant difference was found. According to PN-R-04023 (1996), the soil from location I (the 0–20 cm layer) can be classified as class IV with a low phosphorus content assayed with the Egner–Riehm method. The soil from the other locations (II–IV and Control), on the other hand, was classified as III with an average P content. According to Pan et al. (2013), most salined soils are adequately supplied with phosphorus as the concentration of Na⁺ ions may result in more

soluble Na₃PO₄ formed. There was found no dependence between pH, saline, and the content of available phosphorus in soil. However, one can find little evidence in the applicable literature (Lakhdar et al. 2009; Krzyżaniak and Lemaniowicz 2013) that saline, sodicity and pH can affect forms and dynamics of this nutrient in soil, whereas Jaggi et al. (2005) and Hussain and Thomas (2010), on the other hand, found a tendency of a growing phosphorus availability in soil when accompanied by an increased sulphur content, which is due to a change in soil pH, competition between sulphate ions, the products of mineralization of organic forms of phosphorus and a release of aluminium and iron ions which react more with sulphates than with phosphate ions. There were identified significant differences in the content of available potassium and magnesium depending on the soil sampling location. The highest K content in all the horizons was noted in the soil sampled from location IV (an average increase by 207% as compared with the control), while Mg in the soil from location III (a 16-fold content increase, as compared with the control). Both the content of K and Mg were highest in the 0–20 cm horizon.

The content of sulphates in the soils varied a lot. The lowest content of SO₄²⁻ was identified in the soil sampled from the control (Table 3). The content of available

Table 3 Content of selected macroelements

Sampling	0–20 cm	20–40 cm	40–60 cm	0–20 cm	20–40 cm	40–60 cm
	Phosphorus (mg kg ⁻¹)			Potassium (mg kg ⁻¹)		
I	24.56d±1.413	1.340c±0.141	19.03c±1.421	184.0b±5.657	72.25d±2.828	92.53d±1.414
II	52.17c±1.421	61.71a±0.078	20.49c±1.400	69.45d±1.485	60.57e±1.450	53.55e±1.513
III	62.26b±1.344	64.06a±2.864	58.55b±2.220	132.0c±1.414	137.0c±2.828	140.5b±0.707
IV	60.90b±2.828	64.45a±1.485	63.50a±3.253	423.0a±4.243	368.0a±4.247	176.0a±4.241
Control	79.48a±1.082	32.15b±1.909	8.600d±0.424	185.4b±1.343	166.8b±1.348	114.7c±1.342
	Magnesium (mg kg ⁻¹)			Sulphates (VI) (mg kg ⁻¹)		
I	13.18c±1.415	8.59c±0.707	8.23c±0.283	65.25c±0.360	54.98b±0.053	64.45b±0.318
II	23.66b±1.442	13.55b±1.441	10.50b±0.672	10.25d±1.433	4.913d±0.573	5.973c±0.141
III	69.79a±2.143	62.48a±1.563	47.78a±1.131	184.4a±3.207	232.5a±3.150	170.0a±5.155
IV	4.83d±0.064	3.51d±0.566	5.50d±0.658	92.28b±0.315	12.06c±0.007	8.641c±0.141
Control	4.04d±0.049	4.54d±0.665	2.42e±0.587	10.93d±3.097	7.550 cd±0.141	6.141c±0.238



sulphates (< 15 mg kg⁻¹ for light soils with 0–20% of the fraction < 0.02 mm) classifies that soil as the soil with the natural sulphur content. The soil within the impact zone of the Soda Plant differed significantly in the content of sulphates. In soil test pit II, the content of sulphates was lowest of all the profiles under study (4.913–10.25 mg kg⁻¹), while in profile III the highest (170.0 mg kg⁻¹ to 232.5 mg kg⁻¹) (Table 3). Such content (above 35 mg kg⁻¹ for light soils with 0–20% of the fraction < 0.02 mm) classifies that soil as class 3, which points to a heavy pollution of the soil with sulphur as a result of anthropopressure (Motowicka-Terelak and Terelak 1998). In that soil profile, sulphates leached out from the surface layer (0–20 cm) and accumulated in the 20–40 cm horizon. The soda plant production process uses the Solvay ammonia-soda method which resulted in generating a high amount of waste. The average chemical composition of such waste is dominated by CaCO₃ (40%), and most components include Ca(OH)₂ (18%), CaCl₂ (13%) and NaCl (7%) (Koš and Miakota 1988). Cations Ca²⁺, Na⁺ react with

SO₄²⁻ ions and form sulphates, and under dry conditions they can accumulate considerably, which coincides with the results of research demonstrating a significant positive correlation between K content and the total exchangeable bases and the sulphate content ($r=0.757$; $P=0.0011$ as well as $r=0.757$; $P=0.0011$, respectively) (Table 5). With the value of the coefficient of determination (R^2), it was found that as much as 57% of the variation in the content of potassium is due to a variation in sulphates (Table 5).

The activity of the enzymes showed a varied reactivity depending on the soil sampling location (Table 4). Frankenberger and Bingham (1982), who investigated the activity of amidase, urease, acid phosphatase, alkaline phosphatase, phosphodiesterase, inorganic phosphatase, arylsulphatase, rhodanase, α -glucosidase, α -galactosidase, dehydrogenase and catalase of salined soils, have found that the activity of soil enzymes decreased with increasing ECe. The inhibition varied across the enzymes assayed. Dehydrogenase activity was severely inhibited by saline, whereas hydrolases showed

Table 4 Soil enzymes activities

Sampling	0–20 cm	20–40 cm	40–60 cm	0–20 cm	20–40 cm	40–60 cm
	Catalase (mg H ₂ O ₂ kg ⁻¹ h ⁻¹)			Dehydrogenases (mg TPF g ⁻¹ 24 h ⁻¹)		
I	0.009c ± 0.001	0.009b ± 0.002	0.066a ± 0.006	0.030d ± 0.003	0.360a ± 0.014	0.228a ± 0.003
II	0.015c ± 0.003	0.038ab ± 0.003	0.036ab ± 0.004	3.282b ± 0.005	0.342a ± 0.001	0.018a ± 0.001
III	0.106b ± 0.001	0.034b ± 0.003	0.030b ± 0.003	0.501c ± 0.007	0.498a ± 0.011	0.102a ± 0.003
IV	0.077b ± 0.001	0.070a ± 0.003	0.023b ± 0.003	4.260a ± 0.085	0.618a ± 0.011	0.180a ± 0.014
Control	0.178a ± 0.074	0.013b ± 0.001	0.004b ± 0.001	0.858c ± 0.003	0.320a ± 0.014	0.150a ± 0.028
	Alkaline phosphatase (mM pNP kg ⁻¹ h ⁻¹)			Acid phosphatase (mM pNP kg ⁻¹ h ⁻¹)		
I	0.184e ± 0.001	0.049e ± 0.003	0.106e ± 0.004	0.089e ± 0.001	0.051e ± 0.001	0.100e ± 0.007
II	0.853a ± 0.001	0.510c ± 0.007	0.237c ± 0.003	1.571b ± 0.004	0.823b ± 0.005	0.995a ± 0.006
III	0.784b ± 0.006	0.938a ± 0.004	0.288a ± 0.003	1.001d ± 0.001	0.730c ± 0.006	0.227c ± 0.003
IV	0.771c ± 0.001	0.823b ± 0.003	0.272b ± 0.004	2.769a ± 0.006	0.979a ± 0.010	0.213d ± 0.009
Control	0.657d ± 0.003	0.266d ± 0.003	0.116d ± 0.006	1.225c ± 0.006	0.222d ± 0.004	0.403b ± 0.003
	Rhodanase (μM SCN ⁻ g ⁻¹ h ⁻¹)			Arylsulphatase (mM pNP kg ⁻¹ h ⁻¹)		
I	0.294b ± 0.014	0.033b ± 0.001	0.028b ± 0.001	0.442c ± 0.054	0.466b ± 0.007	0.254a ± 0.007
II	0.033c ± 0.001	0.027b ± 0.001	0.026b ± 0.001	1.783b ± 0.006	0.989b ± 0.163	0.451a ± 0.141
III	0.025c ± 0.001	0.049a ± 0.001	0.083a ± 0.001	0.854bc ± 0.027	0.427b ± 0.061	0.322a ± 0.007
IV	0.099a ± 0.001	0.030b ± 0.001	0.021b ± 0.001	3.446a ± 0.108	0.403b ± 0.271	0.245a ± 0.278
Control	0.036c ± 0.001	0.035b ± 0.001	0.026b ± 0.001	1.027b ± 0.097	4.128a ± 0.071	0.331a ± 0.141

Table 5 Relationship between selected soil properties ($n=30$)

Variables		Equation	r	R^2	P
Dependent	Independent				
ECe	TEB	$y=5.3581x-204.54$	0.561	0.314	0.0297
Sulphur	TEB	$y=3.647x-118.6$	0.592	0.351	0.0199
Phosphorus	Alkaline phosphatase	$y=60.550x+17.209$	0.780	0.608	0.0006
Sulphur	Potassium	$y=0.539x-23.888$	0.757	0.573	0.0011
Phosphorus	Catalase	$y=289x+30.696$	0.537	0.288	0.0390

a much lower inhibition. Similarly Pan et al. (2013) reported on the activities of β -glucosidase, alkaline phosphatase and urease decreasing significantly with salinization. According to Ahmad and Khan (1988) and Telesiński (2012), a decrease in the activity of soil enzymes with an increase in saline can be due to changes in the osmotic potential in soil triggered by toxicity of specific ions and the process of salting-out of enzymatic proteins. The present study, however, showed no correlation between the activity of the enzymes and saline. Catalase can enable the toxic H_2O_2 produced during metabolism to decompose, thus preventing its toxic effects on organisms. The activity of catalase significantly depended on the soil sampling location. In the topsoil, the highest activity was recorded in the control soil ($0.178 \text{ mg } H_2O_2 \text{ kg}^{-1} \text{ h}^{-1}$). There was identified, however, no significant difference between CAT in the soil from locations III and IV as well as I and II. In the 20–40-cm layer, the highest activity was recorded in the soil from location IV. Catalase activity was significantly positively correlated with available phosphorus ($r=0.537$; $P=0.0390$) (Table 5). Different results were reported by Guangminga et al. (2017), investigating the activity of enzymes (catalase, alkaline phosphatase and urease) in coastal natural saline soil in China.

The activity of dehydrogenases was changing depending on the depth and the soil sampling location, and it ranged from 0.030 to $4.260 \text{ mg TPF g}^{-1} \text{ 24 h}^{-1}$ (Table 4). In all the soil test pits, except for I, the highest activity of dehydrogenases was reported in the 0–20-cm soil layer. In the 0–30-cm soil surface layer, one can find the highest count of microorganisms, fungi as well as soil fauna. The activity of dehydrogenase considered an indicator of the total microbiological activity (Masciandaro et al. 2001) pointing to the highest biomass of soil microorganisms in that horizon. Only in the soil from location I in the 0–20-cm layer an even ten-fold lower activity of dehydrogenases than in the 20–40-cm layer was identified. A lowered activity of microorganisms in that soil horizon could have been due to a toxic effect of salt on microorganisms (Rietz and Haynes 2003). Saline can have a toxic effect on plants (Wong et al. 2010), which results in a decrease in the content of organic matter in soil, which, in turn, decreases the activity of microorganisms (Singh et al. 2016).

The ANOVA analysis of variance showed a significant effect of the soil sampling location on the activity of phosphomonoesterases (Table 4). The activity of acid phosphatase was higher than the alkaline one. Our result agrees with earlier reports (Siddikee et al. 2011; Lemanowicz and Bartkowiak 2016) showing that alkaline phosphatase activity was not predominant in neutral or alkaline soils. According to Zhang et al. (2014), if the soil pH varies from 7.38 to 10.00, it activates the alkaline phosphatase decrease exponentially. A significant positive correlation was found between the activity of alkaline phosphatase and the content

of available phosphorus ($r=0.780$; $P=0.0006$) in soil. The linear regression equation shows that with an increase in AIP activity by $1 \text{ mM pNP kg}^{-1} \text{ h}^{-1}$, the content of P increased by 60.5 mg kg^{-1} . With the value of the coefficient of determination (R^2), it was found that as much as 61% of the variation in the content of phosphorus is due to the variation in alkaline phosphatase (Table 5). The results confirm that the enzyme can be used as a marker of susceptibility to changes in the content of phosphorus in soil, unlike acid phosphatase for which we have recorded no significant correlations with the content of P. According to Tripathi et al. (2007), phosphatase activity responded more to pH than to the differences in soil saline. Under high pH, the alkaline form predominates. The (AIP/AcP) ratio of the soil falls within the range of 0.48–4.12 (Fig. 2). In most cases, the values exceed 0.50 (Fig. 2), which in the case of the soil analysed was confirmed with the potentiometer method of pH in KCl measurement, which is due to phosphomonoesterases being the enzymes which are one of the most sensitive indicators of changes of soil pH (Dick et al. 2000, Krzyżaniak and Lemanowicz 2013). A significant positive dependence was found between the value (AIP/AcP), and total exchangeable bases ($r=0.474$; $P=0.0478$) which demonstrates that the enzymatic pH indicator (AIP/AcP) of soil can be used as an indicator of the effect of anthropogenic and natural factors.

The activity of arylsulphatase fell within a wide range from 0.245 to $4.128 \text{ mM pNP kg}^{-1} \text{ h}^{-1}$ (Table 4). The highest activity of the enzyme was found in the soil sampled from the control from the depth of 20–40 cm. In the soil sampled from location I from the same depth, the activity of arylsulphatase was 89% lower. Soil test pit IV recorded the highest activity of arylsulphatase ($3.446 \text{ mM pNP kg}^{-1} \text{ h}^{-1}$) in the 0–20 cm layer, while in the 40–60-cm layer—the lowest ($0.245 \text{ mM pNP kg}^{-1} \text{ h}^{-1}$) of all the objects exposed to the effect of the soda plant. Such a low activity of the enzyme in the 40–60-cm horizon was due to “salting-out,”

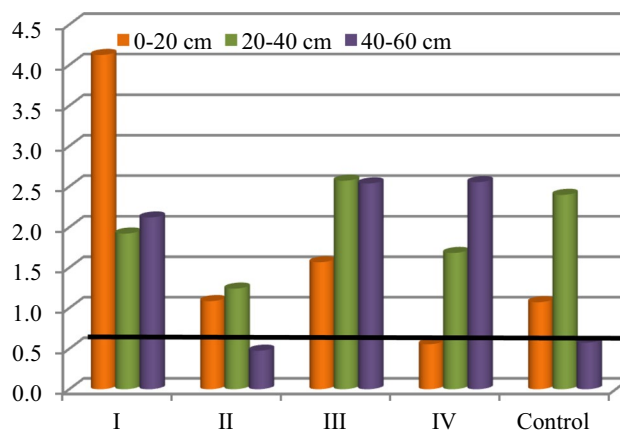


Fig. 2 Enzymatic pH indicator

which is related to a decrease in solubility of the enzyme by dewatering, thus resulting in a change in the structure of the “catalytic place” of the enzyme. According to Garcia and Hernandez (1996), the phenomenon depends on the concentration, type of salt and the chemical composition of the enzyme itself. An excessive concentration of the soil solution resulting in a decrease in water and nutrients availability in that soil layer is confirmed by the highest ECe and TEB value (Table 2). A high activity of arylsulphatase in profile II and IV in the 0–20-cm horizon, on the other hand, can be due to a high microbiological activity since in those layers there was found the highest activity of dehydrogenases (Table 4).

The activity of rhodanase fell within the range from 0.025 to 0.853 $\mu\text{M SCNg}^{-1} \text{h}^{-1}$ and differed from the other soil enzymes analysed. Its highest activity was identified in profile I in which the other enzymes showed the lowest activity (Table 4). Rhodanase is a multifunctional, mitochondrial, sulphur transferase that catalyses the detoxification of cyanide by sulphuration in a double displacement mechanistic reaction. Cyanide is one of the major environmental pollutants produced during certain processes of the chemical and metallurgical industries like steel, electroplating, mining and chemical synthesis (Bhat et al. 2015). Cyanide is a potent cytotoxic agent which kills the cell by inhibiting cytochrome oxidase of the mitochondrial electron transport chain (Saidu 2004). The results suggest that the enzyme can be used as an indicator of environmental pollutants produced during chemical processes.

Conclusion

The present research has shown no one-way changes in the activity of catalase, dehydrogenases, alkaline and acid phosphatase, rhodanase and arylsulphatase and macroelements (P, K, Mg, S) in technogenic soil. The results suggest that the content of macroelements and the activity of the study enzymes differed from naturally saline soils.

The present research did not confirm the results reported by numerous authors (Rietz and Haynes 2003; Siddikee et al. 2011; Telesiński 2012; Guangminga et al. 2017) demonstrating that a high saline decreased the enzymatic activity of the soils.

Further long-term soil research around the plant must be performed to select the adequate revegetation (e.g., phytoremediation) of those soils since changes in the activity of soil enzymes definitely depend on humidity, temperature which often overlap with the consequences of anthropogenic factors.

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References

- Ahmad I, Khan KM (1988) Studies of enzymes activity in normal and saline soils. *Pakistan J Agric Res* 9(4):506–508
- Bardsley CE, Lancaster JD (1960) Determination of reserve sulfur and soluble sulfates in soil. *Soil Sci Soc Am Proc* 24:265–268. <https://doi.org/10.2136/sssaj1960.03615995002400040015x>
- Bhaduri D, Meena HN, Chakraborty K (2016) Variation in phosphorus accumulation in groundnut cultivars as influenced by water salinity. *Legume Res* 39(2):215–220. <https://doi.org/10.18805/lr.v0iOF.6788>
- Bhat A, Riyaz-Ul-Hassan S, Srivastava N, Johri S (2015) Molecular cloning of rhodanase gene from soil metagenome of cold desert of North-West Himalayas: sequence and structural features of the rhodanase enzyme. 3. *Biotech* 5(4):513–521. <https://doi.org/10.1007/s13205-014-0249-2>
- Corwin DL, Lesch SM (2005) Apparent soil electrical conductivity measurements in agriculture. *Comput Electron Agric* 46:1–3. <https://doi.org/10.1016/j.compag.2004.10.005>
- Daliakopoulos IN, Tsanis IK, Koutroulis A, Kourgiyalas NN, Varouchakis AE, Karatzas GP, Ritsema CJ (2015) The threat of soil salinity: a European scale review. *Sci Total Environ* 573:727–739. <https://doi.org/10.1016/j.scitotenv.2016.08.177>
- Dick WA, Cheng L, Wang P (2000) Soil acid and alkaline phosphatase activity as pH adjustment indicators. *Soil Biol Biochem* 32(13):1915–1919. [https://doi.org/10.1016/S0038-0717\(00\)00166-8](https://doi.org/10.1016/S0038-0717(00)00166-8)
- Frankenberger WT Jr, Bingham FT (1982) Influence of salinity on soil enzyme activities. *Soil Sci Soc Am* 46:1173–1177. <https://doi.org/10.2136/sssaj1982.03615995004600060011x>
- Garcia C, Hernandez T (1996) Influence of salinity on the biological and biochemical activity of a calcithid soil. *Plant Soil* 178:255–263. <https://doi.org/10.1080/00103624.2011.542226>
- Guangminga L, Xuechena Z, Xiupingc W, Hongbob S, Jingsongya Y, Xiangping W (2017) Soil enzymes as indicators of saline soil fertility under various soil amendments. *Agric Ecosyst Environ* 237:274–279. <https://doi.org/10.1016/j.agee.2017.01.004>
- Haddad SA, Tabatabai MA, Abdel-Moneim AMA, Loynachan TE (2015) Inhibition of nodulation and nitrogen nutrition of leguminous crops by selected heavy metals. *Air Soil Water Res* 8:1–7
- Haddad SA, Tabatabai MA, Loynachan TE (2017) Effects of liming and selected heavy metals on ammonium release in waterlogged agricultural soils. *Biol Fertil Soils* 53(2):153–158. <https://doi.org/10.1007/s00374-016-1163-z>
- Hulisz P (2007) Proposals of systematics of polish salt-affected soils. *Soil Sci Ann* 58(1/2):121–129
- Hulisz P, Piernik A (2013) Soils affected by soda industry in Inowrocław. In: Charzyński P, Hulisz P, Bednarek R (eds.) *Technogenic soils of Poland*. Polish Society of Soil Science, Toruń, pp 125–140 (2007) Selected aspects research of salt-affected soils in Poland. SOP, Toruń, 40



- Hulisz P, Piernik A, Mantilla-Contreras J, Elvisto T (2016) Main driving factors for seacoast vegetation in the southern and eastern Baltic. *Wetlands* 36:909–919. <https://doi.org/10.1007/s13157-016-0803-2>
- Hussain SS, Thomas T (2010) Effect of nitrogen and sulphur on yield, mineral accumulation and protein content of sunflower (*Helianthus annuus* L.) in Inceptisol. *Res J Agric Sci* 1:89–92. <https://doi.org/10.5897/SRE2013.5618>
- Jaggi RC, Aulakh MS, Sharma R (2005) Impacts of elemental S applied under various temperature and moisture regimes on pH and available P in acidic, neutral and alkaline soils. *Biol Fertil Soils* 41(1):52–58. <https://doi.org/10.1007/s00374-004-0792-9>
- Jesus JM, Danko AS, Fiúza A, Borges MT (2015) Phytoremediation of salt-affected soils: a review of processes, applicability, and the impact of climate change. *Environ Sci Pollut Res* 22:6511–6525. <https://doi.org/10.1007/s11356-015-4205-4>
- Johnson JL, Temple KL (1964) Some variables affecting the measurements of catalase activity in soil. *Soil Sci Soc Am* 28(2):207–209. <https://doi.org/10.2136/sssaj1964.03615995002800020024x>
- Koś R, Miakota B (1988) Utylizacja odpadów stałych na nawozy wapniowe w IZCH. Międzynarodowe Sympozjum Przemysłu Sodego. Toruń: 230–237
- Krzyżaniak M, Lemanowicz J (2013) Enzymatic activity of the Kuyavia Mollic Gleysols (Poland) against their chemical properties. *Plant Soil Environ* 59(8):359–365
- Lakhdar A, Rabhi M, Ghnaya T, Montemurro F, Jedidi N, Abdely Ch (2009) Effectiveness of compost use in salt-affected soil. *J Hazard Mater* 171:29–37. <https://doi.org/10.1016/j.jhazmat.2009.05.132>
- Lemanowicz J, Bartkowiak A (2016) Changes in the activity of phosphatase and the content of phosphorus in salt-affected soils grassland habitat Natura 2000. *Polish J Soil Sci* 49(2):149–165. <https://doi.org/10.17951/pjss/2016.49.2.149>
- Masciandaro G, Ceccanti B, Benedicto S, Lee H (2001) Humic substances to reduce salt effect on plant germination and growth. *Commun Soil Sci Plant Anal* 33:3–4. <https://doi.org/10.1081/CSS-120002751>
- Motowicka-Terelak T, Terelak H (1998) Sulphur in soils of Poland—the status and the risks (in Polish, English summary). *Bibl Monit Środ Pios*, Warszawa
- Munns R (2002) Comparative physiology of salt and water stress. *Plant, Cell Environ* 25(2):239–250. <https://doi.org/10.1046/j.0016-8025.2001.00808.x>
- Ochman D, Jezierski P (2011) Impact of sedimentation waters on the soils absorbing complex in the region of „Żelazny Most” tailings impoundment. *Environ Protect Nat Res* 49:268–277
- Pan Ch, Liu Ch, Zhao H, Wang Y (2013) Changes of soil physicochemical properties and enzyme activities in relation to grassland salinization. *Eur J Soil Biol* 55:13–19. <https://doi.org/10.1016/j.ejsobi.2012.09.009>
- Piernik A, Hulisz P, Rokicka A (2015) Micropattern of halophytic vegetation on technogenic soils affected by the soda industry. *Soil Sci Plant Nutri* 61:98–112. <https://doi.org/10.1080/00380768.2015.1028874>
- PN-R-04020 (1994) Chemical and agricultural analysis. Determination of the content available magnesium. Polish Standards Committee, Warszawa. PKN
- PN-R-04022 (1996) Chemical and agricultural analysis – Determination of the content available potassium in mineral soils. Polish Standards Committee, Warszawa. PKN
- PN-R-04023 (1996) Chemical and agricultural analysis—determination of the content of available phosphorus in mineral soils. Polish Standards Committee, Warszawa. PKN
- Rangasamy P (2006) Soil salinity and sodicity. In: Stevens D, Kelly J, McLaughlin M, Unkovich M (eds) *Growing crops with reclaimed wastewater*. CSIRO Publishing, Collingwood, pp 125–138
- Rangasamy P (2010) Soil processes affecting crop production in salt-affected soils. *Funct Plant Biol* 37:613–620. <https://doi.org/10.1071/FP09249>
- Rietz DN, Haynes RJ (2003) Effects of irrigation-induced salinity and sodicity on soil microbial activity. *Soil Biol Biochem* 35:845–854. [https://doi.org/10.1016/S0038-0717\(03\)00125-1](https://doi.org/10.1016/S0038-0717(03)00125-1)
- Saidu Y (2004) Physicochemical features of rhodanese: a review. *Afr J Biotechnol* 3(4):370–374. <https://doi.org/10.5897/AJB2004.000-2071>
- Siddikee MA, Tipayno SC, Kim K, Chung J, Sa T (2011) Influence of varying degree of salinity-sodicity stress on enzyme activities and bacterial populations of coastal soils of Yellow Sea, South Korea. *J Microbiol Biotech* 21:341–346. <https://doi.org/10.4014/jmb.1012.12015>
- Singh K (2016) Microbial and enzyme activities of saline and sodic soils. *Land Degrad Dev* 27(3):706–718. <https://doi.org/10.1002/ldr.2385>
- Singh K, Trivedi P, Singh G, Singh B, Patra DD (2016) Effect of different leaf litters on car-5 bon, nitrogen and microbial activities of sodic soils. *Land Degrad Dev* 27:1215–1226. <https://doi.org/10.1002/ldr.2313>
- Soil Survey Laboratory Methods Manual (1996) Soil survey investigation report. USA. 42
- Tabatabai MA, Bremner JM (1969) Use of p-nitrophenol phosphate for assay of soil phosphatase activity. *Soil Biol Biochem* 1:301–307. [https://doi.org/10.1016/0038-0717\(69\)90012-1](https://doi.org/10.1016/0038-0717(69)90012-1)
- Tabatabai MA, Bremner JM (1970) Factors affecting soil arylsulfatase activity. *Soil Sci Soc Am Proc* 34:427. <https://doi.org/10.2136/sssaj1970.03615995003400030023x>
- Telesiński A (2012) The effect of salinity on some biochemical indices of soil fertility. *Water Environ Rural Areas* 12(1):209–217
- Thalman A (1968) Zur methodic derestimung der Dehydrogenaseaktivität und Boden mittels Triphenyltetrazoliumchlorid (TTC). *Landwirtschaft Forschung* 21:249
- Tripathi S, Chakraborty A, Chakraborti K, Bandyopadhyay BK (2007) Enzyme activities and microbial biomass in coastal soils of India. *Soil Biol Biochem* 39:2840–2848. <https://doi.org/10.1016/j.soilbio.2007.05.027>
- USDA (2006) Keys to soil taxonomy, 10th edn. United States Department of Agriculture, Natural Resources Conservation Service, Washington, D.C., pp 1–332
- Wong VNL, Greene RSB, Dalal RC, Murphy BW (2010) Soil carbon dynamics in saline and sodic soils: a review. *Soil Use Manag* 26:2–11. <https://doi.org/10.1111/j.1475-2743.2009.00251.x>
- Yan N, Marschner P (2012) Microbial activity and biomass recover rapidly after leaching of saline soils. *Biol Fertil Soils* 49:367–371. <https://doi.org/10.1007/s00374-012-0733-y>
- Yu JB, Li YZ, Han GX, Zhou D, Fu YQ, Guan B, Wang GM, Ning K, Wu HF, Wang JH (2014) The spatial distribution characteristics of soil salinity in coastal zone of the Yellow River Delta. *Environ Earth Sci* 72(2):589–599. <https://doi.org/10.1007/s12665-013-2980-0>
- Zhang TB, Kang Y, Liu SH, Liu SP (2014) Alkaline phosphatase activity and its relationship to soil properties in a saline-sodic soil reclaimed by cropping wolfberry (*Lycium barbarum* L.) with drip irrigation. *Paddy Water Environ*, 12:309–317. <https://doi.org/10.1007/s10333-013-0384-0>

