Int. J. Environ. Res., 10(2):245-254, Spring 2016
ISSN: 1735-6865

Assessment of Selected Heavy Metals and Enzymes in Soil Within the Range of Impact of Illegal Dumping Sites

Bartkowiak, A.[1] Lemanowicz, J.[2] and Siwik-Ziomek, A.[2]

[1]Department of Soil Science and Soil Protection, Faculty of Agriculture and Biotechnology, UTP University of Science and Technology in Bydgoszcz, Bernardyńska 6 St., 85-029 Bydgoszcz, Poland
[2]Sub-Department of Biochemistry, Faculty of Agriculture and Biotechnology, UTP University of Science and Technology in Bydgoszcz, 85-029 Bydgoszcz, Bernardyńska 6 St., Poland

Received 10 Sep. 2015; Revised 31 Feb. 2016; Accepted 7 March 2016

ABSTRACT: Defining the physicochemical and biological parameters in soil under illegally dumping sites provides information on the real threat and the direction of changes in the soil environment. The paper demonstrates the result of changes in the properties in soil as a result of the operation of illegal dumping sites. Soil was sampled from the research points located on the outskirts of the city of Bydgoszcz (Poland) from the site not affected by illegal dumping sites (control C), within the dumping sites, having removed the waste layer (W), and 10 m away from the dumping sites (W 10). In the soil the content of phosphorus, potassium, magnesium and sulphur, total content of copper, zinc, lead and nickel as well as the activity of enzymes were assayed. The content of Pb, Zn, Cu and Ni in the soil samples qualifies the soils as representing the soil category with natural content. The greatest activity of all the enzymes analysed was identified in the soil sampled from the control point affected by waste, whereas the highest content of macroelements was reported in the soil from the dumping sites (W 10). A high variation in the enzymes under study in soils confirms a high value of the coefficient of variation (CV >36%). The analysis of correlation confirmed the relationship between the content of organic carbon compounds and the content of zinc, lead, nickel. The soils show a slight value of the coefficient of contamination for heavy metals (CF<1). The contamination degree (Cdeg) ranged from 1.993 to 5.116, which points to a low level of soil contamination with Zn, Cu, Pb and Ni.

Key words: Heavy metals, Macronutrient, Enzymes, Dumping sites, Waste

INTRODUCTION

Over the last decades a fast economic development has contributed to an intensive increase in the content of waste, accompanied by the problem of disposal (Ogundiran and Afolabi, 2008; Islam *et al.*, 2012). Following the policy of the European Union, we aim at reducing waste origination, however waste management in Poland is much less developed than in many other European countries. Despite the currently binding laws on Maintaining Cleanliness and Order in Communes (Dz. U. item 228 of 25 January 2013) and as well as the Waste Law of 14 December 2012 (Dz. U. 2013 No. 0 item 21), a lack of waste collection contracts has resulted in the emergence of the so-called 'illegal dumping sites'. Illegal waste dumping sites most often appear on the edge of forests and on the outskirts of the cities, in the vicinity of greenbelts separating the road from agricultural land, which results in a progressive contamination of the soil environment by disturbing the microbiological and biochemical processes, as well as physical and chemical properties (Bielińska and Mocek-Płóciniak, 2009; Islam *et al.*, 2012). Illegal dumping sites have neither hydro insulation sealing nor a separated protection zone. Neither are they separated from the soil with the geomembrane layer.

The enzyme assays facilitate a comprehensive evaluation of the soil environment condition since the compounds take part in the transformations of nutrients and affect their availability to plants (Nannipieri *et al.*, 2003; Krzyżaniak and Lemanowicz, 2013). The activity of enzymes is influenced by heavy metals. At low concentrations they have a stimulating effect, however, at large quantities they inhibit the activity of soil enzymes (Bartkowiak and Lemanowicz, 2014). The enzymes also show a susceptibility to the concentration of hydrogen ions: the soil reaction. Alkaline and acid phosphatases are among especially

---

*Corresponding author E-mail: bartkowiak@utp.edu.pl

sensitive and pH-dependent. Dehydrogenase is the most important soil enzyme and a frequently used test for determining the influence of various pollutants (heavy metals, pesticide, crude oil, etc.) on the microbiological quality of soil (Margesin *et al.*, 2000). Their activity can be inhibited from 10 to 90%, depending on the soil contamination. Arylsulphatases play a major role in sulphur cycling in soils by catalysing the hydrolysis of ester sulphates, and thus releasing organically-bound sulphate into the soil solution (Tabatabai and Bremner, 1970).

Open dumping sites present a number of risks to soils due to the capacity for generating toxic chemicals, pathogens and due to altering the natural environment of soil Amuno (2011). Municipal solid waste includes complex organic substances, ammonia, xenobiotics, heavy metals (Longe and Enekwechi, 2007; Tengruit *et al.*, 2007; Ogundiran and Afolabi, 2008). A high concentration of heavy metals in soil as a result of illegal waste deposition points to a lack of responsibility for the natural environment in the society and the natural environment protection institutions (Meller *et al.*, 2012). Moreover, illegal dumping sites may not be located in protected areas (national parks, scenic parks) (Diatta, 2012). Bearing that in mind, one must recognise the level of natural environment contamination and thus launch land rehabilitation treatments, recovering the initial natural environment functions of the areas.

The aim of the paper has been to determine the effect of illegal dumping sites located in the Bydgoszcz commune on selected physical, chemical and biochemical properties of soils, including the accumulation of heavy metals in the soils of their occurrence.

MATERIAL & METHODS

Soil was sampled in spring (April 2013) from 7 research points located on the outskirts of the city of Bydgoszcz (53°12^{1}N; 18°01^{1}E; the Kujawy and Pomorze Province, Poland, Europe) from three horizons (0-15, 15-30, 30-50 cm) from the site not affected by illegal dumping sites (control C), within the dumping sites, having removed the waste layer (W), and 10 m away from the dumping sites (W 10). In total the analysis involved 63 soil material samples.

The city of Bydgoszcz is located in the temperate climate zone, on the left-bank of the fluvial terrace of erosive - accumulative glacial valley of the Vistula River which now runs about 4 km north. The area makes up a high fluvial sandy terrace and outwash plain (the formations produced as a result of the activity of glacial waters built from fluvial sediments of glacial origin), transformed the eolian into dunes.

In the adequately prepared soil samples the following were assayed:
pH in H_2O and pH in 1 M KCl measured potentiometrically (ISO 10390), electroconductivity (EC) with the conductometric method in the water-soil suspension at 1:2.5 (soil-to-water ratio); that property has been assumed as the measure of salinity (EC). Total organic carbon (TOC) was determined with the TOC analyser Primacs provided by Scalar, the content of available phosphorus (P) with the Egner-Riehm method – DL (PN-R-04023, 1996), potassium (K) with the Egner-Riehm method (DL) (PN-R-04022, 1996), sulphate sulphur ($S\text{-}SO_4^{2-}$) in soil according to the Bardsley–Lancaster method modified by COMN-IUNG (Bardsley and Lancaster 1960), as well as the content of magnesium available to plants (Mg) following the Schachtschabel method **(**PN-R-04020, 1994). The total Zn, Cu, Ni and Pb concentrations were assayed after the mineralization of the samples in the mixture of HF and $HClO_4$ as described by Crock and Severson (1980). The total content of heavy metals was assayed with the use of atom absorption spectroscopy with Philips PU 9100X spectrometer.

The activity of selected redox and hydrolytic enzymes: the activity of dehydrogenases (DEH) [E.C. 1.1.1] in soil was determined 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 (AlP) [E.C. 3.1.3.1] and acid (AcP) [E.C. 3.1.3.2] phosphatase – with the Tabatabai and Bremner method (1969) and arylsulphatase (ARS) (EC 3.1.6.1) (Tabatabai and Bremner, 1970).

The values of the contents of heavy metals recorded in the soil were used to calculate the geochemical parameters evaluating the anthropogenic effect on the soil environment (Table 1).

Contamination Factor (CF):

$CF=C_{0-1}/C_n$

where: C_{0-1} - the mean content of metals from at least five sampling sites,

C_n – geochemical background.

Table 1. Categories of contamination factor on the basis of CF value and the contamination degree (C_{deg}) of the ecosystem (Håkanson 1980)

CF	Category	C_{deg}
<1	Low contamination	<8
1=CF<3	Moderate contamination	8= C_{deg}<16
3=CF<6	Considerable contamination	16= C_{deg}<32
6=	Very high contamination	32=

The sum of CF for all the metals studied yields the so-called contamination degree (C_{deg}) of the ecosystem. The coefficient of variation of the parameters analysed was calculated as follows:

CV=(SD/X)*100

where: CV– coefficient of variation (%), SD– standard deviation, X– arithmetic mean.

Values where 0-15%, 16-35%, and > 36% indicate low, moderate, or high variability, respectively.

All the assays were made in three reps; the paper demonstrates the arithmetic means of the results. The results were exposed to the analysis of variance and the significance of differences across the means was verified with the Tukey test at the confidence level of p=0.05. For the purpose of the calculations, there was applied Microsoft Excel-based ANOVA software. Besides the results of the analysis of the features investigated were exposed to the analysis of simple correlation which determined the degree of the dependence between respective features. The analysis of correlation was made with 'Statistica for Windows Pl' software.

RESULTS & DISCUSSION

The content of clay fractions in the soil material analysed ranged from 0.8 to 2.0% (Table 2), which has classified the soils according to the agronomic categories as sandy soils. All the soil samples showed acid reaction. The soils beyond the effect of illegal dumping sites demonstrated a very acid reaction (pH $_{H2O}$ 4.01-4.49; pH $_{KCl}$ 3.90-4.30 depending on the soil sampling depth) (Table 2). The soils sampled under deposited waste and 10 m away showed higher pH values (pH $_{H2O}$ 5.01-6.44; pH $_{KCl}$ 4.56-6.07 as well as pH $_{H2O}$ 4.74-5.32; pH $_{KCl}$ 4.41-5.01), which corresponds to the reaction from acid to slightly acid. Similar results were earlier reported by Bielińska and Mocek–Płóciniak 2009. Literature shows (Malinowski *et al*., 2012) that illegal waste dumping sites, quite common on sandy soils, change their properties, especially the chemical ones. In general, rubble waste with lime mortar enhance the soil reaction they are deposited on.

Electrolytic conductivity (EC) of the soil sampled from the control point was 0.201 – 0.249 mS/cm, beyond the area of the dumping sites 10m away (0.177 – 0.213 mS/cm) as well as at the site of illegal waste deposition (0.182-0.330 mS/cm) did not show any variation (Table 2). The soils demonstrated natural salinity not exceeding the limit value <2.0 mS/cm (Kotuby-Amacher *et al*., 1997). The highest EC value (0.330 mS/cm) was noted in the soil sampled under the dumping site from horizon 0-15cm (Table 2), which must have been due to the anthropogenic pollution of the soil with single elements (Islam *et al*., 2012).

The human activity is a source of inhomogeneous waste with a considerable share of organic matter. The share of organic matter in the waste mass mostly improves the content of total organic carbon and doping agent of industrial and chemical waste result in the accumulation of heavy metals. The content of organic matter in the soil samples varied depending on the object and the soil sampling depth. Its greatest amounts were recorded in the surface horizons from all the objects and the calculated coefficient of variation (CV 76.83%) pointed to a high variation of the results (Table 3).

The content of available phosphorus of the soil ranged from 10.01 to 29.17 mg/kg P, with an average content of 17.32 mg/kg P, which according to PN-R-04023 (in Polish) (1996), classifies it as class V with a very low content of that nutrient. The potassium accumulation fell within the range from 39.72 to 86.43 mg/kg K (on average 58.81 mg/kg K). The contents of those macroelements point to a high variation of the results, which was confirmed with a high value of the

Table 2. Selected physicochemical properties

Objects	Horizon cm	pH H_2O	pH KCl	Hh cmol(+)/kg	EC mS/cm	Fractions % 2.0-0.05 mm	0.05-0.002mm	< 0.002 mm
C^*	0-15	4.01	3.90	7.95	0.201	79.80	19.2	0.80
	15-30	4.16	4.04	4.05	0.249	85.50	12.8	1.70
	30-50	4.49	4.30	2.33	0.239	90.6	7.63	1.77
W^{**}	0-15	6.44	6.07	1.05	0.330	80.69	17.45	1.43
	15-30	5.29	5.09	1.65	0.208	78.94	19.10	1.96
	30-50	5.01	4.56	0.83	0.182	89.97	8.03	2.00
W 10^{***}	0-15	5.32	5.05	2.03	0.213	89.37	8.93	1.70
	15-30	4.74	4.41	2.10	0.183	83.10	15.20	1.70
	30-50	5.11	5.01	0.83	0.177	93.07	5.16	1.77

C^* - Control, W^{**} - Waste dumping site, W 10^{***} – 10m away from the waste dumping site coefficient of variation (CV 60.50% for phosphorus and CV 49.99% for potassium) (Table 3). The results of the magnesium content showed an average variation, which was confirmed by the value of the coefficient of variation (CV =35.45%).

The significantly lowest content of available phosphorus (10.01 mg/kg), potassium (42.24 mg/kg) and magnesium (32.21 mg/kg) was found in the control soil (Table 3). In the soil samples 100 m away from the dumping sites the content of the macroelements was highest (29.17 mg/kg P, 86.43 mg/kg K, 44.73 mg/kg Mg, respectively) (Table 3), which can be related to the content of the elements in washing agents, bleaches, food residue (Islam *et al.*, 2012). The results of the study by Islam *et al.* (2012) revealed that the highest available phosphorus content in soils was recorded in solid waste dumping site and not the organic one, which was connected with a low activity of phosphomonoesterases in those soils. 30 mgP/kg of soil is considered to be the critical content of phosphorus for plants. Considering that value, it was found that the content of available phosphorus was lower than the critical value in all the soil sampling points. In the soil sampled just under illegally deposited waste, the phosphorus content was very low (12.79 mg/kg), which, according to PN-R-04023 (in Polish) (1996), classifies it as class V. The potassium content, according to PN-R-04022 (1996), was low (47.77 mg/kg) (IV soil richness class), while the magnesium content (34.16 mg/kg) was high, which classifies it, according to PN-R-04020 (1994), as class II of soil richness with that element.

Based on the analysis of variance, there was reported a significant effect of the soil sampling depth. The highest contents of phosphorus (22.56 mg/kg), potassium (72.78 mg/kg) and magnesium (47.87 mg/kg) were noted in the soil sampled from horizon 0-15 cm. The greater the depth, the lower the contents of those elements (Table 3). A high content of sulphates was recorded in the soil samples. The content of sulphate sulphur was highest (41.757 mg/kg) in the soil sampled in the control point (Table 3). According to the sulphur content scale developed by IUNG Puławy, the content of SO_4^{2-} in sandy soil above 35 g/kg corresponds to the content elevated due to the anthropogenic impact on the environment (Motowicka-Terelak and Terelak, 2000). Most probably the control point is located at the place of sulphur oxides emissions and, most probably, in that control location a dry and wet deposition of sulphur oxides occurred. Sulphur is a controversial chemical element. On the one hand, sulphur has a negative effect on the natural environment and causes its acidification, however, on the other hand, sulphur as an elemental and necessary component of amino acids e.g. methionine and cysteine is a requisite for protein synthesis necessary for biomass growth (Ostowska *et al*., 2008). While organic sulphur compounds are largely immobile, inorganic sulphur is more mobile and sulphate (SO_2^{4-}) is most mobile **(**Scherer, 2009). Sulphate transport is delayed by adsorption, whereby adsorption and desorption are predominantly controlled by SO_2^{4-} concentration in soil solution, soil pH, the character of colloidal surfaces, and other anions in solution.

A significant effect of the soil sampling depth on the content of sulphates in soil was identified (Table 3). The highest concentration of sulphur ions (36.76 mg/kg) was assayed in the surface horizon. The adsorption of sulphates by iron and aluminium oxides is the main mechanism of sulphur retention in soil. The size of the sorption phenomenon depends mostly on the properties, the content of clay minerals, iron and aluminium oxide-hydroxides, the soil level, the presence of other ions and the soil reaction (Scherer, 2009). The sorption of sulphates is intensive when exposed to low soil pH, being non-significant at pH 6.0. In the soil sampled from the control point the highest values of hydrolytic acidity were determined (Table 2). The dependence of the content of sulphates in soil on hydrolytic acidity is confirmed by a high value of the coefficient of correlation for those parameters ($r=0.916$; $P<0.05$) (Table 7). The positive value of the coefficient of correlation between the activity of dehydrogenases being an indicator of the biological activity of soils and the content of sulphates suggests also a possibility of binding ions SO_4^{2-} by organic matter. According to Blair *et al*. (1994), organic matter in specific conditions, thanks to atmospheric nature, identifies positive charges and thus initiates the process of sorption of sulphate ions. A higher content of sulphates (VI) in the layer 30-50 cm than in horizon 15-30 cm suggests the process of sulphates leaching deep down the soil profile. The phenomenon takes place when water moves following the gravitational forces stronger than it is uptaken by plants or gets evaporated (Blair *et al*., 1994). That phenomenon is enhanced by e.g. a high soil pollution with sulphur. A high variation in the content of sulphates in the soils confirms a high value of the coefficient of variation CV 85.60% (Table 3).

The total amount of pollution introduced from waste dumping sites depends on the type of waste deposited there. The research has demonstrated that the highest concentration of heavy metals was noted right under the waste dumping sites. The analysis of variance also confirmed a significant effect of the soil sampling depth (Table 4). The highest amounts of zinc, copper, lead and nickel were reported right under the waste in the surface soil horizon. Of all the metals studied, the following got accumulated in soil: Zn (35.80 mg/kg), Pb (15.54 mg/kg) as well as Cu (14.07 mg/kg), respectively. The contents exceeded the concentration of those metals in the soil sampled from the control point considerably. A low homogeneity of the results for zinc, lead and copper was found, which was confirmed by high values of the coefficients of variation CV: 72.56%, 88.72% and 222.7%, respectively. Evaluating the contamination degree of the soils with selected heavy metals, under Regulation of Minister of Environment of September 2, 2002 pertaining to the soil and land quality standards (Dz. U. No 165, item 1359), one finds that the values of maximum permitted contents are not exceeded, which points to their natural content in soil, which can be due to a short time of the existence of illegal dumping sites in that area. An important factor determining not only the content but also the mobility of heavy metals in soils is the grain size composition affecting its sorption potential. Sandy soils, with an inconsiderable content of the clay fraction, contain, on average, less trace elements than loamy soils (Kabata-Pendias and Pendias, 2001). Such relationships were not confirmed by the analysis of correlation. Elevated contents of metals in the surface layer of sandy soils are a result of an increased amount of organic matter and its capacity for point-like retention of nutrients **(**Malinowski *et al*., 2012). The analysis of correlation confirmed the relationship between the content of total organic carbon compounds and the content of zinc (r=0.815, $P<0.05$), lead (r=0.762, $P<0.05$) as well as nickel (r=0.751, $P<0.05$) (Table 7).

The Contamination Factor (CF) facilitates qualifying the soils into respective groups depending on how many times the geochemical background has been exceeded (Diatta, 2012). According to the criterion developed by Håkanson (1980), the soils analysed show an inconsiderable value of the Contamination Factor for heavy metals (CF<1) (Table 5). Only in the soil sampled from the surface horizon, right under the dumping sites, there was noted an average contamination with those elements, and in the case of copper – a very heavy contamination. Similarly Ideriah et al. (2010) reported that the waste dumps contribute to high copper levels in the soils. The comprehensive evaluation of the state of contamination of the soil under study was made based on the value of the level of contamination (C_{deg}) The level of contamination ranged from 1.993 to 5.116, which, according to the Håkansona classification **(**1980), points to a low level of soil contamination with heavy metals, except for the soil sampled from horizon 0-20 cm right under the deposited waste (C_{deg} 19.458) with a considerable level of contamination. The findings by Amuno (2011) indicate that soil from two dump sites can be classified as moderate to extremely contaminated with heavy metals, such as lead and cadmium. It is also observed that the soil contamination ranges from low to high with zinc, molybdenum, copper and arsenic.

The enzymatic activity of soil reflects the level and the size of the natural environment contamination (Lemanowicz and Bartkowiak, 2013). The activity of enzymes is definitely affected by heavy metals. At low concentrations they act as stimulants, while at high concentrations they inhibit the soil enzymes activity. The activity of the soil enzymes depended significantly on the soil sampling site and depth and demonstrated a high value of the coefficient of variation (CV >36%) (Table 6). The greatest activity of all the enzymes analysed: dehydrogenases (4.498 mgTPG/g/d), catalase (0.106 mgH_2O_2 /g/h), alkaline phosphatase (1.300 mM pNP/kg/h), acid phosphatase (2.033 mM pNP/kg/h) arylsulphatase (0.051 mM pNP/kg/h) was recorded in the soil sampled from the control point not exposed to the effect of waste (Table 6). However, in the soil sampled right under the deposited waste, a significant process of inhibition of the activity of those enzymes was reported; (DEH–2.573 mgTPG/g/d, KAT-0.053 mgH_2O_2/g/h, AlP–0.689 mM pNP/kg/h, AcP–0.872 mM pNP/kg/h). Different results were recorded by Bielińska and Mocek-Płóciniak (2009) who noted the activity of the enzymes (dehydrogenases, acid alkaline phosphatase urease, protease) about 1.5-2.0-fold higher in the soils at the waste dumping sites than in the forest soils beyond their reach. The authors claim that the greater intensity of the enzymatic activity of soils from the area of the waste dumping sites was connected with the richness of organic compounds contained in the deposited waste, which, by activating additional sources of energy, triggers the development of microorganisms and stimulates the biosynthesis of enzymes. The waste of different origin left shows, in general, negative biological soil properties. The enzymatic activity could have been lowered due to a greater concentration of heavy metals which, together with complex substrate-enzyme, inhibited active groups of enzymes (Renella *et al*., 2003; Liu *et al*., 2008). A high content of heavy metals can cause oxidative stress (Dong *et al*., 2006), which usually lowers the activity of dehydrogenases and soil catalase. The activity of alkaline (1.038 mM pNP/kg/h) and acid phosphatase (1.334 mM pNP/kg/h) in the soil 100m away from the deposited waste showed that the range of the effect of

Table 3. Content of total organic carbon (TOC), available phosphorus (P), potassium (K), magnesium (Mg), sulphur (S) in soil

		TOC g/kg	P mg/kg	K mg/kg	Mg mg/kg	S mg/kg
Objects	C*	2.622 bc	10.01 e	42.24 c	32.21 bc	41.76 a
I factor	W**	4.173 ab	12.79 d	47.77 c	34.13 b	29.24 c
	W 10***	5.236 ab	29.17 a	86.43 a	44.73 a	23.34 d
Horizon	0-15	7.047 a	22.56 b	72.78 b	47.87 a	36.76 b
cm	15-30	3.783 bc	17.40 c	63.94 b	35.03 b	26.45 d
II factor	30-50	1.201 c	12.01 d	39.72 c	28.16 c	31.09 c
Standard Deviation		3.081	10.48	29.21	13.13	9.485
CV %		76.83	60.50	49.66	35.46	30.16

C* - Control, W** - Waste dumping site, W 10*** – 10m away from the waste dumping site
a, b, c, d, e – values followed by the same letter are not significantly different at $p<0.05$

Table 4. Content of total heavy metals in soil

		Pb mg/kg	Zn mg/kg	Cu mg/kg	Ni mg/kg
Objects	C*	9.167 c	12.93 c	1.947 c	3.007 a
I factor	W**	15.54 b	35.80 a	14.17 a	4.557 a
	W 10***	9.270 c	23.65 b	1.317 c	3.930 a
Horizon	0-15	20.31 a	37.16 a	15.39 a	4.557 a
[cm]	15-30	9.217 c	22.05 b	1.208 c	5.057 a
II factor	30-50	4.543 d	13.17 c	0.934 c	2.880 a
Standard Deviation		10.07	17.51	13.02	1.04
CV %		88.72	72.56	222.79	27.15

C* - Control, W** - Waste dumping site, W 10*** – 10m away from the waste dumping site
a, b, c, d, e – values followed by the same letter are not significantly different at $p<0.05$

Table 5. Coefficients and degrees of soil contamination

Variable	Horizon cm	CF^{1}			(%) CF in C_{deg}^{2}		
		C	W	W10	C	W	W 10
Pb	0-15	1.166	4.362	1.536	31.94	22.42	30.02
	15-30	1.214	0.844	1.532	38.80	23.73	33.81
	30-50	0.740	0.487	0.542	33.45	18.57	27.20
Zn	0-15	0.774	3.683	1.737	21.20	18.93	33.95
	15-30	0.714	1.380	1.581	22.82	38.81	34.89
	30-50	0.667	0.904	0.625	30.15	34.48	31.36
Cu	0-15	0.793	10.125	0.630	21.72	52.04	12.31
	15-30	0.363	0.219	0.325	11.60	6.16	7.17
	30-50	0.350	0.213	0.183	13.79	8.12	9.18
Ni	0-15	0.918	1.288	1.213	25.12	6.62	23.71
	15-30	0.838	1.113	1.093	26.78	31.30	24.12
	30-50	0.500	1.018	0.643	22.60	38.83	32.26
C_{deg}	0-15	3.651	19.458	5.116			
	15-30	3.129	3.556	4.531			
	30-50	2.212	2.622	1.993			

^{1}(Contamination Factor, CF), ^{2}(Degree of Contamination, C_{deg}) C_{deg}=”(CF Pb,Zn,Cu,Ni)]

Table 6. Activity of dehydrogenases (DEH), catalase (CAT), alkaline phosphatases (AlP) and acid (AcP), arylsulphatase (ARS) in soil

		DEH	CAT	AlP	AcP	ARS
		mg TPF/kg/d	mgH_2O_2/g/h	mM pNP/kg/ h		
Character of	C^{*}	4.489 a	0.106 a	1.300 b	2.033 b	0.051a
objects	W^{**}	2.573 b	0.053 c	0.689 e	0.872 e	0.033 b
I factor	W 10^{***}	2.793 b	0.098 b	1.038 d	1.334 c	0.030 b
Horizon	0-15	4.360 a	0.166 a	1.435 a	2.373 a	0.028 c
[cm]	15-30	2.933 b	0.065 c	1.132 c	1.275 d	0.051 a
II factor	30-50	2.572 b	0.027 d	0.460 f	0.591 f	0.036 b
Standard Deviation		1.189	0.068	0.549	0.952	0.015
CV %		36.20	79.06	54.41	67.42	39.50

C^{*} - Control, W^{**} - Waste dumping site, W 10^{***} – 10m away from the waste dumping site
a, b, c, d, e, f – values followed by the same letter are not significantly different at $p<0.05$

Table 7. Correlation coefficients among the investigated parameters (*n=63*)

Variables		Equation	r	r^2
Dependent	Independent			
Lead	Total organic carbon	y=1.3678+2.4922x	0.763	0.581
Zinc	Total organic carbon	y=5.5485+4.6352x	0.816	0.665
Nickel	Total organic carbon	y=2.8106+0.2546x	0.752	0.565
Available phosphorus	Total organic carbon	y=8.0042+2.3254x	0.683	0.467
Catalase	Total organic carbon	y=0.0237+0.0156x	0.699	0.488
Acid phosphatase	Dehydrogenases	y=-1.153+624.263x	0.953	0.907
Alkaline phosphatase	Dehydrogenases	y=-0.249+306.059x	0.810	0.656
Hydrolytic acidity	Acid phosphatase	y= -0.1405+1.894x	0.798	0.636
Hydrolytic acidity	Sulphate	y=0.1172+0.5769x	0.916	0.840
Hydrolytic acidity	Dehydrogenases	y= -3.1251+1376.91x	0.885	0.783

contamination around the waste dumping sites was limited (Bielińska and Mocek-Płóciniak, 2009). Catalase is active over a wide pH range, and its activity does not drop until its pH is below 3.5. In the present research pH fell within the ranges pH_{H2O} 4.01-6.44 as well as pH_{KCl} 3.90-6.07. The greater the soil sampling depth, the lower the activity of the enzymes (Table 4), which is connected with the spatial distribution of humus, a decreasing amount of carbon substrates available to microorganisms and enzymes (Fierer *et al.*, 2003; Kizilkaya and Dengiz, 2010). The results of the activity of alkaline and acid phosphatase showed a high variation, which was confirmed by the values of the coefficient of variation (CV=54.41% as well as CV=67.42%).

A positive high dependence was also observed between the activity of acid phosphatase in soil and hydrolytic acidity (r=0.797; $P < 0.05$) since in acid soils the growth of the activity of acid phosphomonoesterase usually occurs. Similar results were recorded by Wyszkowska and Kucharski (2004). A high positive dependence was reported between the activity of dehydrogenases and acid phosphatase (r=0.952; $P<0.05$) and dehydrogenases and alkaline phosphatase (r=0.809; $P<0.05$) suggesting the microbiological origin of phosphatases as active dehydrogenases occur in soil as an integral part of undisturbed cells.

There was reported a high dependence between the content of total organic carbon compounds in soil and the activity of catalase (r=0.698, $P<0.05$). The relationships between catalase activity and soil organic matter have been described by Kizilkaya *et al.* (2004); Uzun and Uyanöz (2011). However, no dependence between the content of TOC and the activity of the other soil enzymes (dehydrogenase, alkaline and acid phosphatase, arylsulphatase) can be connected with a low share of humus substances in the total content of organic matter of the soils exposed to anthropogenic pressure.

A significant negative correlation was observed between the activities of catalase with clay contents in all the soils.

CONCLUSIONS

The research has demonstrated that the surface soil horizon which is found directly in the area of the effect of illegal waste dumping sites showed a greater concentration of heave metals. The waste deposited in the area of the waste dumping site did not have a considerable effect on the contamination of soils with heavy metals. The content of Pb, Zn, Cu and Ni in the soil samples qualifies the soils into the natural content category. The above contents of metals in the surface layer of sandy soils are a result of an increased amount of organic matter and its capacity for point-like retention of nutrients. The analysis of correlation confirmed the relationship between the content of carbon of organic compounds and the content of zinc, lead and nickel.

Neither was there noted an increased electrolytic conductivity which could point to a greater salinity of the soil environment.

A lack of a negative effect of the illegal waste dumping sites on the content of available forms of phosphorus, potassium and magnesium in the soils located about 10 m away from their edge shows that the effect of contamination in the vicinity of waste dumping sites is limited.

However, there was identified a high content of sulphates in the soil samples analysed. The highest content of sulphate sulphur assayed in the soil sampled in the control point corresponds to the content increased due to the human impact on the environment.

The highest activity of all the enzymes analysed: dehydrogenases, catalase, alkaline phosphatase, acid phosphatase and arylsulphatase was reported in the soil sampled from the control point not exposed to the effect of the waste. There was found no direct effect of illegal waste dumping sites on the activity of the enzymes analysed. However, such research should be continued as it facilitates an ecology-minded evaluation of the effects of a gradual accumulation of contamination in the soils surrounding illegal municipal waste dumping sites. The lower intensity of biochemical processes in soils due to deposited waste must have been due to a lack of the inflow of waste of organic origin to the soil environment.

REFERENCES

Amuno, S.A. (2011) Trace elements analysis and contamination degree of soils affected by municipal solid wastes. Journal of Applied Technology in Environmental Sanitation**, 1(4)**, 393-398.

Bardsley, C.E. and Lancaster, J.D. (1960) Determination of reserve sulfur and soluble sulfates in soil. Soil Science American Proceedings, **24**, 265-268.

Bartkowiak, A. and Lemanowicz, J. (2014) Application of biochemical testes to evaluate the pollution of the Unislaw Basin soils with heavy metals. International Journal of Environmental Research, **8(1)**, 93-100.

Bielińska, E.J. and Mocek-Płóciniak, A. (2009) Impact of uncontrolled waste dumping on soil chemical and biochemical properties. Archives of Environmental Protection, **35(3)**, 101-107.

Blair, G.J., Lefroy, R.D.B., Chinoim, N. and Anderson, G.C. (1994) The development of a soil test for sulphur. Norwegian Journal of Agricultural Sciences Supplement, **15**, 83-95.

Crock, J.G., and Severson, R. (1980) Four reference soil and rock samples for measuring element availability in the western energy regions. Geochemical Survey Circular, **841**, 1-16.

Diatta, J.B. (2012) Application of geochemical indices for assessing lead and cadmium contamination in recreational parks of the city Poznan, Ecological Chemistry and Engineering A, **19(1-2),** 35-43. doi: 10.2428/ecea.2012.19(01)003.

Dong, J., Wu, F. and Zhang, G. (2006) Influence of cadmium on antioxidant capacity and four microelement concentration in tomato seedlings *(Lycopersicon esculentum*). Chemosphere, **64**, 1659-1666.

Dz. U. No.165 item 1359 (2002) Regulation of the Minister of Environment dated 9 September 2002 on standards soil quality and land quality standards (in Polish).

Dz. U. item 228 (2013) Act of 25 January 2013 on Maintaining Cleanliness and Order in Communes (in Polish). Dz. U. No. 0 item 21 (2013) Act of 14 December 2012 on Waste Law (in Polish).

Fierer, N., Schimel, J.P. and Holden, P.A. (2003) Variations in microbial community composition through two soil depth profiles. Soil Biology Biochemistry, **35**, 167-176.

Håkanson, L. (1980) An Ecological Risk Index for Aquatic Pollution Control: A Sedimentological Approach. Water Research, **14**, 975–1001.

Ideriah, T.J.K., Harry, F.O., Stanley, H.O. and Igbara, J.K. (2010) Heavy Metal Contamination of Soils and Vegetation around Solid Waste Dumps in Port Harcourt, Nigeria. Journal of Applied Sciences and Environmental Management, **14(1)**, 101 – 109.

Islam, Md.S., Tusher, T.R., Mustawa, M. and Mamun, S. (2012) Investigation of soil quality and heavy metal concentrations from a waste dumping site of Konabari industrial area at Gazipur in Bangladesh. Journal of Environmental Science, Toxicology and Food Technology, **2(1)**, 1-7.

Johnson, J.I. and Temple, K.L. (1964) Some variables affecting the measurements of catalase activity in soil. Soil Science Society America, **28**, 207-216.

Kabata-Pendias, A. and Pendias, P. (2001) Trace Elements in Soils and Plants. 3re.ed., CRC Press.

Kandeler, E., Tscherko, D., Bruce, K.D., Stemmer, M., Hobbs, P.J. and Bardgett, R.D. (2000) The structure and function of the soil microbial community in microhabitats of a heavy metal polluted soil. Biology and Fertility of Soils, **32**, 390–400.

Kizilkaya, R., Aþkýn T., Bayrakli, B. and Saðlam, M. (2004) Microbiological characteristics of soils contaminated with heavy metals. European Journal of Soil Biology, **40**, 95–102.

Kizilkaya, R. and Dengiz, O. (2010).Variaton of land use and land cover effects on some soil physic-chemical characteristics and soil enzyme activity. Zemdirbyste-Agriculture, **97**, 15-24.

Kotuby-Amacher, J., Koenig, R. and Kitchen, B. (1997) Salinity and Plant Tolerance. Electronic Publication AG-SO-03, Utah State University Extension, Logan, UT, 84322.

Krzyżaniak, M. and Lemanowicz, J. (2013) Enzymatic activity of the Kuyavia Mollic Gleysols (Poland) against their chemical properties. Plant Soil Environmental, **59**, 359-365.

Lemanowicz, J.(2013) Mineral fertilization as a factor determining selected sorption properties of soil against the activity of phosphatases. Plant Soil Environmental, **59**, 439-445.

Lemanowicz, J. and Bartkowiak, A. (2013) Diagnosis of the content of selected heavy metals in the soils of the Pałuki region against their enzymatic activity. Archives of Environmental Protection, **39(3)**, 23-32. doi: 10.2478/aep-2013-0026.

Liu, J., Xie, J., Chu, Y., Sun, C., Chen, C. and Wang, Q. (2008) Combined effect of cypermethrin and copper on catalase activity in soil. Journal Soils Sediments, **8**, 327–332.

Longe, E.O. and Enekwechi, L.O. (2007) Investigation on potential groundwater impacts and influence of local hydrology on natural attenuation of leachate at a municipal landfill. International Journal of Environmental Science and Technology, **4(1**), 133-140.

Malinowski, R., Niedźwiecki, E., Meller, E., Sammel, A., Wojcieszczuk, M. and Jarnuszewski, G. (2012) Some chemical properties of sandy soils affected by uncontrolled dump sites in the west pomeranian province. Soil Science Annual, **63(2)**, 31-35 doi: 10.2478/v10239-012-0021-4.

Margesin, R., Zimmerbauer, A. and Schinner, F. (2000) Monitoring of bioremediation by soil biological activities. Chemosphere, **40**, 339–346.

Meller, E., Niedźwiecki, E., Protasowicki, M., Malinowski, R., Sammel, A. and Jarnuszewski, G. (2012) Influence of uncontrolled dump sites on some chemical properties of organic and mineral soils developed from clay and loam in west Pomeranian. Soil Science Annual, **63(2**), 36-41 doi: 10.2478/v10239-012-0022-3.

Motowicka-Terelak, T. and Terelak, H. (2000) The heavy metals and sulphur status of agricultural soils in Poland. M. Wilson, B. Maliszewska-Kordybach (Eds). In: Soil Quality, Sustainable Agriculture and Environmental Security in Central and Eastern Europe, Kluwer Academic Publishers Printed in Netherlands, 37-47.

Nannipieri, P., Ascher, J., Ceccherini, T., Landi, L., Pietramellara, G. and Renella, G. (2003) Microbial diversity and soil functions. European Journal of Soil Science, **54**, 655-670.

Ogundiran, O.O. and Afolabi, T.A. (2008) Assessment of the physicochemical parameters and heavy metal toxicity of leachate from municipal solid waste open dumpsite. International Journal of Environmental Science and Technology, **5(2**), 243-250.

Ostowska, D., Pietkiewicz, S., Ciesinski, M., Kucinska, K. and Gozdowaski, D. (2008) Biomass accumulation and absorption of Photosynthetic active radiation by rapeseed Plantd depending on sulphur fertilization. World Journal of Agriculture Sciences, **4(2**), 133-136.

PN-R-04020, (1994) Chemical and Agricultural Analysis. Determination of the content available magnesium. Polish Standards Committee, Warszawa. (in Polish).

PN-R-04022, (1996) Chemical and Agricultural Analysis – Determination of the content available potasium in mineral soils. Polish Standards Committee, Warszawa. (in Polish).

PN-R-04023, (1996) Chemical and Agricultural Analysis – Determination of the content available phosphorus in mineral soils. Polish Standards Committee, Warszawa. (in Polish).

Renella, G., Ortigoza, A.L.R., Landi, L. and Nannipieri, P. (2003) Additive effects of copper and zinc on cadmium toxicity on phosphatase activities and ATP content of soil as estimated by the ecological dose (ED50). Soil Biology Biochemistry, **35**, 1203–1210.

Scherer, H.W. (2009) Sulphur in soils. Journal of Plant Nutrition and Soil Science, **172**, 326–335.

Siwik–Ziomek, A., Koper, J. and Zamorski, R. (2010) The effect of long term fertilizationon arylsulphatase activity and sulphates (VI) content in a lessive soil. Chemistry and Ecology, **26**, Supplement 117-122.

Tabatabai, M.A. and Bremner, J.M. (1969) Use of p–nitrophenol phosphate for assay of soil phosphatase activity. Soil Biology Biochemistry, **1**, 301-307.

Tabatabai, M.A. and Bremner, J.M. (1970) Factors affecting soil arylsulfatase activity. Soil Science Society of America Proceedings, **34**, 427-429.

Thalmann, A. (1968) Zur methodic derestimung der Dehydrogenaseaktivität i Boden mittels Triphenyltetrazoliumchlorid (TTC). Landwirdschaft Forschung, **21**, 249-258.

Tengrui, L., Al-Harbawi, A.F., Lin, M.B., Jun, Z. and Long X.U. (2007) Characteristics of nitrogen removal from old landfill leachate by sequencing batch biofilm reactor. American Journal of Applied Sciences, **4(4**), 211-214.

Uzun, N. and Uyanöz, R. (2011) Determination of urease catalase activities and CO2 respiration in different soils obtained from in Semi Arid Region Konya, Turkey. Trends Soil Science Plant Nutrition Journal, **2(1**), 1-6.

Wyszkowska, J. and Kucharski, J. (2004) Biochemical and physicochemical properties of soil contaminated with herbicide triflurotox 250 EC. Polish Journal of Environmental Studies, **13**, 223–231.