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Ecochemical condition of soils located in river valleys of urban areas

Ekochemiczny stan gleb położonych w dolinach rzecznych na terenach miejskich

Summary. The paper deals with assessment of the ecochemical condition of soils within river valleys in the areas of selected cities of the Lublin region. The assessment was based on the determination of enzymatic activity and content of polycyclic aromatic hydrocarbons (PAHs) in soils located directly in river valleys and out of their range. The study was located in valleys of the most important rivers of Lublin region: Vistula, Wieprz, and Bystrzyca within the administrative borders of Kazimierz Dolny, Krasnystaw, and Lublin, respectively. The research areas were selected around busy roads and bridges with a potentially high level of anthropogenic pressure. The present research showed that the enzymatic activity of soils located in river valleys was about 1.5 times higher than in the soils beyond their reach. The determined content of PAHs in the soils from the river valleys was clearly lower than in the soils out of their range, which proves that habitat conditions of river valleys have a beneficial effect on detoxification of the soil environment.

Key words: anthropopressure, river valleys, soils, enzymatic activity, detoxication, PAHs

INTRODUCTION

River valleys, i.e. the most open spaces in the urban tissue, play an important role in creating and shaping the urban environment. They function as bands stabilizing the cli-

matic conditions, producing oxygen, retaining water, and constituting a refuge of many species of flora and fauna. Due to numerous barriers related to urbanization and infrastructure development, river valleys within urban borders are often the only route for the spread of species [Zimny 2005, Szczepańska 2009]. They are also valuable refuges of the city's green spaces [Trzaskowicka et al. 2009]. In the 1970s and 1980s, the multi-directional values of riverside areas in cities began to be seen where the whole industry was located in the past and water was used for production and as a source of energy. After withdrawal of all industrial and economic activities from the riverside areas, river valleys became degraded in most Polish cities, posing a serious burden for local governments [Janucha-Szostka 2011].

Soils are the basis for functioning and an integral part of urban ecosystems [Stuczyński et al. 2008]. Research in the field of soil quality assessment within river valleys is important from the point of view of ecological and landscape problems and their consequences for the entire city area. In contamination of the urban environment, the dominant role is played by road transport generating soil pollution with polycyclic aromatic hydrocarbons (PAHs) [Bielińska et al. 2018]. These xenobiotics are subject to various changes in the soil environment. Some of them are easily decomposed, volatilized, and leached, while others are subject to biological sorption or strongly combine with soil components. Many chemical compounds become toxic or mutagenic after metabolic transformations in living organisms [Bielińska and Mocek-Płóćiniak 2009]. These compounds are not determined during routine analysis. Therefore, in the assessment of the pollution status of urban soils, it is advisable to apply an integrated research system based on the use of chemical analytics and biological tests. It is important to determine the level of pollution that causes permanent disturbances in homeostasis in the soil environment and threatens living organisms. Assessment of the impact of anthropogenic pollution on changes in the biological status of soils is possible through measuring the activity of a number of soil enzymes [Bielińska et al. 2018]. The aim of the work is to assess the ecochemical state of soils within river valleys in the areas of selected cities in the Lublin region. This assessment was made by determination of enzymatic activity and the content of polycyclic aromatic hydrocarbons (PAHs) in soils located directly in river valleys and out of their range.

MATERIAL AND METHODS

The research was carried out in the valleys of rivers that are most important for the Lublin region: Vistula, Wieprz, and Bystrzyca within the administrative boundaries of Kazimierz Dolny (51°18'58.7"N 21°55'23.2"E), Krasnystaw (50°59'8.4"N 23°10'36.2"E), and Lublin (51°14'22.5"N 22°33'33.3"E), respectively. The research areas were selected around busy roads and bridges with a potentially high level of anthropogenic pressure. Soils located directly in the river valleys and beyond their reach at a distance of about 100 m from their edge were the objects in this study. The soils in the areas covered by the study developed of silty formation; the soils of river valleys were classified as lessive rainfall-gley soils (Stagnic Luvisol – LVst), while the soils beyond the range of the valleys were typical lessive soils (Haplic Luvisol – LVha) [Polish Soil Classification 2011, Soil Survey Staff 2014]. The basic chemical properties of the investigated soils are shown in Tab. 1.

Table 1. Basic chemical properties of studied soils

Locality	Areas	pH	Corg	Nt	C : N
		KCl	(g · kg ⁻¹)		
Kazimierz Dolny	I A	6.30	21.86	1.68	13.01
	I B	6.94	19.74	2.20	8.97
Krasnystaw	II A	6.48	20.09	1.52	13.21
	II B	7.05	18.90	2.12	8.91
Lublin	III A	6.50	18.22	1.38	13.20
	III B	7.34	12.48	1.43	8.72

A – areas of river valleys; B – areas beyond the reach of river valleys

The data provided in Tab. 1 show that the soils from the river valleys are slightly acidic: pH_{KCl} 6.30–6.50, whereas the soils beyond the valley range exhibit clearly higher values of pH_{KCl} : 6.94–7.34. Alkalinization of urban soils is associated with the precipitation of alkaline dust and the use of snow removal agents. The values of the C : N ratio in the soils beyond the range of the river valleys were clearly higher than in the soils from the river valleys (Tab. 1). This is associated with an increased inflow of organic matter of anthropogenic origin to urban soils, the so-called *black coal*, i.e. the remnant of incomplete combustion of biomass and fuels containing soot and charcoal [Oleszczuk 2007].

Soil samples for the tests were taken from a depth of 0–25 cm in the spring 2018. Tab. 2 presents the characteristics of the soil sampling sites with indication of possible sources of contamination.

Table 2. Characteristics of soil sampling sites

Area	Locality	Source of pollution
I A; I B	Kazimierz Dolny	cars, buses, river transport, increased tourist traffic, dense buildings
II A; II B	Krasnystaw	cars and trucks, buses, dense buildings, occasional events (Chmielaki beer event)
III A; III B	Lublin	cars and trucks, city and intercity buses, bicycle route, sporting events

A – areas of river valleys; B – areas beyond the reach of river valleys

The following enzymes were determined: dehydrogenases [Thalmann 1968], acid phosphatase and alkaline phosphatase [Tabatabai and Bremner 1969], and urease [Zantua and Bremner 1975]. These enzymes are involved directly in the biogeochemical carbon cycle (dehydrogenases), nitrogen cycle (urease), and phosphorus cycle (phosphatase) in ecosystems. Additionally, they respond clearly to stress factors, and the magnitude of changes in their activity is related to the intensity of the influencing factors [Russel et al. 2006].

The PAH content in the studied soils was determined by means of HPLC with UV detection (254 nm) according to the methodology developed by Baran and Oleszczuk [2001]. Soil samples (30 g) were extracted with dichloromethane in an ultrasonic bath (Sonic-3, Polsonic). The obtained extract was centrifuged and then evaporated to dryness. After dissolution, the residue was purified by solid phase extraction using C18 columns. Determination of PAHs was performed on a liquid chromatograph (ThermoSeparation Product).

Each analyzed soil sample was the average of 5 samples taken from each surface. All determinations were carried out in three replicates. Statistical analysis of the research results was carried out using the Microsoft Office Excel 2003 spreadsheet and Statistica ver. 10 PL software. The significance of differences between mean values was verified on the basis of the t-Tukey test at the significance level $\alpha \leq 0.05$. In order to assess the relationship between the PAH content and the activity of the studied enzymes, values of Pearson's linear correlation coefficients (r) were calculated at the significance level $p < 0.05$. The work assumes a maximum 5% spread between measurements in chemical analysis.

RESULTS AND DISCUSSION

The enzyme activity in the studied soils varied significantly depending on the location of the research areas. The intensity and direction of the observed changes was dependent on the type of the enzyme tested (Tab. 3).

The activity of dehydrogenases, acid phosphatase, and alkaline phosphatase in soils from Krasnystaw and Lublin (areas II and III) was significantly lower than in soils located in the area of Kazimierz Dolny. The lowest activity of these enzymes was exhibited by the soils from the Lublin area (Tab. 3). The lower enzymatic activity of the soils from areas II and III was associated with increased anthropogenic pressure reflected in the increased inflow of PAHs to the soil environment (Tab. 4). Data presented by many authors [Maliszewska-Kordybach and Smreczak 1997, Caravaca and Rodán 2003, Baran et al. 2004, Wyszowska et al. 2006, Bielińska et al. 2012] confirm the special sensitivity of dehydrogenases and phosphatases to soil pollution with PAHs. Their activity can be used as an indicator of soil environment pollution with these xenobiotics [Bielińska et al. 2014, 2018].

Table 3. Enzymatic activity of studied soils

Locality	Areas	ADh	PhacA	PhalA	AU
Kazimierz Dolny	I A	7.64e	10.85f	8.89f	9.30b
	I B	5.08c	7.04d	5.78d	6.18a
	\bar{x}	6.36d	8.94e	7.33e	7.69a
Krasnystaw	II A	5.14c	7.30d	6.01d	10.32b
	II B	3.42b	4.82b	3.97b	6.70b
	\bar{x}	4.28bc	6.06c	4.99c	8.51a
Lublin	III A	3.31b	4.70b	3.95b	11.71b
	III B	2.18a	3.35a	2.77a	7.76a
	\bar{x}	2.74a	4.02a	3.36a	9.73b

DhA – dehydrogenases in $\text{mg TPF} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$; PhacA and PhalA – acid and alkaline phosphatase in $\text{mg PNP} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$, UA – urease in $\text{mg N-NH}_4^+ \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$. Means followed by the same letters do not differ significantly ($p > 0.05$). A – areas of river valleys; B – areas beyond the reach of river valleys

During the observation period, no univocal influence of the research location (Kazimierz Dolny, Krasnystaw, and Lublin) on urease activity (Tab. 3) was found. Urease is resistant to external factors and an increase in its activity is observed even in extreme conditions. The only factor limiting urease activity is the availability of the urea substrate, because as an extracellular enzyme, it is synthesized only in its presence [Carbrera et al. 1994]. Especially large urban agglomerations are significant producers of urea. The source of urea in urban soils include e.g. animal droppings, household waste, fragments of tissues and cells of micro-, meso-, and soil

macrofauna, and plant debris. Based on urease activity, the degree of anthropogenization of the soil environment can be assessed [Bielńska et al. 2014].

In all cases, there was a significant stimulating effect of the river valley habitats on the activity of the analyzed enzymes. The activity of the studied enzymes in the soils from the river valleys was about 1.5 times higher than in the soils beyond their reach (Tab. 3). This may be related to the presence of abundant vegetation in river valleys. Higher plants can directly and indirectly enrich the soil with enzymes. Litter, plant debris, and roots are the direct sources of enzymes. After decay, cells of higher plants undergo autolysis resulting in release of their content, including enzymes, into the soil. The indirect influence of plants is based on the stimulation of the synthesis of microbial enzymes by plant residues and root exudates. Similar to plants, also mesofauna contributes to the soil enzyme pool [Bielńska et al. 2014]. An important role is played by microorganisms that represent PGPR – *Plant Growth Promoting Rhizobacteria* [Kohler et al. 2009]. Besides bacteriorrhiza and mycorrhiza as well as the association of microorganisms with plants, the influence of the root system on the physical properties of soil cannot be neglected, since it plays a role in drainage, allowing appropriate oxygenation of soils, which stimulates enzyme activity. Other factors stimulating the enzymatic activity of soils in river valleys include relatively favorable local soil and habitat conditions. This is evidenced by the lower PAH content, lower pH_{KCl} values, and a narrower C:N ratio in the river valley soils than in the non-valley soils (Tabs. 1 and 4), as well as the lower amplitude of seasonal changes in soil temperature and humidity [Zimny 2005]. The soils in the studied areas were characterized by remarkable diversity of the content of PAHs (Tab. 4). The highest total PAH content was found in soil originating from the Lublin area.

Table 4. PAHs content in studied soils ($\mu\text{g}\cdot\text{kg}^{-1}$)

PAHs	Locality					
	Kazimierz Dolny		Krasnystaw		Lublin	
	areas					
	A	B	A	B	A	B
Na	171	184	86	106	181	209
Ace	33	36	41	52	78	80
Ac	52	56	48	50	94	111
Fl	132	150	172	197	294	330
Fen	70	80	120	138	390	420
Ant	8	9	24	16	41	48
Fln	68	79	161	172	443	542
Pir	72	82	180	204	492	525
BaA	9	11	42	44	122	140
Ch	42	42	57	58	137	144
BbF	11	11	33	33	128	138
BkF	12	13	29	38	65	68
BaP	11	17	12	18	34	52
DahA	28	32	22	19	26	27
BghiP	3	5	5	8	14	22
Ind	11	15	12	15	33	39
$\Sigma 16\text{PAHs}$	733	822	1044	1168	2572	2895

Na – naphthalene, Ace – acenaphthalene, Ac – acenaphthylene, Fl – fluorene, Phen – phenanthrene, Ant – anthracene, Fluo – fluoranthene, Pyr – pyrene, 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

A – areas of river valleys; B – areas beyond the reach of river valleys

The PAH content determined in this area exceeded the value of $2500 \mu\text{g}\cdot\text{kg}^{-1}$ and was about 3.5 and 2.5 times higher than in the soil from the area of Kazimierz Dolny and Krasnystaw, respectively (Tab. 4). According to the classification proposed by Maliszewska-Kordybach [1996], soils from the city of Lublin and Krasnystaw belong to the polluted soil group and the soil originating from the area of Kazimierz Dolny represents slightly contaminated soils. In all cases, the content of PAHs determined in the soils of the river valleys was lower than in the soils located out of their range (Tab. 4). The reduced level of PAHs in the river valley soils may be related to their physical, chemical, and biological transformations and the uptake of these compounds by plant roots [Sample et al. 2003, Oleszczuk and Baran 2005]. This trend may also be related to the fact that river valleys are open spaces in the urban tissue, where emitted pollutants are transmitted by long-range air currents [Kluska and Kroszczyński 2000, Futa et al. 2016]. This suggestion is also confirmed by the ca. 1.5 times lower content of benzo(*a*)pyrene and benzo(*ghi*)perylene in the soil samples from the river valleys, compared with the soils out of their range (Tab. 4). These PAHs are emitted on very fine dust particles and can be effectively transferred over long distances [Bielińska et al. 2018].

In all cases, the analysis of individual PAHs showed predominance of 2–4 ring hydrocarbons: naphthalene, fluorene, phenanthrene, fluoranthene, and pyrene, the content of which in the studied soils accounted for approximately 70% of all PAHs (Tab. 4). As demonstrated in other studies [Baran and Oleszczuk 2001, Bielińska et al. 2018], the presence of 2–4 ring PAHs in the environment is associated with low emission. The total level of PAHs with the strongest carcinogenic and mutagenic effects (benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenz(*a,h*)anthracene, indeno(*1,2,3-cd*)pyrene) did not exceed 20% of the total content of compounds determined in the studied soils (Tab. 5).

Table 5. Share (%) of carcinogenic PAHs in total PAHs determined

WWA	Locality					
	Kazimierz Dolny		Krasnystaw		Lublin	
	areas					
	A	B	A	B	A	B
BaA	1.23	1.34	4.02	3.77	4.74	4.84
BbF	1.50	1.34	3.16	2.83	4.98	4.77
BkF	1.64	1.58	2.78	3.25	2.53	2.35
BaP	1.50	2.07	1.15	1.54	1.32	1.80
DahA	3.82	3.89	2.11	1.63	1.01	0.93
Ind	1.50	1.82	1.15	1.28	1.28	1.35
$\Sigma 16\text{PAHs}$	11.19	12.04	14.37	14.30	15.86	16.03

BaA – benzo(*a*)anthracene, BbF – benzo(*b*)fluoranthene, BkF – benzo(*k*)fluoranthene, BaP – benzo(*a*)pyrene, DahA – dibenzo(*a,h*)anthracene, Ind – indeno(*1,2,3-cd*)pyrene

A – areas of river valleys; B – areas beyond the reach of river valleys

Table 6. Significant (at $\alpha = 0.05$) values of correlation coefficients between the $\Sigma 16$ PAHs and individual PAHs content and investigated properties of the soils) N = 12

PAHs	DhA	PhacA	PhalA
Ace	-0.58	-0.68	-0.54
Fl	-0.59	-0.66	-0.56
Phen	-0.69	-0.61	-0.77
Ant	-0.65	-0.58	-0.72
Fluo	-0.64	-0.59	-0.74
Pyr	-0.62	-0.72	-0.59
BaA	-0.71	-0.62	-0.78
Ch	-0.68	-0.59	-0.76
BbF	-0.68	-0.60	-0.77
BkF	-0.65	-0.58	-0.73
BaP	-0.62	-0.71	-0.56
DahA	-0.62	-0.68	-0.52
BghiP	-0.61	-0.68	-0.54
Ind	-0.59	-0.63	-0.55
$\Sigma 16$ PAHs	-0.56	-0.62	-0.58

DhA – dehydrogenases, PhacA and PhalA – acid and alkaline phosphatase

Ace – acenaphthene, Fl – fluorene, Phen – phenanthrene, Ant – anthracene, Fluo – fluoranthene, Pyr – pyrene, 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

The assessment of the relationships between the analyzed soil parameters showed a significant negative correlation between the sum of 16 PAHs and all PAH compounds determined vs. the activity of dehydrogenases and phosphatases. The effect of PAHs on urease activity was not significant (Tab. 6), which confirms the special sensitivity of dehydrogenases and phosphatases to soil pollution with PAHs.

CONCLUSIONS

1. The enzymatic activity of soils located in the river valleys was about 1.5 times higher than in soils out of their range, which indicates that, despite the intense anthropogenic pressure, the soil of the river valleys has the ability to self-reproduce and renew the resources necessary for the growth and development of soil microorganisms and plants.
2. The activity of dehydrogenases, acidic phosphatase, and alkaline phosphatase in the soils from the area of Krasnystaw and Lublin was significantly lower than in the soils located in Kazimierz Dolny, which was associated with increased anthropogenic pressure reflected by an increased inflow of PAHs to the soil environment.
3. The present research showed that the content of PAHs in the soils from the river valley areas was clearly lower than in the soils outside their range. This proves that the habitat conditions of the river valleys have a beneficial effect on the detoxification of the soil environment.
4. The results indicate that river valleys create spatial structures with a beneficial impact on the functional biodiversity of soils located therein, and in consequence, on the ecological status of urban ecosystems.

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Streszczenie. W pracy podjęto próbę oceny ekochemicznego stanu gleb w obrębie dolin rzecznych na obszarach wybranych miast z terenu Lubelszczyzny. Oceny tej dokonano na podstawie określenia aktywności enzymatycznej i zawartości wielopierścieniowych węglowodorów aromatycznych (PAHs) w glebach położonych bezpośrednio w dolinach rzek i poza ich zasięgiem. Badania zlokalizowano w dolinach najważniejszych dla Lubelszczyzny rzek – Wisły, Wieprza i Bystrzycy – odpowiednio w granicach administracyjnych miast: Kazimierza Dolnego, Krasnegostawu i Lublina. Powierzchnie badawcze wytypowano na terenach wokół uczęszczanych dróg i mostów, o potencjalnym wysokim poziomie presji antropogenicznej. Przeprowadzone badania wykazały, że aktywność enzymatyczna gleb położonych w dolinach rzek była około 1.5-krotnie większa niż w glebach poza ich zasięgiem. Oznaczona zawartość PAHs w glebach z obszarów dolin rzecznych była wyraźnie mniejsza niż w glebach położonych poza ich zasięgiem. Świadczy to o tym, że uwarunkowania siedliskowe dolin rzecznych wpływają korzystnie na detoksykację środowiska glebowego.

Słowa kluczowe: antropopresja, doliny rzeczne, gleby, aktywność enzymatyczna, detoksykacja, WWA

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