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## THE RELATIONSHIP BETWEEN THE ACTIVITY OF DEHYDROGENASES AND PHOSPHATASES AND THE CONTENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN SOILS

### Summary

*The humus horizons of soils in 12 park gardens located in cities of eastern and south Poland and Upper Silesia were the objects of study. Gardens situated in city centres and suburbs were included in the test. The location of park gardens and the related intensity of anthropogenic pressure were factors significantly affecting the activity of dehydrogenases and phosphatases, and the PAH content in the studied urban soils. The relationship between the dehydrogenase and phosphatases activity and the PAH content in soils varied, depending on the location of the park gardens, which shows that it is determined mostly by the condition of the environment, as shaped by the intensity of anthropogenic pressure.*

**Key words:** dehydrogenases activity, phosphatases activity, PAHs, urban soils

## RELACJE MIĘDZY AKTYWNOŚCIĄ DEHYDROGENAZ I FOSFATAZ A ZAWARTOŚCIĄ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W GLEBACH MIEJSKICH

### Streszczenie

*Obiektami badań były poziomy próchniczne gleb 12 parków zlokalizowanych na obszarze Górnego Śląska i miast południowej i wschodniej Polski. Badaniami objęto jednocześnie parki położone w centrach miast oraz na przedmieściach. Lokalizacja ogrodów parkowych i związana z nią intensywność presji antropogenicznej była czynnikiem wpływającym istotnie na aktywność dehydrogenaz i fosfataz oraz zawartość WWA w badanych glebach miejskich. Relacje między aktywnością dehydrogenaz i fosfataz a zawartością WWA w glebach miały zróżnicowany charakter w zależności od lokalizacji ogrodów parkowych, co świadczy, że są one determinowane głównie stanem środowiska kształtowanego intensywnością presji antropogenicznej.*

**Słowa kluczowe:** aktywność dehydrogenaz, aktywność fosfataz, WWA, gleby miejskie

### 1. Introduction

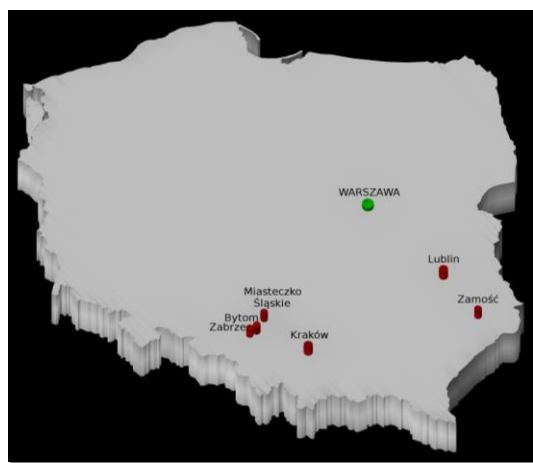
Soil quality evaluation is not easy due to the complexity of the soil environment, changeability of the existing physico-chemical and biological conditions and the capability of soils for compensation of these transformations. A key role is played, in this respect, by changing conditions associated with the buffer capacity of the sorptive complex as well as with the retention and accumulation of constituents in soil [4, 10]. Evidence of Polycyclic Aromatic Hydrocarbons (PAHs) in the soil does not always fully reflect the real ecotoxicological threat associated with their presence in the environment, since incomplete degradation of such compounds may lead to the formation of metabolites with properties more harmful than those of the contaminants from which they were created [11]. Changes in the activity of soil enzymes reflect the disturbances in the environment influencing the soil as well as plants [7, 16] Occurring in microorganisms, dehydrogenases - enzymes connected with carbon circulation - reflect an environmental pollution level that poses a threat to living organisms, regardless of their quantity [20]. The activity of phosphatases may be a good indicator of the soil polluted with polycyclic aromatic hydrocarbons (PAHs) [3]. The results obtained by Bielińska et al. [5] also confirmed the sensitivity of phosphatases to

content of PAHs in soils. The objective of the study was to investigate the potential relationship between dehydrogenases and phosphatases activity and PAHs content in the soils of parks situated in Upper Silesia, and in the cities of Eastern and Southern Poland.

### 2. Materials and Methods

The studied objects were the humus levels of soils in 12 parks located in the area of the Upper Silesia and cities of the Southern and Eastern Poland (Figure 1). The studies simultaneously covered parks located in the city centres, on territories with strong pressure of anthropogenic contaminations and on the outskirts of cities, of similar physiographic conditions, but not subject to such strong anthropogenic factor. Research works were carried out within the administrative borders of the following cities: Bytom, Cracow, Lublin, Miasteczko Śląskie, Zabrze, and Zamość. According to the classification of urban soils by Burghardt [8] the soils of studied parks were Hortisol. On the territory of each of the 12 selected objects one representative surface was chosen within the large lawns situated in the central part of parks. The analysed soil sample was an average of 5 samples collected from each surface. Soil samples for laboratory analyses from the selected surfaces were collected in

May of 2014. In soil samples, activities of the following enzymes were determined: dehydrogenases [19], acid phosphatase and alkaline phosphatase [18], while the PAHs content was determined by means of HPLC with UV detection (254 nm) [15]. Statistical analysis was conducted using the Statistica package [17].



Source: Own work / Źródło: opracowanie własne

Figure 1. The localizations of sampling sites

### 3. Results and Discussion

The studies showed high enzymatic inactivation of soils on territories under high pressure of the anthropogenic factor (Table 1). The activity of studied enzymes in soils of park gardens situated on the outskirts was several times greater than in soils of city-centre parks – dehydrogenases ca. 3-4 times, and phosphatases ca. 2 times (Table 1). Earlier studies of the author [2, 6] show that great weakening of the enzymatic activity of soils in city centres is strictly related with the contamination of soil environment with heavy metals and Polycyclic Aromatic Hydrocarbons, inhibiting the biosynthesis of enzymes with soil microorganisms [12, 21]. The lowest enzymatic activity characterised soils from the Upper Silesia (Table 1). In soils of this area (Bytom, Miasteczko Śląskie, Zabrze) the activity of enzymes was several times lower than in soils of parks located in Kraków and cities on the territory of the Eastern Poland (Lublin, Zamość). Particularly high

inactivation was observed for dehydrogenases, especially in city centres, where the activity of this group of enzymes was in the range of 0.54-0.61  $\text{cm}^3 \text{H}_2 \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$  (Table 1). It means lowered general microbiological activity of the environment caused by strong human pressure generating disturbances in groups of microorganisms and intensification of biochemical processes [13, 14].

The total content of PAHs in the studied soils ranged considerably, but clearly depended on the intensity of anthropogenic pressure (Table 2). The greatest PAH amounts were found in soils coming from Upper Silesia. The content of 16 PAHs identified in soils taken from downtown parks exceeded 19,000-20,000  $\mu\text{g} \cdot \text{kg}^{-1}$ , and in soils of parks situated on the outskirts of those cities it ranged from approx. 4,000 to 5,000  $\mu\text{g} \cdot \text{kg}^{-1}$ . Soils from other study areas had lower PAHs content ( $< 3,000 \mu\text{g} \cdot \text{kg}^{-1}$ ). Analysis of individual PAHs showed a predominance of 4-ring hydrocarbons, whose content, in the majority of samples, exceeded 30% of the total content of the studied compounds. The lowest content was observed for 3-ring compounds, whose share did not exceed 10% of the total content of the PAHs under study (Figure 2). An analysis of results showed that the dominant source of PAHs in the urban soils studied results from processes connected with carbon combustion, as confirmed by the phenanthrene/anthracene ratios, which did not exceed 10 (ranging instead from 1.2 to 4.4), and in the case of the fluoranthene/pyrene ratio, were greater than 1.

The study evaluated the relationship between dehydrogenases and phosphatases activity and PAHs content based on correlation coefficients (Table 3). This evaluation was undertaken for the whole study area, as well as by the location of park gardens, i.e. by the intensity of anthropogenic pressure. A significant negative relationship between dehydrogenase and phosphatases activity and PAHs content was found only in the case of soils coming from parks situated in downtown zones. Conversely, soils of parks situated on the outskirts exhibited the opposite tendency, even though the correlation coefficients were not statistically significant (Tab. 3). This may prove that some microflora have adapted to the presence of PAHs, especially in soils with low PAHs contamination, and used them as a source of carbon and energy [1, 9]. Wang et al. [21] demonstrated a totally destructive impact of the hydrocarbon mixture on the activity of soil dehydrogenases.

Table 1. Enzymatic activity of soils

Locality No	Dehydrogenases	Acid Phosphatase	Alkaline Phosphatase
Bytom 1	0.54a	4.98a	3.22a
Bytom 2	2.39b	10.27ab	8.34ab
Kraków 1	1.69b	27.94b	14.98b
Kraków 2	5.32c	60.12c	35.11c
Lublin 1	1.95b	37.49bc	14.61b
Lublin 2	5.61c	71.88cd	31.78c
Miasteczko Śląskie 1	0.63a	7.39a	6.23a
Miasteczko Śląskie 2	1.82b	14.16ab	12.90b
Zabrze 1	0.61a	5.56a	3.97a
Zabrze 2	2.69b	11.92ab	9.25ab
Zamość 1	2.78b	52.85c	20.67cd
Zamość 2	8.43d	99.12d	39.65d

Dehydrogenases in  $\text{cm}^3 \text{H}_2 \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$ , Acid Phosphatase and Alkaline Phosphatase in  $\text{mmol PNP} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$ ; values in the column followed by the same letter are not significantly at  $p < 0,05$ , „t”- test; 1 – city centre; 2 – outskirts of the city

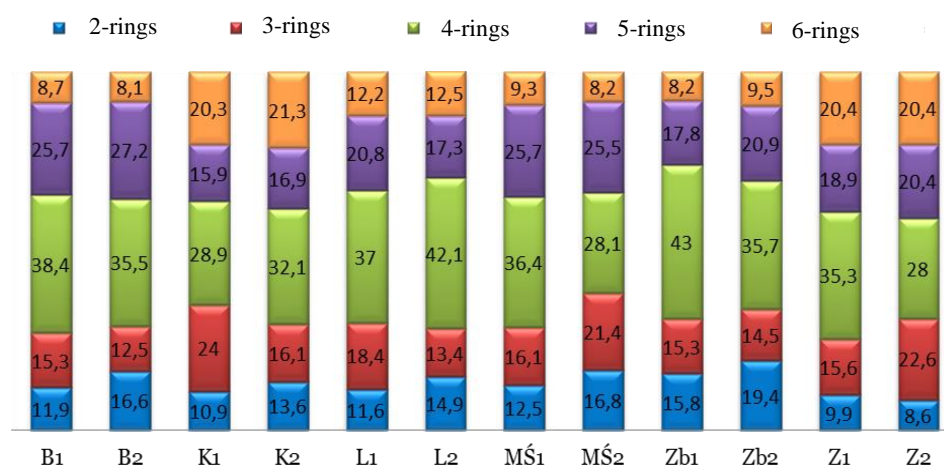
Source: Own work / Źródło: opracowanie własne

Table 2. Polycyclic aromatic hydrocarbons (PAHs) content in soils in  $\mu\text{g}\cdot\text{kg}^{-1}$  s.d.

PAHs	Object – city centre					
	Bytom	Kraków	Lublin	Miasteczko Śl.	Zabrze	Zamość
Na	2932	201	322	2693	3106	59
Ace	2544	242	296	2290	1824	43
Ac	0	119	34	0	0	29
Fl	465	33	69	382	377	0
Fen	608	28	92	572	568	16
Ant	153	19	21	234	239	5
Fln	3667	188	335	2950	2986	69
Pir	3041	171	278	2646	2144	36
BaA	1518	95	223	1289	2128	25
Ch	1229	76	192	983	1219	81
BbF	4486	192	226	3992	1119	71
BkF	1443	89	143	1361	1305	42
BaP	389	12	209	210	1088	0
DahA	174	217	44	199	366	43
BghiP	968	93	142	896	553	33
Ind	1012	62	153	909	694	46
$\Sigma 16\text{PAHs}$	24629	1837	2779	21606	19716	598
PAHs	Object – outskirts of the city					
	Bytom	Kraków	Lublin	Miasteczko Śl.	Zabrze	Zamość
Na	873	160	81	899	852	8
Ace	408	141	29	857	339	9
Ac	0	0	5	0	0	6
Fl	98	16	18	111	152	0
Fen	115	20	7	149	116	4
Ant	39	12	3	30	32	2
Fln	511	143	74	608	417	9
Pir	453	129	62	456	409	8
BaA	328	48	52	233	168	3
Ch	578	56	41	210	572	6
BbF	1124	141	11	986	344	11
BkF	263	52	67	328	302	8
BaP	45	5	16	52	273	0
DahA	68	124	8	36	121	2
BghiP	191	77	31	215	130	11
Ind	169	49	29	188	165	6
$\Sigma 16\text{PAHs}$	5263	1173	544	5358	4392	93

PAHs: Na – naphthalene, Ace – acenaphthylene, Ac – acenaphthalene, Fl – fluorene, Fen – fenanthrene, An – anthracene, Fln – fluoranthene, Pir – pirenene, BaA – benzo[a]anthracene, Ch – chrysene, BbF – benzo[b]fluoranthene, BkF – benzo[k]fluoranthene, BaP – benzo[a]pyrene, DahA – dibenzo[a,h]anthracene, BghiP – benzo[ghi]perylene, Ind – indeno[1,2,3-cd]pyrene

Source: Own work / Źródło: opracowanie własne



B – Bytom, K – Kraków, L – Lublin, MŚ – Miasteczko Śląskie, Zb – Zabrze, Z – Zamość; 1 – city centre, 2 – outskirts of city

Source: Own work / Źródło: opracowanie własne

Figure 2. Contribution (%) of individual PAHs in investigated soils in relation to number of rings

Table 3. Correlation coefficients between dehydrogenases and phosphatases activity and Polycyclic Aromatic Hydrocarbons ( $\Sigma 16\text{PAHs}$ ,  $N = 9$ )

Enzymes	Polycyclic Aromatic Hydrocarbons ( $\Sigma 16\text{PAHs}$ )	
	city centre	outskirts of the city
Dehydrogenases	(-)0,62	n.s.
Acid Phosphatase	(-)0,52	n.s.
Alkaline Phosphatase	(-)0,51	n.s.

\* significant at  $p = 0.05$ , n.s. = non-significant

Source: Own work / Źródło: opracowanie własne

#### 4. Conclusions

1. The location of park gardens and the related intensity of anthropogenic pressure were factors significantly affecting the activity of dehydrogenases and phosphatases and the PAHs content in the urban soils studied.
2. Coefficients calculated from the phenanthrene/anthracene and fluoranthene/pyrene ratios show that the main source of PAHs in the studied soils results from processes connected with carbon combustion.
3. The relationship between the dehydrogenase and phosphatase activity and the PAH content in soils varied, depending on the location of the park gardens, which shows that it is determined mostly by the condition of the environment, as shaped by the intensity of anthropogenic pressure.

#### 5. References

- [1] Baran S., Bielińska E.J., Oleszczuk P.: 2004. Enzymatic activity in an airfield soil polluted with polycyclic aromatic hydrocarbons. *Geoderma* 118, 221-232, 2004.
- [2] Baran S., Bielińska E.J., Kawecka-Radomska M.: Content of heavy metals in urban park influenced by various anthropogenic changes. *Zesz. Naukowe Uniwersytetu Zielonogórskiego*, 137, Inżynieria Środowiska, 17, 131-137, 2010.
- [3] Bielińska E.J., Mocek-Płóćiniak A.: Fosfatazy w środowisku glebowym. Monografia, Wydawnictwo Uniwersytetu Przyrodniczego w Poznaniu, Poznań 2009.
- [4] Bielińska E.J., Pranagal J.: Enzymatic activity of soil contaminated with triazine herbicides. *Polish J. of Environ. Stud.* 16, 2, s. 295-300, 2007.
- [5] Bielińska E.J., Mocek-Płóćiniak A., Kaczmarek Z.: Indices of the eco-chemical condition of forest soils on a large-area forest fire. *Polish J. of Environ. Stud.* 17, 5, 665-671, 2008.
- [6] Bielińska E.J., Kawecka-Radomska M., Kłos A.: Impact of urban factors on the content of Polycyclic Aromatic Hydrocarbons in soils of park gardens. *Rocz. Glebozn.*, 62, 2, 16-22, 2011.
- [7] Bielińska E.J., Puchała A., Wnuczek A.: Enzymatyczne wskaźniki przeobrażeń gleb na terenach zurbanizowanych. *Journal of Research and Applications in Agricultural Engineering* 55 (3), 20-23, 2012.
- [8] Burghardt W.: Boden und Böden in der Stadt. Substrate der Bodenbildung urban, gewerblich und industriell überformter Flächen [In: *Urbaner Bodenschutz*]. Springer Verlag, 7-44, 1996.
- [9] Byun, I.-G., Nam, H.-K., Song S., K., Hwang I.-S., Lee T.-H., Park T.-J., 2005. Monitoring of bioventing process for diesel-contaminated soil by dehydrogenase activity, microbial counts and the ratio of n-alkanes/isoprenoid. *Korean J. Chem. Eng.* 22(6), 917-921.
- [10] Janowska E., Czępińska-Kamińska D.: Trace Elements Dynamics in the Upper Soil Horizons of the Puszcza Kampinowska Biosphere Reserve. *Polish J. of Environ. Stud.*, 13, 367-371, 2005.
- [11] Meyer S., Steinhart H.: Fate of PAHs and hetero-PAHs during biodegradation in a model soil compost-system: formation of extractable metabolites. *Water Air Soil Poll.* 132, 215-231, 2001.
- [12] Moreno J.L., Bastida F., Ros M., Hernandez T., Garcia C.: Soil organic carbon buffers heavy metal contamination on semiarid soils: Effect of different metal thresholds levels on soil microbial activity. *Eur. J. Soil Biol.*, 45, 220-228, 2009.
- [13] Nannipieri P., Kandler E., Ruggiero P.: Enzyme activities and microbiological and biochemical processes in soil. IN. *Enzymes in the environment. Activity, Ecology, and Applications*. (Eds. Burns R., Dick R.), New York, 1-33, 2002.
- [14] Nannipieri P., Ascher J., Ceccherini M.T., Landi L., Pietramellara G., Renella G.: Microbial diversity and soil functions. *Eur. J. Soil Sci.*, 54, 655-670, 2003.
- [15] Oleszczuk P., Baran S.: Degradation of individual polycyclic aromatic hydrocarbons (PAHs) in soil polluted with aircraft fuel. *Pol. J. Environ Stud.* 12, 431-437, 2003.
- [16] Puglisi E., Del Re A.A.M., Rao M.A., Gianfreda L.: Development and validation of numerical indexes integrating enzyme activities of soils. *Soil Biol. Biochem.* 38, 1673-1681, 2006.
- [17] Statistica: Data analysis, version 8.0. [www.statsoft.pl](http://www.statsoft.pl). StatSoft, Inc., 2007.
- [18] Tabatabai M.A., Bremner J.M.: Use of p-nitrophenyl phosphate for assay of soil phosphatase activity. *Soil Biol. Biochem.* 1, s. 301-307, 1969.
- [19] Thalmann A.: Zur Methodik der Bestimmung der Dehydrogenase Aktivität in Boden mittels Triphenyltetrazoliumchlorid (TTC). *Landwirtsch. Forsch.* 21, 249-258, 1968.
- [20] Turgay O.C., Erdogan E.E., Karaca A.: Effect of humic deposit (leonardite) on degradation of semi-volatile and heavy hydrocarbons and soil quality in crude-oil-contaminated soil. *Environ. Monit. Assess.* 170, 45-58, 2010.
- [21] Wang J., Zhan X., Zhou L., Lin Y.: Biological indicators capable of assessing thermal treatment efficiency of hydrocarbon mixture-contaminated soil. *Chemosphere* 80, 837-844, 2010.