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# Variability of edaphic parameters in the area affected by a municipal waste landfill\*\*

Agata Bartkowiak<sup>1</sup><sup>1</sup>, Piotr Hulisz<sup>2</sup>, Joanna Lemanowicz<sup>3</sup>, Barbara Kalisz<sup>4</sup>

<sup>1</sup>Department of Soil Science and Soil Protection, Bydgoszcz University of Science and Technology, Bernardyńska 6,

85-029 Bydgoszcz, Poland

<sup>2</sup>Department of Soil Science and Landscape Ecology, Nicolaus Copernicus University in Toruń, Lwowska 1,

87-100 Toruń, Poland

<sup>3</sup>Department of Biogeochemistry and Soil Science, Bydgoszcz University of Science and Technology, Bernardyńska 6,

85-029 Bydgoszcz, Poland

<sup>4</sup>Department of Soil Science and Microbiology, University of Warmia and Mazury in Olsztyn, Plac Łódzki 3, 10-727 Olsztyn, Poland

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Abstract. Monitoring the soil quality in municipal landfill sites is critical. It poses challenges because of the diversity of municipal waste, soil properties, and hydrogeological conditions at a landfill. This study aimed to assess the variability of soil properties in the zone of impact of a municipal waste landfill in the city of Bydgoszcz (Poland, Central Europe). The soil material was taken from ten sampling points, including the control sample located in a nearby forest that was not influenced by the municipal waste landfill. The basic physicochemical properties of soils, the content of selected heavy metals and enzymatic activities were determined. To evaluate the risk resulting from the toxicity of heavy metals in the soils, the contamination factor (CF), enrichment factor (EF), Nemerow's pollution index (PN) and pollutant load index (PLI) were calculated. Additionally, the soil quality indices, *i.e.* the geometric mean of enzyme activities (GMea), total enzyme activity index (TEI), and metabolic activity index (MAI), were calculated. The study showed that the heavy metal content in the soils was acceptable, with the following order of concentration: Cd < Pb < Ni < Cu < Cr < Zn. Some enrichment was noted and the enzymatic analysis indicated that anthropogenic activities significantly influenced the activity of soil dehydrogenases and phosphatases. The findings highlight the complexity of soil dynamics in such areas and emphasise the importance of long-term monitoring.

K e y w o r d s: heavy metals, oxidoreductive enzymes, technogenic soils, soil quality

# **1. INTRODUCTION**

For many countries, municipal solid waste management is a challenge exacerbated by population growth, while waste is a part of every urban landscape. Waste is inherently generated by human economic activity, and waste management is a problem for all societies and economies. For cost reasons, the deposition of untreated mixed municipal solid waste in landfills is a popular waste disposal method in most countries (Madon et al., 2019). Under Art. 3 section 1 of the Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste, waste should be understood as any substance or object that its owner rejects, intends to dispose of, or is required to dispose of (Directive 2008/98/European Parliament and Council, 2018). Landfills are, therefore, the main place where solid waste is disposed of, which results in severe environmental pollution and the spread of diseases (Bakis and Tuncan, 2011; Vongdala et al., 2018). The spread of many pollutants, mainly due to solid waste disposal in insufficiently secured facilities, puts significant pressure on the environment because some pollutants are very toxic and dangerous to all life forms. Environmental pollution by heavy metals is one of the most hazardous contamination elements and is particularly dangerous to human health. Urban solid waste landfills are a potential source of the heavy-metal contamination of groundwater, soil and plants (Prechthai, 2008; Xie et al., 2015; Gworek et al., 2016; Makuleke

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<sup>\*</sup>Corresponding author e-mail: bartkowiak@utp.edu.pl

<sup>\*\*</sup>Bydgoszcz University of Science and Technology, Faculty of Agriculture and Biotechnology, Laboratory of Soil Science and Biochemistry (grant BN-WRiB-2/2022). University of Warmia and Mazury in Olsztyn. Faculty of Agriculture and Forestry, Department of Soil Science and Microbiology (grant 30.610.005-110). Nicolaus Copernicus University in Toruń (1752/2020 IDUB Urban Soil Environment).

and Ngole-Jeme, 2020; Kekelidze *et al.*, 2022). Therefore, numerous engineering measures have been taken to limit the spread of contaminants from landfills, such as using liners, covers, leachate systems and vertical barriers (Othman *et al.*, 2010; Koda *et al.*, 2013).

Heavy metals remain key contaminants in municipal waste due to their harmfulness and behaviour associated with leaching. The literature contains many publications on identifying heavy-metal contamination in landfill soils (e.g., Liu and Sang, 2010; Ishchenko, 2019; Baziene et al., 2020; Yaashikaa et al., 2022; Wang et al., 2022). Soil contamination by metals is often assessed alongside an analysis of enzymatic activity (Bartkowiak et al., 2017; Lemanowicz, 2019; Lemanowicz et al., 2020). Soil enzymes are good indices of changes in soil impacted by natural and anthropogenic factors (Gil-Sotres et al., 2005; Lemanowicz et al., 2023a, b). Enzymatic tests provide quantitative information on the functional diversity of microbial activity, soil chemical processes, soil mineralisation rates and organic matter accumulation (Zouboulis et al., 2001). Soil quality can be determined by measuring individual enzymes or using complex equations with mathematical combinations (Gil-Sotres et al., 2005).

The aim of this study was to examine the impact of the municipal waste landfill in Bydgoszcz (northern Poland) on the variability of physicochemical, chemical, and enzymatic parameters of soils. The results were used to assess the soil quality based on such indices as contamination factor (CF), enrichment factor (EF), pollutant load index (PLI), Nemerow's pollution index (PN), the geometric mean of enzyme activities (GMea), total enzyme activity index (TEI), and metabolic activity index (MAI). Due to the heterogeneity of municipal waste, the continuous overlaying of new waste on the landfill, the possibility for waste to be moved around within the landfill, the original soil properties and the prevailing hydrogeological conditions at the landfill, it may be difficult to clearly determine the factors influencing the concentration of heavy metals in landfill soils and the migration of these metals to surface water and groundwater (Oman and Junested, 2008; Makuleke and Ngole-Jeme, 2020; Kekelidze et al., 2022; Elanga et al., 2022). Considering these facts, it was also assumed that the variability of the properties of the tested soils might be largely dependent on conditions occurring locally at the landfill. This research complements and develops past research on issues regarding the impact that landfills have on seasonal changes in the content of macro- and micronutrients against the background of soil biological activity (Lemanowicz et al., 2023a).

# 2. MATERIALS AND METHODS

# 2.1. Study area

The investigated waste landfill is located about 14 km southeast of the centre of Bydgoszcz (53°03'N; 18°08'E; Fig. 1). The landfill is located on the premises of a waste management plant and is the most significant modern controlled landfill in Bydgoszcz and the entire Kuyavian-Pomeranian Voivodeship. The waste deposited at the landfill is mainly mixed directly with household waste (Lemanowicz et al., 2023a). The landfill is classified as a landfill for non-hazardous and neutral waste. This is due to its location, operation and expected method of sealing, which considers the natural and geological conditions of the designated area and the control system. The landfill bottom is sealed with PVC foil, fitted with a drainage system, and equipped in accordance with environmental protection requirements. The inflow of rainwater and leachate polluting groundwater and the spread of gas from the landfill to the air have been reduced, and the surrounding area has been protected against the spread of dust and pathogenic bacteria and fungi, all as part of a project carried out at the landfill and co-financed by the EU. Most of the waste admitted to the landfill, as much as 65.4%, is unsegregated (mixed) municipal waste originating from households and directly related to non-industrial human activity. There are three landfills on the premises, including two reclaimed landfills (in operation from 1985 to 2003) and one currently in operation (Lemanowicz et al., 2023a).

The original soils within the landfill are Brunic Arenosols (http://mapy.infoteren.pl/glebowe/; IUSS Working Group WRB, 2022). They developed from sandy materials underlain by clays in the central and southwestern sections (below 1 m b.g.l.). The soil cover in the research areas outside the landfill area was similar.

# 2.2. Fieldwork

Before starting the research, the area in and around the landfill was investigated. Based on the on-site visit and interview with the facility manager, eight soil sampling points were randomly selected within the landfill (S1-S8): S1 - by the pumping station at a closed sector (53°03'48.34"N, 18°07'54.16"E); S2 - in a closed-off sector (53°03'48.11"N, 18°07'47.92"E); S3 - near the leachate outflow from a closed-off sector (53°03'47.74"N, 18°07'50.46"'E); S4 – waste landfill near the active sector (landfill basin) (53°03'34.81"N, 18°08'06.68"E), S5 - 5 m from the active sector basin (53°03'37.20"N, 18°08'07.95"'E); S6 - 10 m from the active sector  $(53^{\circ}03'39.99"N, 18^{\circ}08'09.04" E); S7 - 50 m$  from the active sector (53°03'44.17"N, 18°08'10.95"E) and S8 areas adjacent to the plant perimeter fence (53°03'45.28"N, 18°08'12.98"'E). The two remaining research sites were designated in areas outside the landfill (Fig. 1). Site S9 was located within a field with a maize monoculture



**Fig. 1.** Location of the study area and sampling points. C – control site outside the landfill's zone of impact, S1 – by the pumping station at a closed sector, S2 – in a closed-off sector, S3 – near the leachate outflow from a closed-off sector, S4 – waste landfill near the active sector (landfill basin), S5 – 5 m from active sector basin, S6 – 10 m from the active sector, S7 – 50 m from the active sector, S8 – areas adjacent to the plant perimeter fence, S9 – arable field with a maize monoculture.

 $(53^{\circ}03'50.77"N; 18^{\circ}08'16.52"E)$ . The control site (C) was located in a forest area outside the protection zone, about 1000 m from the edge of the landfill and outside the zone of impact of leachates  $(53^{\circ}03'27.25"N; 18^{\circ}08'39.65"E)$  (Lemanowicz *et al.*, 2023a).

To better reflect the local variability of environmental conditions in individual landfill sectors, soil samples were collected in two series: I (spring) and II (autumn) of 2018. The second sampling (series II – autumn 2018) was performed analogously to the first date. Samples were taken from the topsoils at 0-20 cm depth. Each average sample consisted of 10 primary samples taken from a square of 4 m<sup>2</sup>.

# 2.3. Laboratory analysis

The soil samples were air-dried, homogenised and sieved through a 2-mm mesh. The following properties were determined:

 grain-size composition with the laser method using the Mastersizer MS 2000 particle analyser (Malvern Instruments, Malvern, UK). Based on established percentages of granulometric fractions, the granulometric group and subgroup were established according to the USDA classification (2022); pH in 1M CaCl<sub>2</sub> potentiometrically using a CPC-551
 pH meter (PN-ISO 10390;1997);

- total organic carbon (TOC) and total nitrogen (TN) using a multi-N/C 3100 analyser (Analytik, Jena, Germany);

– hydrolytic acidity (Hh) and total exchangeable base cations (TEB) using the Kappen method. Using TEB and Hh, the cation exchange capacity (CEC) was calculated, and the sorption complex's degree of saturation with bases (BS) was calculated from CEC and TEB;

– soil salinity analysis using 1:5 soil–water extracts (van Reeuwijk, 2002). The following properties were determined: electrical conductivity (EC<sub>1:5</sub>) with the conductometric method, chloride ion concentration (Cl<sup>-</sup>) using the argentometric method, and sulphate ion concentration (SO<sub>4</sub><sup>2-</sup>) with the turbidimetric method using a Rayleigh UV-1601 spectrophotometer;

– the content of total forms of selected heavy metals (Zn, Cu, Pb, Ni, Cd, Cr) after prior mineralisation in 65% HNO<sub>3</sub> in an Ultrawave Milestone microwave mineraliser using an iCAP 7400 ICP-OES spectrophotometer (Thermo Stientific, USA). The factory performance test using defined certified standards (ICAP Series Multi-Element Test Solution, No. 430122821401, Thermo Scientific) was run before and in the middle of the analysis.

The activity of selected enzymes from the oxidoreductase class was tested in fresh-sieved ( $\phi < 2 \text{ mm}$ ) soils stored at 4°C for two weeks. Each activity was assayed in triplicate. The activity of dehydrogenases (DEH) [EC 1.1.1] in the soil was determined with the Thalmann method (1968) after sample incubation with 2,3,5-triphenyl tetrazolium chloride and measurement of triphenyl formazan (TPF) absorbance at 546 nm and expressed in mg TPF  $kg^{-1}$ 24 h<sup>-1</sup>. The catalase activity (CAT) [EC 1.11.1.6] was determined using the method of Johnson and Temple (1964) with a 0.3% hydrogen peroxide solution as a substrate. The remaining  $H_2O_2$  was determined by titration with 0.02M KMnO<sub>4</sub> under acidic conditions. The activity of peroxidases (PER) [EC 1.11.17] was determined according to Bartha and Bordeleau (1969) by measuring the amount of purpurogallin (PPG) produced by oxidation of pyrogallol in the presence of  $H_2O_2$ .

# 2.4. Soil quality indices

Due to the expected significant impact of anthropogenic transformations, the soils were also assessed using the percentage enrichment factor (*EF*) determined by Zonta *et al.* (1994) and Loska and Wiechuła (2003), according to the formula:

$$\% EF = \frac{C - Cmin}{Cmax - Cmin} 100,$$
(1)

where: C – average concentration in the soil, Cmin – minimum concentration, Cmax – maximum concentration.

The *EF* index can be used to distinguish an anthropogenic source from a natural one. Based on the enrichment factor, five categories of impurities are recognised, where EF<2 means deficiency to minimal enrichment, EF 2-5 is moderate enrichment, EF 5-20 is significant enrichment, EF 20-40 is very high enrichment, and EF>40 is extremely high enrichment (Sutherland *et al.*, 2000).

To determine the degree of heavy-metal contamination of the soil in the landfill, the heavy-metal contamination factor (*CF*) was calculated for each of the analysed heavy metals using Eq. (1) and according to the recommendations of Hakanson (1980) and Ngole-Jeme (2016):

$$CF = \frac{Cm \, sample}{Cm \, backgroud} \,, \tag{2}$$

where: *Cm sample* is the concentration of the metal in the soil from the landfill, and *Cm background* is the concentration of the same heavy metal in the background samples (which in this case was a sample from the control point).

According to Sutherland *et al.* (2000), heavy metal values of CF < 1 refer to low contamination,  $1 \le CF < 3$  indicates moderate contamination,  $3 \le CF \le 6$  indicates significant contamination, and CF > 6 indicates very high contamination.

The pollutant load index (*PLI*), which indicates the degree of soil contamination with heavy metals, was also calculated to determine which site was most contaminated regarding all the heavy metals analysed (Al-Juboury, 2009). Pollution load index values of <1 indicate no pollution, while values of >1 indicate pollution (Seshan *et al.*, 2010). The *PLI* for each site was calculated according to Seshan *et al.* (2010) and Tomlinson *et al.* (1980), as shown in the following equation:

$$PLI = n\sqrt{CF_{Zn} CF_{Cu} CF_{Pb} CF_{Ni} CF_{Cd} CF_{Cr}}, \qquad (3)$$

where: CF is the contamination factor, and n is the number of elements, which in this study was 6.

In the case of *PLI*, there are four categories: low contamination (*PLI* $\leq$ 1), moderate contamination (1<*PLI* $\leq$ 2), high contamination (2<*PLI* $\leq$ 5), and very high contamination (*PLI*>5).

Nemerow's pollution index (*PN*) is a multi-factor environmental quality indicator considering extreme values, especially the most polluting factors. *PN* describes the integrated pollution level in the study area and is calculated as follows (Huang *et al.*, 2018; Martínez-Guijarro *et al.*, 2019):

$$PN = \sqrt{\frac{(CF)^2 max + (CF)^2 mean}{2}},$$
 (4)

where: CF(max) and CF(mean) are, respectively, the maximum and average CF values for all target heavy-metal elements. The degree of heavy-metal contamination is classified according to the following criteria: safe ( $PN \le 0.7$ ), warning ( $0.7 < PN \le 1$ ), light contamination ( $1 < PN \le 2$ ), moderate contamination ( $2 < PN \le 3$ ) and heavy contamination (PN > 3).

The following indices were calculated based on enzyme activity:

The geometric mean GMea (Hinojosa et al., 2004) is given by:

$$GMea = \sqrt[3]{DEH CAT PER}, \qquad (5)$$

where: *DEH*, *CAT*, and *PER* are dehydrogenases, catalase, and peroxidase.

To determine the total level of soil enzyme activity, the total enzyme activity index (*TEI*) was calculated (Tan *et al.*, 2014) as:

$$TEI = \sum \frac{Xi}{Xi}, \tag{6}$$

where *xi* is the activity of soil enzyme *i* and is the mean activity of enzyme *i* in all samples.

The metabolic activity index (*MAI*) (Picariello *et al.*, 2021) of the soil was also calculated as:

$$MAI = \sum \frac{Pij}{Pcij},\tag{7}$$

where:  $P_{ij} = \frac{A_{ij}}{Ref_j}$ ,  $Pc_{ij} = \frac{Ac_{ij}}{Refc_j}$ , Aij is the value of the activity of each enzyme, Refj is the reference parameter TOC, Acij is the value of the activity of each enzyme in the control soil, and  $Refc_j$  is the reference parameter in the control soil.

#### 2.5. Statistical analysis

The measurement data on soil physical and chemical properties and enzymatic activity were analysed using one-way ANOVA. The mean-variance for objects was determined by identifying homogeneous groups based on the LSD test with a significance level of  $\alpha = 0.05$ . The research factor was spatial – the place from which soil samples were taken for the analysis. The results are expressed as an arithmetic mean and standard deviation (SD). The statistical analysis was performed using the Statistica.PL 13.3 package (2019).

The Shapiro-Wilk test results showed that most studied soil parameters did not exhibit a normal distribution (p<0.05). Therefore, to determine the relationships between basic soil properties, salinity, heavy metal content, and enzyme activities, Spearman's rank correlation coefficients (rs) were calculated using the PAST 4.13 software (Hammer *et al.*, 2001).

#### **3. RESULTS AND DISCUSSION**

#### 3.1. Impact of landfill on variability of soil properties

The analysed soil samples differed widely in the grainsize composition (Table 1). The sand fraction predominated in most samples, and the clay fraction was the least abundant. The content of the sand fraction ranged from 35 to 89%, the silt fraction from 10 to 60%, and the clay fraction from 1 to 5%. According to the USDA classification (2022), four granulometric groups are distinguished: loamy sand (samples S1, S7, S9), sandy loam (S2, S5, S6, S8), sand (S4, C), and silt loam (S3). Soils belonging to these textural groups are characterised by high porosity and permeability, which may facilitate the migration of leachate into surrounding environments (Makuleke and Ngole-Jeme, 2020).

The total organic carbon (TOC) content ranged from 0.68 to 2.71% in series I and from 0.73 to 2.33% in series II (Table 1). The TOC values in both series were the highest at point S3 and the lowest at point C. However, the total nitrogen (TN) content was low and did not exceed 0.16% in the first series and 0.18% in the second series. Similar TOC and TN content levels were recorded in landfill soils by Amos-Tautua *et al.* (2014) and Agbeshiea *et al.* (2020). Those authors suggested that the increased content of TOC and TN in the soil was caused by household organic waste.

Soil pH and sorption properties showed significant differences between the soil sampling points in the landfill area (Table 2). The tested soils collected in series I and II from the landfill area were neutral (pH 6.9-7.4 for series I; pH 6.8-7.4 for series II). Maphuhla *et al.* (2021) and Odom *et al.* (2021) obtained similar results regarding soil pH in their studied landfill soils. However, the control (C) and the cultivated field (S9) soils were acidic (pH 4.6 and 5.5, respectively). The balance of sorption and desorption processes of hydrogen cations and metal cations is reaction-dependent. pH values from 5.5 to 7.2 are considered to be in the optimal range for biological processes.

The hydrolytic acidity (Hh) determines the degree of hydrogen saturation and includes the total acidity of the soil. The test results showed significant changes in Hh of the soil layer depending on the sites (the average value

Table 1. Soil texture and content of total organic carbon (TOC) and total nitrogen (TN)

Sites	Ре	ercentage of fraction	(%)	TOC	(%)	TN (%)		
	Sand (2-0.05 mm)	Silt (0.05-0.002 mm)	Clay (<0.002 mm)	Series I	Series II	Series I	Series II	
С	88	11	1	$0.68 \!\pm\! 0.01$	$0.73 \pm 0.14$	$0.04 \pm 0.03$	$0.04 \pm 0.01$	
S1	75	21	4	$0.74 \!\pm\! 0.02$	$1.46 \!\pm\! 0.02$	$0.05 \pm 0.08$	$0.10 \pm 0.02$	
S2	58	37	5	$1.00 \pm 0.01$	$2.06 \pm 0.28$	$0.08 \pm 0.02$	$0.18 \pm 0.02$	
S3	35	60	5	$2.71 \pm 0.06$	$2.33 \pm 0.05$	$0.16 {\pm} 0.10$	$0.10 \pm 0.03$	
S4	89	10	1	$2.07 \pm 0.01$	$1.71 \pm 0.01$	$0.04 \pm 0.01$	$0.04 \pm 0.01$	
S5	55	40	5	$1.01 \pm 0.10$	$1.23 \pm 0.05$	$0.04 \pm 0.02$	$0.04 \pm 0.01$	
S6	55	40	5	$0.89 \pm 0.01$	$0.95 \!\pm\! 0.08$	$0.04 \pm 0.01$	$0.01 \pm 0.03$	
<b>S</b> 7	85	13	2	$0.69 \pm 0.09$	$1.39 \pm 0.06$	$0.04 \pm 0.01$	$0.09 \pm 0.02$	
<b>S</b> 8	66	30	4	$1.00 \pm 0.01$	$1.02 \pm 0.02$	$0.06 \pm 0.02$	$0.06 \pm 0.03$	
S9	80	18	2	$0.98 \!\pm\! 0.02$	$0.89 \pm 0.01$	$0.07 \pm 0.02$	$0.05 \pm 0.01$	
Mean	69	28	3	1.17	1.38	0.07	0.07	
$LSD_{0.05}$	_	-	_	0.20	0.41	0.05	0.10	

C – control site outside the landfill's zone of impact, S1 – by the pumping station at a closed sector, S2 – in a closed-off sector, S3 – near the leachate outflow from a closed-off sector, S4 – waste landfill near the active sector (landfill basin), S5 – 5 m from active sector basin, S6 – 10 m from the active sector, S7 – 50 m from the active sector, S8 – areas adjacent to the plant perimeter fence, S9 – arable field with a maize monoculture, TOC – total organic carbon, TN – total nitrogen,  $\pm$  standard deviation.

Sita	pН	Hh	TEB	CEC	BS	EC <sub>1:5</sub>	Cl	SO4 <sup>2-</sup>
Sile	CaCl <sub>2</sub>	(cmol kg <sup>-1</sup> )		0	%		$(mg dm^{-3})$	
		Series I						
С	4.6	$2.5 \pm 0.1$	$8.9 \pm 0.1$	$11.4 \pm 0.1$	$78.0 \pm 1.2$	$15.2 \pm 0.9$	$36.0 \pm 0.1$	$35.7 \pm 0.3$
S1	7.2	$0.4 \pm 0.0$	$49.8 \pm 1.3$	$50.2 \pm 2.6$	$99.1 \pm 3.9$	$98.7 \pm 1.5$	$33.7\!\pm\!0.8$	$112 \pm 0.4$
S2	7.2	$0.4 \pm 0.0$	$49.2 \pm 1.3$	$49.6 \pm 2.3$	$99.2 \pm 4.1$	$437 \pm 11.3$	$99.1 \pm 2.7$	$126 \pm 0.1$
S3	7.0	$0.5\!\pm\!0.0$	$58.7 \pm 2.0$	$59.2 \pm 2.3$	$99.1 \pm 4.0$	$960 \pm 44.6$	$260 \pm 7.7$	$95.7 \pm 0.4$
S4	7.4	$0.4 \pm 0.0$	$59.1 \pm 1.5$	$59.5 \pm 2.7$	$99.3 \pm 3.5$	$2630 \pm 0.5$	$472 \pm 7.2$	$216\pm0.9$
S5	7.5	$0.5\!\pm\!0.0$	$57.9 \pm 1.3$	$58.3 \pm 1.9$	$99.2 \pm 4.1$	$133 \pm 3.5$	$66.1 \pm 0.8$	$106 \pm 0.7$
S6	7.4	$0.5\!\pm\!0.0$	$55.3 \pm 1.9$	$55.7 \pm 1.2$	$99.8 \pm 3.8$	$120 \pm 3.5$	$51.9\!\pm\!0.2$	$54.2 \pm 0.5$
S7	7.3	$0.5\!\pm\!0.0$	$51.3 \pm 1.4$	$51.8 \pm 1.1$	$99.1 \pm 4.1$	$104 \pm 3.2$	$33.0 \pm 0.5$	$50.9 \pm 0.1$
<b>S</b> 8	6.9	$0.4 \pm 0.0$	$36.2 \pm 1.4$	$36.6\!\pm\!0.9$	$98.8 \pm 3.5$	$108 \pm 2.0$	$47.2 \pm 0.9$	$68.0 \pm 0.2$
S9	5.5	$1.8\!\pm\!0.0$	$12.1 \pm 1.1$	$13.8 \pm 0.7$	$87.4 \pm 3.8$	$41.9\!\pm\!4.8$	$33.0 \pm 0.8$	$42.7 \pm 0.1$
Mean		0.8	43.8	44.6	95.8	202	113	9.1
$LSD_{0.05}$		0.1	10.8	8.85	10.0	19.4	13.9	1.8
				Series	II			
С	4.6	$2.4 \pm 0.1$	$7.4 \pm 0.1$	$9.8 \pm 0.9$	$75.5 \pm 3.4$	$15.4 \pm 1.0$	$26.0\!\pm\!1.0$	$38.2 \pm 0.1$
S1	7.1	$0.5\!\pm\!0.0$	$46.6 \pm 1.6$	$47.8 \pm 2.1$	$99.0 \pm 4.6$	$99.4 \pm 2.3$	$47.2 \pm 0.7$	$72.6 \pm 0.1$
S2	7.0	$0.4 \!\pm\! 0.0$	$46.3 \pm 1.9$	$46.6 \pm 1.9$	$99.1 \pm 5.2$	$239\!\pm\!7.8$	$94.4 \pm 1.6$	$40.7 \pm 0.0$
S3	6.8	$0.5\!\pm\!0.0$	$56.4 \pm 1.7$	$56.9 \pm 2.1$	$99.1 \pm 4.1$	$1640 \pm 0.8$	$519\pm1.1$	$148 \pm 0.3$
S4	7.4	$0.4 \pm 0.0$	$56.8 \pm 1.3$	$57.2 \pm 2.0$	$99.3 \pm 4.0$	$309\!\pm\!9.9$	$70.8\!\pm\!0.8$	$61.4 \pm 0.1$
S5	7.3	$0.5\!\pm\!0.0$	$55.5 \pm 1.5$	$55.9 \pm 1.6$	$99.2 \pm 4.0$	$146 \pm 4.2$	$42.5\!\pm\!0.5$	$81.4 \pm 0.1$
S6	7.2	$0.5\pm0.0$	$52.3 \pm 2.4$	$52.8 \pm 1.4$	$99.1 \pm 3.9$	$117 \pm 2.0$	$47.2 \pm 0.7$	$70.1 \pm 0.1$
<b>S</b> 7	7.2	$0.5\!\pm\!0.0$	$48.9 \pm 1.1$	$49.3 \pm 1.5$	$99.0 \pm 4.1$	$69.9 \pm 0.2$	$30.7 \pm 0.7$	$48.3\!\pm\!.0.1$
<b>S</b> 8	7.0	$0.4\pm0.0$	$33.6 \pm 1.0$	$34.0 \pm 1.6$	$98.7 \pm 4.2$	$105\!\pm\!1.9$	$42.5\!\pm\!1.4$	$62.7 \pm 0.1$
S9	5.5	$1.6 \pm 0.1$	$9.60 \pm 0.1$	$11.2 \pm 0.9$	$85.7 \pm 2.9$	$36.4 \pm 0.2$	$23.6 \pm 0.5$	$43.9 \!\pm\! 0.2$
Mean		0.8	41.3	42.1	95.4	114	94.4	6.7
$LSD_{0.05}$		0.1	9.9	8.1	9.8	17.3	3.9	0.5

Table 2. Selected soil properties (mean  $\pm$  standard deviation)

Hh - hydrolytic acidity, TEB - total exchangeable bases, CEC - cation exchange capacity, BS - base saturation, EC<sub>1:5</sub> - electrical conductivity of 1:5 soil-water extract, Cl<sup>-</sup> - chloride ion concentration in 1:5 soil-water extract, SO<sub>4</sub><sup>2-</sup> - sulphate ion concentration in 1:5 soil-water extract. Site description as in Table 1.

in series I was 0.79 cmol kg<sup>-1</sup> and in series II 0.77 cmol kg<sup>-1</sup>) (Table 2). The significantly highest value was found at point C (control) both in series I (2.51 cmol kg<sup>-1</sup>) and in series II (2.40 cmol kg<sup>-1</sup>), which shows a significant decrease in Hh in the soils from sites S1-S8 located in the municipal landfill.

The soil sorption complex is saturated with alkaline cations and constitutes an essential pool of plant nutrients. In soils sampled near the impact of the municipal landfill (S1-S8), the content of total exchangeable bases (TEB) was found to be significantly higher in both series I (36.2-59.1 cmol kg<sup>-1</sup>) and series II (33.6-56.8 cmol kg<sup>-1</sup>) (Table 2). The significantly highest TEB value was obtained at point S4 (59.1 cmol kg<sup>-1</sup> in series I and 56.8 cmol kg<sup>-1</sup> in series II). The lowest TEB values were recorded at points C and S9 and were 8.91 cmol kg<sup>-1</sup> and 12.1 cmol kg<sup>-1</sup> (series I) and 7.40 cmol kg<sup>-1</sup> and 9.60 cmol kg<sup>-1</sup> (series II), respectively (Table 2). Cation exchange capacity (CEC) is the ability of the soil to retain and release positive ions. Since the value of this parameter depends on pH and clay and organic matter fraction content, it is used as an indicator of soil quality (Adam et al., 2021). The CEC values from sites S1-S8

in both series I (36.6-59.5%) and series II (34.0-56.9%) were significantly higher than in the control (C): 11.42 and 8.90%, respectively (Table 2). Research by Aryampa et al. (2023) showed that the CEC in landfill soils was 20.8 cmol kg<sup>-1</sup>, indicating that they have good potential to provide nutrients to plants. The CEC values were significantly higher at points S3 (near the outflow of leachates from the non-active sector) and S4 (landfill basin). According to Jones (2012), CEC in the range of 11-50 cmol kg<sup>-1</sup> is highly desirable because it is associated with high OM content. The high cation exchange capacity of the landfills was probably the result of the decomposition of municipal waste, which resulted in a greater abundance of exchangeable basic cations, thereby increasing the fertility of the landfill soils. Anikwe and Nwobodo (2002) also showed that CEC was higher in waste dump soils than in soils from control areas. The degree of saturation of the sorption complex with basic cations (BS) in S1-S8 was up to 99% (Table 2). Meanwhile, in the control and S9 soil, significantly lower BS values were obtained in both series I and series II. According to Plak et al. (2017), complete saturation of the sorption complex with basic cations can be associated with the presence of calcium carbonate. In a study by Anikwe and Nwobodo (2002), the degree of saturation of the sorption complex was higher at waste storage sites than at sites without waste. The higher percentage saturation with alkaline ions in landfill soils compared to soils outside landfills suggests that landfill soils have more exchangeable cations.

To determine the possible impact of waste storage on the salinity level of the tested soils, electrical conductivity  $(EC_{1:5})$  and the concentration of chloride and sulphate ions in the soil-water extract 1:5 were determined (Table 2). On both sampling dates, there was a clear enrichment of soils in easily soluble salts at points S2, S3 and S4 (EC1:5 437, 960 and 2630  $\mu$ S cm<sup>-1</sup> in spring and 329, 1640 and 309  $\mu$ S cm<sup>-1</sup> in autumn, respectively), compared to the control sample (EC<sub>1:5</sub> 15.2 and 15.4  $\mu$ S cm<sup>-1</sup>, respectively). A similar trend was observed in the concentrations of the analysed anions. The maximum values were recorded at point S4 in spring (Cl<sup>-</sup> 472 mg dm<sup>-3</sup>, SO<sub>4</sub><sup>2-</sup> 216 mg dm<sup>-3</sup>) and at point S3 in autumn (Cl<sup>-</sup> 519 mg dm<sup>-3</sup>, SO<sub>4</sub><sup>2-</sup> 148 mg dm<sup>-3</sup>). This confirms that the source of salinity is anthropogenic. Some authors suggest a significant impact of landfill leachates on the salinity of soils and groundwater (Hernández et al.,

1999; Rodríguez-Rastrero *et al.*, 2023). However, it should be noted that the analysed soil materials varied in organic matter content and grain size. These factors are the main determinants of water-holding capacity (Richards, 1954) and may influence differences in the salinity level at individual research points (Hulisz *et al.*, 2018).

Due to the heterogeneity of the stored waste and soil properties and the prevailing hydrogeological conditions in landfills, it is challenging to define typical phenomena and universal characteristics of heavy metal contamination for the soil of landfills (Wanga *et al.*, 2022). With regard to the standards resulting from the Regulation of the Minister of the Environment (2016), the content of all the tested heavy metals in the analysed area was considered acceptable, and the soil was classified as unpolluted. Table 3 shows that the content of the tested heavy metals was higher in the landfill soils than in the soils from the nearby locations (control site and agricultural field). Zinc had the largest share in the amount of the analysed metals, and its content ranged from 38.1 to 70.0 mg kg<sup>-1</sup> (series I) and from 33.1 to 161 mg kg<sup>-1</sup> (series II). Cadmium was present in the smallest amounts

Table 3. Total content of Zn, Cu, Pb, Ni, Cd, and Cr in soil in series I and II (mean ± standard deviation)

Sitas	Zn	Cu	Pb	Ni	Cd	Cr				
Siles	(mg kg <sup>-1</sup> )									
			Series I							
С	$29.9 \pm 3.3$	$10.1 \pm 1.1$	$8.6 \pm 0.9$	$3.2 \pm 0.1$	$0.2 \pm 0.0$	$9.4 \pm 1.3$				
S1	$69.1 \pm 6.2$	$17.9 \pm 2.0$	$8.8 \pm 1.2$	$9.2 \pm 4.2$	$0.8 \!\pm\! 0.0$	$30.0 \pm 3.1$				
S2	$48.7 \pm 3.1$	$14.4 \pm 1.2$	$15.3 \pm 2.8$	$7.8 \pm 3.5$	$0.3 \pm 0.0$	$20.3 \pm 2.3$				
S3	$73.1 \pm 6.3$	$20.4 \pm 0.2$	$7.3 \pm 2.7$	$16.0 \pm 6.3$	$0.4 \pm 0.1$	$36.0 \pm 2.1$				
S4	$70.0 \pm 5.2$	$23.1 \pm 1.1$	$3.6 \pm 1.2$	$16.0 \pm 4.1$	$0.4 \pm 0.1$	$27.1 \pm 4.2$				
S5	$60.0 \pm 6.1$	$14.0 \pm 0.1$	$7.1\!\pm\!0.9$	$9.0 \pm 1.1$	$0.3 \pm 0.0$	$19.6 \pm 1.3$				
S6	$38.1 \pm 3.1$	$13.7 \pm 0.2$	$4.2 \pm 0.4$	$9.3 \pm 3.2$	$0.2 \pm 0.0$	$19.8 \pm 2.3$				
<b>S</b> 7	$28.2 \pm 1.5$	$10.2 \pm 1.2$	$3.4 \pm 1.6$	$3.9 \pm 1.2$	$0.2 \pm 0.1$	$17.2 \pm 3.3$				
<b>S</b> 8	$48.2 \pm 2.8$	$13.0 \pm 4.0$	$8.5 \!\pm\! 0.6$	$6.2 \pm 2.2$	$0.3 \pm 0.2$	$17.8 \pm 1.3$				
S9	$47.0 \pm 3.2$	$17.1 \pm 2.0$	$11.0 \pm 1.0$	$4.9 \pm 1.2$	$0.2 \pm 0.1$	$16.7 \pm 1.3$				
Mean	51.2	15.4	7.8	8.5	0.3	21.4				
$LSD_{0.05}$	3.1	0.7	2.6	1.4	0.2	7.5				
			Series II							
С	$30.0 \pm 3.6$	$6.8 \pm 2.2$	$10.5 \pm 0.2$	$2.9 \pm 1.1$	$0.2 \pm 0.0$	$9.6 \pm 1.3$				
S1	$79.8 \!\pm\! 8.4$	$31.6 \pm 3.7$	$16.4 \pm 0.6$	$18.0 \pm 2.3$	$1.5 \pm 0.2$	$57.0 \pm 17.3$				
S2	$98.8 \pm 6.9$	$19.7 \pm 2.2$	$30.0 \pm 1.3$	$9.0 \pm 1.0$	$0.3 \pm 0.1$	$25.1 \pm 11.0$				
S3	$67.9 \pm 4.1$	$22.0 \pm 3.2$	$6.1 \pm 0.1$	$15.9 \pm 1.2$	$0.3 \pm 0.1$	$38.1 \pm 15.0$				
S4	$95.6 \pm 7.2$	$38.6 \pm 6.2$	$19.7 \pm 1.4$	$12.2 \pm 1.2$	$0.5 \pm 0.1$	$27.3 \pm 9.6$				
S5	$46.1 \pm 4.1$	$13.9 \pm 5.1$	$5.6 \pm 0.4$	$8.3 \pm 0.9$	$0.2 \pm 0.0$	$18.8 \pm 2.3$				
S6	$33.1 \pm 2.1$	$9.2 \pm 2.1$	$3.3 \pm 0.4$	$9.1 \pm 1.1$	$0.2 \pm 0.1$	$19.9 \pm 4.5$				
<b>S</b> 7	$161 \pm 3.2$	$51.4 \pm 9.2$	$27.1 \pm 0.1$	$21.3 \pm 5.1$	$1.3 \pm 0.3$	$75.8 \pm 20.5$				
<b>S</b> 8	$48.7\!\pm\!1.8$	$11.9 \pm 1.3$	$11.0 \pm 0.6$	$6.1(\pm 1.1)$	$0.2 \pm 0.1$	$19.6 \pm 2.6$				
S9	$39.0 \pm 4.1$	$12.0 \pm 1.1$	$10.2 \pm 0.6$	$3.6 \pm 1.1$	$0.2 \pm 0.1$	$10.4 \pm 1.6$				
Mean	60.6	21.7	14.0	10.6	0.4	30.2				
LSD <sub>0.05</sub>	5.9	1.5	3.9	0.9	0.7	4.2				

Site description as in Table 1.

(Table 3). Metal concentrations in the soils collected from the landfill in both sampling series were ordered as follows: Cd<Pb<Ni<Cu<Cr< Zn. Moreover, higher amounts of the analysed metals were found in series II (autumn). The significantly highest content of all the analysed metals in series II was recorded at site S7 (Table 3). A study by Tałałaj (2014) showed that larger loads of pollutants are released from waste in spring. During this time, the percentage of the annual load released was 94% for lead, 75% for copper, 75% for zinc, and 96% for cadmium. The metal release rate may also increase due to the transient oxidation of metal sulphides to soluble sulphates. This author also showed that the release of heavy metals from waste into the soil is not significant and is limited by processes favouring metal immobilisation, such as sorption, precipitation, and a higher pH value (Tałałaj, 2014). Moreover, waste contains organic matter, which, at a pH ranging from neutral to higher, has a high sorption capacity, favouring metal immobilisation. The acidic state of leachates causes slow leaching of heavy metals, and leachates are, therefore, one of the sources of heavy metal pollution (Kanmani and Gandhimathi, 2013). The correlation analysis confirmed significant correlations between soil pH, hydrolytic acidity (Hh), organic carbon content (TOC), and heavy metal content in both sampling series (Fig. 2). Other causes of variation in heavy metal concentrations in landfill leachate include the composition of buried waste and the age of the landfill (Pasalari et al., 2019). Even if the composition of buried waste is similar,

the concentration of heavy metals in soils may vary due to progressive changes in their pH (Beinabaj *et al.*, 2023). The strong positive correlations between the content of individual metals (Fig. 2) mean that each paired element was dependent on common technogenic sources. This may be due to the geochemical associations of metals and may also provide information about their sources (Guo *et al.*, 2012; Mafuyai *et al.*, 2015). The correlation analysis confirmed such relationships for the analysed metals.

# 3.2. Impact of landfill on soil enzymatic activity

The results of the one-way ANOVA analysis for dehydrogenases (DEH), catalase (CAT), and peroxidase (PER) are presented in Table 4. It was shown that the enzymatic activity in the soil varied widely. The activity of the tested redox enzymes varied significantly depending on the soil sampling location. The highest DEH activity (0.648 mg TPF kg<sup>-1</sup> 24 h<sup>-1</sup> in series I and 0.612 mg TPF kg<sup>-1</sup> 24 h<sup>-1</sup> in series II), CAT activity (0.289 mg H<sub>2</sub>O<sub>2</sub> kg<sup>-1</sup> h<sup>-1</sup> in series I and 0.242 mg H<sub>2</sub>O<sub>2</sub> kg<sup>-1</sup> h<sup>-1</sup> in series II) and PER activity  $(1.756 \text{ mM PPG kg}^{-1} \text{ h}^{-1} \text{ in series I and } 1.698 \text{ mM PPG kg}^{-1}$ h<sup>-1</sup> in series II) were found in the soil samples taken from S3 (near the outflow of leachates from the non-active sector). Soils collected from S9 (the arable field of maize monoculture about 200 m north of the landfill premises) were characterised by significantly higher activity of the tested enzymes, compared to the control soil (except for CAT in series II).



**Fig. 2.** Correlogram showing relationships between analysed soil properties: a) series I, b) series II. Hh – hydrolytic acidity, TEB – total exchangeable bases, CEC – cation exchange capacity, BS – base saturation, EC<sub>1:5</sub> – electrical conductivity of 1:5 soil–water extract,  $CI^-$  – chloride ion concentration in 1:5 soil-water extract,  $SO_4^{2-}$  – sulphate ion concentration in 1:5 soil water extract, PLI – pollution load index, DEH – dehydrogenases, CAT – catalase, PER – peroxidases, GMea – geometric mean, TEI – total enzyme activity index, MAI – metabolic activity index.

Sites —	DEH (mg TF	PF kg <sup>-1</sup> 24 h <sup>-1</sup> )	CAT (mg H	$_{2}O_{2} \text{ kg}^{-1} \text{ h}^{-1}$	$PER (mM PPG kg^{-1} h^{-1})$		
	Ι	II	Ι	II	Ι	II	
С	$0.049 \pm 0.001$	$0.036 \pm 0.006$	$0.121 \pm 0.006$	$0.070 \pm 0.005$	$0.839 \pm 0.017$	$0.721 \pm 0.011$	
S1	$0.048 \pm 0.001$	$0.039 \!\pm\! 0.003$	$0.102 \!\pm\! 0.003$	$0.098 \!\pm\! 0.005$	$0.723 \!\pm\! 0.014$	$0.695 \!\pm\! 0.009$	
S2	$0.235 \!\pm\! 0.004$	$0.220 \pm 0.001$	$0.189 \!\pm\! 0.002$	$0.072\!\pm\!0.006$	$1.521 \!\pm\! 0.021$	$1.428 \!\pm\! 0.012$	
S3	$0.648 \!\pm\! 0.004$	$0.612\!\pm\!0.007$	$0.289 \pm 0.003$	$0.166 \!\pm\! 0.006$	$1.756 \pm 0.023$	$1.698 \pm 0.014$	
S4	$0.161 \!\pm\! 0.005$	$0.158 \!\pm\! 0.008$	$0.135 \!\pm\! 0.001$	$0.242 \!\pm\! 0.011$	$1.194 \!\pm\! 0.015$	$1.122 \pm 0.008$	
S5	$0.111 \!\pm\! 0.006$	$0.099 \!\pm\! 0.001$	$0.155 \!\pm\! 0.010$	$0.113 \!\pm\! 0.006$	$1.086 \pm 0.008$	$0.907 \!\pm\! 0.012$	
S6	$0.173 \!\pm\! 0.001$	$0.165 \!\pm\! 0.013$	$0.129 \!\pm\! 0.003$	$0.117 \!\pm\! 0.010$	$1.324 \!\pm\! 0.014$	$1.267 \!\pm\! 0.013$	
<b>S</b> 7	$0.049 \!\pm\! 0.002$	$0.037 \pm 0.011$	$0.080 \!\pm\! 0.005$	$0.108 \!\pm\! 0.005$	$0.708 \!\pm\! 0.009$	$0.635 \!\pm\! 0.008$	
<b>S</b> 8	$0.131 \!\pm\! 0.003$	$0.119 \!\pm\! 0.001$	$0.169 \!\pm\! 0.006$	$0.060 \pm 0.018$	$1.289 \pm 0.011$	$1.023 \pm 0.009$	
S9	$0.071 \!\pm\! 0.003$	$0.065 \!\pm\! 0.006$	$0.095 \!\pm\! 0.007$	$0.123 \pm 0.004$	$0.927 \!\pm\! 0.013$	$0.826 \!\pm\! 0.007$	
Mean	0.168	0.155	0.146	0.117	1.137	1.032	
$LSD_{0.05}$	0.013	0.028	0.020	0.034	0.198	0.189	

Table 4. Activity of dehydrogenases (DEH), catalase (CAT) and peroxidases (PER) in the two series

DEH - dehydrogenases, CAT - catalase, PER - peroxidases. Site description as in Table 1.

Similarly, Datta et al. (2021) showed an increase in enzyme activity (dehydrogenase, alkaline phosphatase, acid phosphatase, urease, and nitrate reductase), compared to the control. The nature of the waste probably resulted in an increase in the organic carbon content in the soil, which increased the mineralisation rate by microorganisms and thus increased enzymatic activity. Similar trends were presented by Wiesmeier et al. (2019). By comparing the DEH activity value in the soil samples (the average of the two series), the activity was determined as follows: S3>S2>S6>S4>S8>S5>S9>C=S7>S1. In their study of soils exposed to leachate from municipal solid waste, Shailaja et al. (2021) showed higher dehydrogenase activity in leachate-exposed soil compared to soils partially exposed to leachate and control soil. This suggests that dehydrogenases indicate the soil's potential to support biochemical processes needed to maintain soil fertility. According to Gianfreda and Rao (2004), oxidoreductases may have a protective function by oxidising toxic soluble products to insoluble ones. These enzymes facilitate the breakdown of harmful environmental pollutants by lowering the activation energy. Oxidoreductases catalyse the transfer of electrons from a donor to an acceptor. The acceptor can be an organic and inorganic compound and oxygen. Determination of dehydrogenase activity is used to indicate the intensity of respiratory metabolism of all soil microbial populations (Furtak and Gajda, 2017). The function of catalase is to dismutate hydrogen peroxide. Peroxidase also catalyses the decomposition of hydrogen peroxide while oxidising various organic and inorganic substances. These enzymes mediate key processes of the soil ecosystem, e.g. lignin degradation, humification, and carbon mineralisation by determining dissolved organic carbon content (Baldrian and Šnajdr, 2011). According to Lee et al. (2020), the sensitivity of enzymes as indices for assessing contamination and monitoring soil remediation is higher for oxidoreductases than hydrolases.

The activity of the tested enzymes varied depending on the date of soil sample collection. The activities of DEH (average 0.168 mg TPF kg<sup>-1</sup> 24 h<sup>-1</sup>), CAT (0.146 mg H<sub>2</sub>O<sub>2</sub> kg<sup>-1</sup> h<sup>-1</sup>), and PER (1.137 mM PPG kg<sup>-1</sup> h<sup>-1</sup>) were higher in soil samples collected in July than in autumn, when the analogous values were as follows: DEH-average 0.155 mg TPF kg<sup>-1</sup> 24 h<sup>-1</sup>, CAT - 0.117 mg H<sub>2</sub>O<sub>2</sub> kg<sup>-1</sup> h<sup>-1</sup>, and PER -1.032 mM PPG kg<sup>-1</sup> h<sup>-1</sup> (Table 5). Both temperature and precipitation significantly affect the activity of soil enzymes (Maphuhla et al., 2021), which is associated with seasonal or climatic changes in activity (Steinweg et al., 2013). These last-cited authors found that the activity of enzymes (β-glucosidase, cellobiohydrolase, xylosidase, acid phosphatase, N-acetyl glucosaminidase, leucine-amino peptidase) increased with temperature, peaked at medium warming, and then decreased at the highest warming. Soil moisture affects the diffusion of substrates, enzymes, and products, and drought conditions can significantly reduce this process. According to Steinweg et al. (2013), the rate of enzymatic reactions increases with temperature. However, Xiao et al. (2018) suggest that warming and increased precipitation tend to accelerate the carbon cycle and, therefore, significantly impact the activity of soil enzymes. Increasing soil moisture accelerates the transformation and availability of organic matter (OM). This activates microbial biomass, which contributes to increasing the overall enzymatic activity of the soil (Spohn et al., 2013). However, adding nutrients has a more significant impact on enzymatic activity than atmospheric and climatic changes. The correlation analysis showed no relationship between the analysed enzymes and total organic carbon (TOC) content (Fig. 2). According to Bielińska et al. (2013), the lack of correlation between TOC content and enzyme activity may be due to the low share of humic substances in total soil OM content. This limits access to bioavailable C, which stimulates the

number of bacteria producing soil enzymes. Also, Guan *et al.* (2019) and Lemanowicz (2019) found no relationship between OC and enzymatic activity, which was explained by the addition of anthropogenic organic substances to the soil. These substances do not occur in natural soil organic matter, so they do not act as substrates for enzymes. The total nitrogen (TN) content was significantly correlated in series I with *DEH* activity (r=0.74) and *PER* (0.64). According to Olander and Vitousek (2000), TN content may activate soil enzymes (*e.g.*, phosphatases) because N is necessary to produce some of them.

The activity of the tested redox enzymes was significantly and positively correlated with microelements, but these relationships varied depending on the date of soil samples collected and the enzyme itself. In series I, a significant positive correlation was found between Cu and both DEH (r=0.52) and PER (r=0.55), between Pb and both DEH (r=0.88) and PER (0.55), and between Cd and DEH (r=0.69). No significant correlations were obtained between CAT and micronutrients (Fig. 2). However, in series II, CAT activity was positively correlated with Cu (r=0.58), Pb (r=0.79), Ni (r=0.58), Cd (r=0.79), and Cr (r=0.78) (Fig. 2). The R<sup>2</sup> value showed that 33, 62, 33, 63, and 61% of the CAT variability was related to the content of heavy metals in the soil. Similar relationships were presented by Bartkowiak et al. (2024). There were also no significant negative correlations between DEH, CAT, and PER and the content of the tested heavy metals in the soil. This was probably due to the optimal content of all the tested heavy metals in the soil (Regulations of the Minister of the Environment, 2016). At low concentrations, metals can stimulate the activity of enzymes, while at high concentrations they cause a complete loss of the enzyme's catalytic functions. Enzyme inhibition in soil depends on the concentration and nature of heavy metals, and levels vary among enzymes. However, some heavy metals can increase enzyme activity at certain concentrations (Aziza et al., 2020). This happens when the enzymatic protein is unable to activate the substrate due to the absence of an appropriate metal ion. Metals may also be necessary to form bonds between a substrate and an enzyme or between a substrate, an enzyme and a coenzyme. Some of them also have an affinity for functional groups of amino acids that are the active site of some enzymes. The resistance of enzymes to metals can also be attributed to OM, which inactivates the effects of metals. OM-metal complexes prevent direct interaction between metals and the active sites of enzymes. However, Aponte et al. (2020) found that heavy metal content decreased enzyme activity in the following order: arylsulfatase > dehydrogenase >  $\beta$ -glucosidase > urease > acid phosphatase > alkaline phosphatase > catalase. This

means that heavy metals have a stronger effect on soil microorganisms and their endoenzymes than on extracellular enzymes that are stabilised on clay minerals and organic matter. Karaca et al. (2010) reported that different metals differently affect enzyme activity due to various chemical affinities of enzymes found in soil; for example, Pb significantly reduced the activity of urease, catalase, invertase, and acid phosphatase. Positive correlations were obtained between EC<sub>1:5</sub> and the activity of redox enzymes. A study by Lemanowicz et al. (2021) also showed a positive correlation between CAT and EC activity (r=0.623). Usually, soil salinity inhibits the enzymatic activity of the soil (Lemanowicz, 2019). As a result of the salting out of proteins, enzymes lose their biological activity (Bartkowiak et al., 2017). The solubility of the enzyme decreases as a result of dehydration and, consequently, the structure of the enzyme's active centre changes. However, even at high EC values, enzyme activity may persist due to enzyme production by microorganisms adapted to soil salinity. According to Telesiński (2012) and Bartkowiak et al. (2017), of all soil enzymes, the most sensitive to salinity are oxidoreductases, especially catalase. Dinesh et al. (1995) found that higher soil Cl<sup>-</sup> concentrations could reduce acid phosphatase activity. The growth of microflora is inhibited, which negatively affects the production of soil enzymes. As shown by Kalwasińska et al. (2023), the assessment of the impact of technogenic salinity on the activity of dehydrogenases may be made less clear by the effects of other environmental factors, such as interactions between microbiota and plants and the impact of root systems. This probably accounted for the significant positive relationships between the Cl<sup>-</sup> content and DEH, CAT, and PER activity in both series I and II. The correlation analysis showed significantly positive relationships between the features characterising the soil sorption properties and the enzyme activities in the landfill soils. The sorption capacity of soil increases with humus and clay content and the pH value, which have a positive effect on the enzymatic activity of the soil (Lemanowicz et al., 2023b).

## 3.3. Assessment of soil quality

Contamination factor (*CF*), enrichment factor (*EF*), Nemerow's index (*PN*), and pollutant load index (*PLI*) were determined to assess pollution and determine potential risks arising from heavy-metal toxicity in the soil. *CF* allowed the tested soils to be classified into appropriate groups depending on how many times greater values were than the background, which in our case was the concentration of a metal in the sample from the control station. According to Wang *et al.* (2016), among indices of soil pollution levels,

Sites -	Z	Zn		Cu		Pb		Ni		Cd		Cr	
	Ι	II	Ι	II	Ι	Π	Ι	II	Ι	II	Ι	II	
<b>S</b> 1	2.3	2.7	1.8	4.6	1.0	1.6	2.9	6.3	4.3	7.4	3.2	5.9	
S2	1.6	3.3	1.4	2.9	1.8	2.8	2.4	3.1	1.6	1.4	2.2	2.6	
S3	2.4	2.3	2.0	3.2	0.8	0.6	5.0	5.5	2.2	1.6	3.8	4.0	
S4	2.3	3.2	2.3	5.7	0.4	1.9	5.0	4.2	2.0	2.6	2.9	2.8	
S5	2.0	1.5	1.4	2.0	0.8	0.5	2.8	2.9	1.6	1.1	2.1	2.0	
S6	1.3	1.1	1.4	1.4	0.5	0.3	2.9	3.2	1.2	1.1	2.1	2.1	
<b>S</b> 7	0.9	5.4	1.0	7.5	0.4	2.6	1.2	7.4	0.9	6.8	1.8	7.9	
<b>S</b> 8	1.6	1.6	1.3	1.7	1.0	1.0	2.0	2.1	1.6	1.2	1.9	2.0	
S9	1.6	1.3	1.7	1.8	1.3	1.0	1.5	1.2	1.2	1.1	1.8	1.1	

Table 5. Degree of contamination with heavy metals (CF) calculated for the two measurement series

Site description as in Table 1.

*CF* meets the strictest criteria for assessing the pollution of an area. According to the criterion developed by Sutherland *et al.* (2000), the analysed soils were classed as uncontaminated at only a few measurement points (Table 5). During the first sampling (series I), significant contamination was recorded at sites S3 and S4 for Cu, at site S1 for Cd and Cr, and at site S3 for chromium. However, in series II, only one measurement point (S7) recorded a high level of contamination with Cu, Ni, Cd, and Cr. Significant Zn contamination was recorded during this period at the S4 site, and Ni and Cd contamination at the S1, S3 and S4 sites. In the other cases, the contamination was mainly moderate.

Due to the significant impact of anthropogenic transformations in the study area, the intensity of anthropogenic deposition of pollutants was assessed using *EF*. Using this coefficient, series I enrichment was found to be very high (*EF*>40%) for Zn, Cu, and Ni and high for the other metals. However, in series II, very high enrichment was found only for Ni, while the other metals were found to have high enrichment (20 < EF > 40) (Fig. 3).

The comprehensive Nemerow's pollution index (*PN*) method also assessed soil contamination with heavy metals. Figure 3b shows that the average values of Nemerow's pollution index for the measured heavy metals were above 1. According to the principle of the comprehensive *PN* index method, values in the range from 1.0 to 2.0 can be assessed as light pollution (class 2). Such values were recorded in both sampling series only for lead. The results show that copper, nickel, cadmium and chromium contamination was high in series II (*PN*>3).

The degree of heavy metal contamination was also assessed using the pollutant load index (*PLI*), which detects the deterioration in soil quality caused by heavy metal contamination. With overlapping levels of the six heavy metals tested in spring, the *PLI* values ranged from 0.95 to 2.37 and were classified as low and moderate contamination levels. The lowest *PLI* value was recorded at point S7. In the second sampling series, the *PLI* values were higher and ranged from 1.2 to 4.1, which indicated a moderate and high level of contamination with the tested metals (Fig. 3).

The *CF*, *EF*, *PN* and *PLI* indicators calculated to assess contamination and determine the potential risk resulting from heavy-metal toxicity in the soil had values similar



**Fig. 3.** Pollution assessment: a) enrichment factor (*EF*), b) Nemerow's pollution index (*PN*), c) pollution load index (*PLI*).



**Fig. 4.** Enzymatic indices of soil quality: a) geometric mean (GMea), b) total enzyme activity index (*TEI*), c) metabolic activity index (*MAI*).

to those obtained by other authors (Bhutiani et al., 2017; Uzoekwe and Glory, 2020; Beinabaj et al., 2023). In light of the results, both closed (S1-S3) and active (S4-S8) landfill sectors may be the source of heavy metals, but their levels were not high. The causes of the irregular distribution of heavy metal soil contamination may be complex. It seems likely that the most critical factor influencing the variability of the quality indices of the tested soils in relation to the content of heavy metals is the variation in the primary properties of the deposited technogenic materials, which was confirmed by the soil texture and the total organic carbon content (Table 1). Therefore, it is difficult to indicate any spatial trend within the landfill. Site S9 was located out of the landfill in the arable field. It can be assumed that the similar PLI value at this point and nearby points S5, S6, and S8 may result from the direct influence of municipal waste. In addition, another source of metals related to agricultural cultivation techniques cannot be ruled out.

It is known that heavy metals are potential long-term soil pollutants. They are easily leached by water and cannot be decomposed by soil microorganisms. Still, their levels can be enriched by organisms activity, which often results in the gradual accumulation of heavy metals in the soil environment and transfer that is difficult to remove (Wanga *et al.*, 2022). Another potential cause of soil contamination with heavy metals in the impact zone of landfills is dust generated during waste transport and open storage (Wang *et al.*, 2022). In addition, it is also necessary to consider that some soil materials used to establish the geochemical background may have naturally high element concentrations, and global reference values may be higher or lower than local conditions. This factor could also influence the levels of the calculated soil quality indices (Mafuyai *et al.*, 2015).

Based on the results for CAT, DEH, and PER activity, soil fertility indices (GMea, TEI, MAI) were calculated (Fig. 4). Due to the multi-faceted function of soil, it is not sufficient to measure the activity of a single enzyme. Determining the activity of soil enzymes and, based on that, calculating multiparametric indices is one of the fastest and most sensitive ways of indicating natural and anthropogenic changes in the soil. Therefore, based on the results of CAT, DEH, and PER activity, soil fertility indices (GMea, TEI and MAI) were calculated as dimensionless parameters. The value of the GMea coefficient ranged from 0.141 (S7) to 0.690 (S3) (series I) and from 0.112 (S7) to 0.631 (S3) (series II). The highest values in both series I and II were obtained in the soils from sites S2 and S3. The GMea value was higher in series I than in series II (Fig. 4). According to Paz-Ferreiro et al. (2012) and Jat et al. (2021), higher GMea values indicate better soil fertility without taking into account its physicochemical properties. It follows that S2 and S3 (inactive sites) were less exposed to the impact of heavy metals in the area adjacent to the municipal landfill. In soil samples in both series, the GMea values were in the following order: S3>S2>S6>S4>S8>S5>S9>C>S1>S7 (Fig. 4). According to Tan et al. (2014), the total enzyme activity index (TEI) allows comparison of total enzymatic activity in the soil among all sampling points. The highest TEI value was obtained in S3 in series I (7.39) and series II (7.66). However, the lowest TEI was obtained in S7 – the site 50 m from the active sector (1.46 in series I; 1.37 in series II) (Fig. 4). The ratio of the total enzymatic activity of the soil in the area affected by the municipal landfill to the activity in the control soil was expressed as the MEI index. The DEH, CAT and PER activities were normalised to the soil's organic carbon (OC) content. The MAI value varied significantly according to the soil sampling point. It was the highest at S2 (5.56) for series I and at S3 (6.87) for series II (Fig. 4).

The Pearson correlation analysis demonstrated the relationship between enzymatic indices (GMea, TEI, and MAI) and other soil parameters. The results of the correlation analysis (spring) showed that the content of TOC and TN in the soil had a significantly stronger effect on GMea and TEI than did the other soil properties (Fig. 2). Mierzwa-Hersztek et al. (2019) showed that TEI is usually positively correlated with TOC and TN content. This was not shown in a study by Lemanowicz et al. (2023b). It was also found that the clay, Cl<sup>-</sup>, EC<sub>1:5</sub> and Ni content positively correlated with the values of GMea and TEI. The correlation indices (series II) showed that EC<sub>1:5</sub> and Cl<sup>-</sup> were each significantly positively correlated with the values of GMea and TEI (Fig. 2). However, MAI was positively correlated with clay in both series (respectively, r=0.56 and r=0.69). The activity of soil enzymes can be intensified or maintained if adsorption to clay minerals stabilises their structure, allowing the enzymes to maintain their catalytic activity (An et al., 2015). GMea and TEI had stronger correlations with soil physicochemical properties than did the activities of individual enzymes (Fig. 2). A similar relationship was demonstrated by Tan et al. (2014) and Nurzhan et al. (2022). The results indicate that changes in soil use strongly affect enzyme activities, with GMea and TEI providing a more sensitive biological indicator of soil quality than MAI.

# 4. CONCLUSIONS

Our findings highlight the complexity of soil dynamics in areas strongly transformed by human activity, such as municipal landfill sites. Local environmental conditions significantly controlled by technogenic factors closely related to the method of waste storage and land use within the landfill site were particularly influential in the variability of soil properties. It was found that the average content of total forms of the analysed heavy metals was in the order Cd<Pb<Ni<Cu<Cr<Zn. The contents of all the tested heavy metals in the study area were considered acceptable, and the soils were classified as uncontaminated. However, some enrichment in the analysed metals was observed, compared to the control sample. The results of the enzyme activity analysis revealed that anthropogenic changes in the soil in the municipal waste landfill strongly determined the activity of dehydrogenases, catalase, and alkaline and acid phosphatase. The multiparametric enzymatic soil fertili-ty indices calculated on their basis the geometric mean of enzyme activities (GMea), total enzyme activity index (TEI), and metabolic activity index (MAI) indicated that GMea and TEI are more sensitive soil quality indices than MAI. The content of heavy metals did not cause enzymatic inhibition of the soil.

This research provides valuable insights into environmental management, indicating that while the soil may currently be classified as uncontaminated, ongoing monitoring and strategic interventions remain crucial to maintaining soil quality amidst changing environmental conditions.

**Conflicts of interest.** The authors declare no conflict of interest.

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