

PAH SOIL CONCENTRATIONS IN THE VICINITY OF CHARCOAL KILNS IN BIESZCZADY

EWA LISOWSKA

W. Szafer Institute of Botany, Polish Academy of Sciences
Lubicz str. 46, 31- 512 Kraków

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Abstract: The aim of the study was to assess the degree of soil contamination by PAHs in the area of charcoal kiln basis, located in the East Carpathian Biosphere Reserve. The concentrations of PAH in soil samples derived from various sampling locations pointed to a strong or a very strong contamination of the ecosystem by these compounds ($8,95 \mu\text{g} \cdot \text{g}^{-1}$ – $283,53 \mu\text{g} \cdot \text{g}^{-1}$). PAH concentrations in the soil differed significantly between the sampling locations. Analysis of samples from different soil layers (to 30 cm) pointed to a threat of washing out into groundwater. The highest concentrations of PAH corresponded to soil samples collected near kilns (distance of 1.5 m), and were in the range of $17.81 \mu\text{g} \cdot \text{g}^{-1}$ – $435.54 \mu\text{g} \cdot \text{g}^{-1}$. PAH content in soil gradually decreased with increasing distance from the kilns to values $< 1 \mu\text{g} \cdot \text{g}^{-1}$. The analysis of the data from three sampling periods (June-August) pointed to higher concentrations of PAHs in soil collected in the middle of the burning season, what was probably due to their more intense emission and a relatively small amount of precipitation.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are classified as a group of semi-volatile organic compounds (SOCs), occurring both in the solid and gas phase. The widespread occurrence of polycyclic aromatic hydrocarbons is due to their structure and physical-chemical properties. Their molecules are composed of two or more benzene rings. Lower (two- and three-ring) homologues are more volatile and more soluble in water than four-ring hydrocarbons, which are better soluble in oils and organic solvents [16, 27]. These compounds show toxic properties, both for animals (they can be built in nucleotides of DNA and RNA), and for plants, because they are precursors for the synthesis of tropospheric ozone. Due to the mutagenic properties, PAHs have been classified by the European Commission and the U.S. Environmental Protection Agency as major air pollutants, 16 of which were deemed most harmful to human health [6, 18].

Polycyclic aromatic hydrocarbons are formed as a result of natural and anthropogenic processes. Human activity introduces large amounts of these compounds into the environment. They are outcome of incomplete combustion of various types of fuel, such as wood, charcoal, oil, gas oils, and as a result of industrial activity. Significantly high concentrations of these compounds have been identified in samples from large urban agglomerations, where industry and traffic are the main source of pollution [7]. Factors that increase the intensity of PAH emission into the atmosphere are the incomplete combus-

tion of organic matter with low oxygen concentration and temperatures in the range of 650–900°C. Contamination of non-industrialized and agricultural areas may occur as a result of using fuel to heat homes and charcoal burning [6, 18, 37].

Almost 90% of the total amount of PAHs in the environment concentrates in soil [8]. Due to the sorption and accumulation properties of soil, PAHs may remain in it even for decades. PAH binding in soil depends on the amount of organic matter and increases along with its increasing content in soil [22, 34]. PAH low solubility in water limits migration to deeper soil layers and leaking into groundwater [22].

During the active burning season in the East Carpathian Biosphere Reserve, there are about 200 charcoal kilns, acting as the major point sources of PAH contamination in this area. The Reserve was recognized under UNESCO's Man and Biosphere (MAB) Program in 1992. Bilateral Polish-Slovak Biosphere Reserve was extended to Ukrainian part in 1995 and presently covers a total area of 2,132.11 km² [5]. Polish part (1089 km²) was divided into 3 zones: core and buffer zone – Bieszczady National Park, transitional zone – Ciśniańsko-Wetliński Landscape Park and Dolina Sanu Landscape Park. Local economic activities may occur only in the transitional zone, according to environmental protection regulations [20]. Reserve became one of the most important area of the Nature 2000 network in the European Union and includes the areas of special bird and habitat protection. The East Carpathian Biosphere Reserve has a significant value for conservation of biodiversity, natural ecosystems and genetic resources. It provides the ability of ecological and environmental research and creating conditions for popular and specialist education [12, 20].

For this region, with exception of some specific reports, there is no information on the level of organic pollutants in the environment. Neither industry nor road network is developed in the Reserve nor in the adjacent area, and the total territory is assumed to be unpolluted. Research conducted in 1997–1999 in the whole territory of Carpathians showed high concentrations of ground tropospheric ozone (approximately 100 mg m⁻³) in the Bieszczady region, both in the Polish and Ukrainian part [9]. It seems that residential heating and charcoal kilns may constitute a major source of pollution in the area. The degrading effect of charcoal production on soil was under the study in the East Carpathian in 1998 [10, 31]. It showed increasing intensity of soil metabolism after a long-term exposure to smoke.

The purpose of this study is to assess the degree of soil contamination with PAHs and the risk from the charcoal kilns activity for the environment of the East Carpathian Biosphere Reserve.

MATERIALS AND METHODS

Area of research

Area of research was located in the vicinity of 6 charcoal kiln bases, placed directly in the forest within the East Carpathian Biosphere Reserve (southern Poland) (Fig. 1). Six sampling locations spread up to 60 m from each charcoal kiln basis. The bases differed in their burning activity and the number of kilns. These were: 1 – Wola Michowa (seven active kilns for 10 years) 2 – Balnica (closed in 1998), 3 – Wola Michowa (four closed kilns, three – in 2008, one in 2006), 4 – Maniów (ten kilns operating since 2004), 5 – Szczerbanówka (three kilns closed in 2007), 6 – Habkowce (two kilns operating since

2006). Samples representativeness was conditioned by similar physical and chemical soil properties in all sampling locations which are presented in Figure 1.

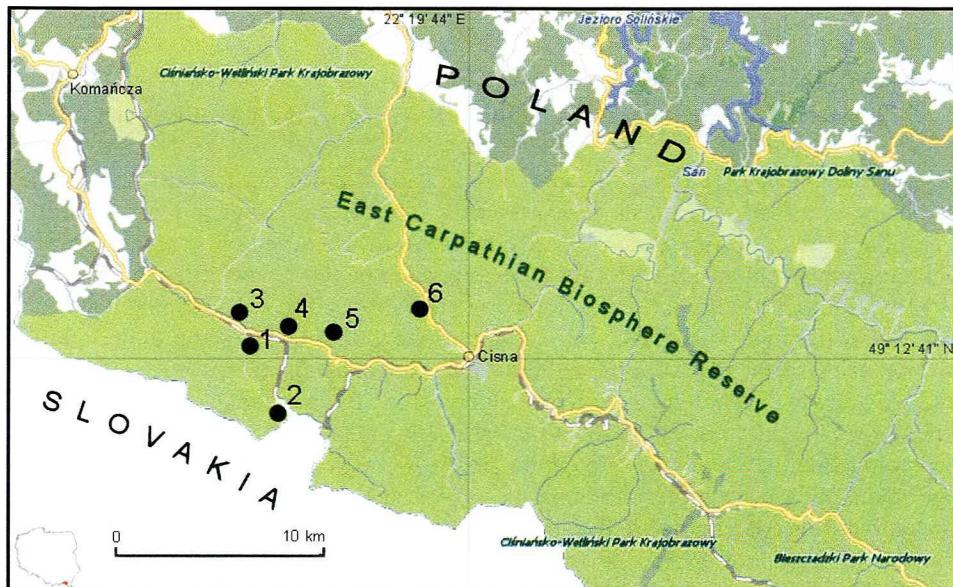


Fig. 1. Sampling locations 1–6 (1 – Wola Michowa, 2 – Balnica, 3 – Wola Michowa, 4 – Maniów, 5 – Szczerbanówka, 6 – Habkowce).

Locations 1–5 were in Komańcza Forest District, location 6 – in Cisna Forest District. Sampling points were located in the respective distances to avoid overlapping of emission from individual kilns. The choice of kilns was conditioned by using the same technology. In the area of 5 charcoal kiln bases (1–5) portable ring kilns of the capacity of 15 m³ were used, however, in Szczerbanówka (6th charcoal kiln base) there was a closed stable kiln of the capacity of 20 m³. In 5 charcoal bases (1–5) beech wood (approx. 90%) with an admixture of grey alder, silver birch and aspen poplar were used for charcoal production. Only in the base in Habkowce (6) gray alder and sycamore maple were used.

Charcoal is formed as a result of destructive distillation process of wood, running without air. The phase of wood carbonization lasts 24 hours and is characterized by emission of white, thick smoke from the kiln. During burning process the temperature inside the kiln is 400°C. Wood burning is a source of different gaseous and atmospheric particle bound pollutants (CO, CO₂, CH₄, H₂, NO, NO₂, O₂), PAHs, heavy metals as well as liquid products (tar, methanol, water) and solids (charcoal, coke breeze) [15].

Sampling collection

In each of the sampling location, 4 sampling points were set up, up to 60 m from the kilns in a downwind direction. The first sampling point was located 1.5 m from the kilns, the second – 20 m from the kilns, the third – 40 m from the kilns and the fourth – 60 m from the kilns. The total number of sampling points was 24 (4 sampling points for each of 6 sampling locations). One surface sample (0–5 cm) was collected at each sampling point, with two-month intervals during a season (June–October). Samples from each sampling

location were collected during three sampling periods, except those from the 6th location, where the first collection was not included. Additionally, soil samples were collected from the depths of 5, 15 and 30 cm at the distance of 1.5 m from the kilns, in three sampling locations (1, 4 and 5). Soil samples were transported and stored in closed polyester bags.

Analytical methods

In dried, sieved fractions, concentration of 16 PAHs (from the U.S. EPA) and soil pH value were determined.

Extraction of PAH from soil samples was carried out using the ASE-200 Dionex Company extractor, nitrogen shortened the time. The method validation was performed according to Dionex Application [3]. The extraction was carried out with a mixture of dichloromethane and acetone (1:1) at the temperature of 100°C and nitrogen pressure of 14 MPa. In order to eliminate fresh water from the analyzed samples, approximately 7.0 g of each soil sample was mixed with sodium sulfate [30]. Then the samples were further purified using membrane SPM (Semi Permeable Membranes), made from a semi-permeable polyethylene foil 80 µm thick. Purification using SPM membranes was based on the diffusion of analytes from the extract placed inside the membrane sleeve to the solvent located outside the membrane through the pore with the diameter of about 1 nm, retaining fat and other macromolecular impurities. N-hexane was used as the receiver solvent. The extract was concentrated in the air stream, and dissolved in 1 ml of acetonitrile, then injected into the HPLC system column.

Isolation of PAH from water samples was carried out by shaking twice with n-hexane. In order to improve wettability of potential suspensions and glass surface, before extraction, 1% (v/v) methanol was added to samples [4]. The concentrated extracts after dissolution in acetonitrile were analyzed.

Determination of extracted compounds was carried out by HPLC using the DX-500 Dionex Company chromatograph, with the VYDAC 201TP5415 column. The mobile phase was acetonitrile - water given with gradient of 50–100% acetonitrile in 45 min. at a flow of 1 ml/min. Quantitative determination of PAH (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, pyrene, benzo/a/anthracene, chrysene, benzo/b/fluoranthene, benzo/a/pyrene, benzo/k/fluoranthene, benzo/g, h, i/perylene, dibenz/a, h/anthracene, indeno/1,2,3-c, d/pyrene) was carried out using UV-VIS detector with wavelength 254 nm at 30°C. Chromatograph calibration and quantitative analysis control were carried out using the external standard method based on certified reference material CR104. The PAH concentration in soil samples was converted to dry weight equivalent.

Soil pH was determined potentiometrically in 1 mol KCl×dm⁻³ solution in redistilled water [35].

Statistical methods

PAH concentrations [$\mu\text{g} \times \text{g}^{-1}$] in soil samples from 6 sampling locations were used in statistical calculations. For each location, the following descriptive statistical parameters were calculated: arithmetic mean, standard deviation, and coefficient of variation.

The data were statistically evaluated using one and two factor analysis of variance without repetition test (ANOVA, MANOVA) and post hoc NIR, accepting the likelihood of error p = 0.05. ANOVA was performed for 5 sampling locations (1–5). The sixth location was excluded due to the presence of an additional source of emission. The data used in the statistical analysis was transformed into a natural logarithm.

RESULTS

PAHs in soil

Mean concentrations of total PAH in soil from six locations ranged from $8.96 \mu\text{g} \times \text{g}^{-1}$ (location 3) to $283.53 \mu\text{g} \times \text{g}^{-1}$ (location 6) (Table 1). Mean concentrations of light and heavy fractions of PAH and B(a)P were in the range: $1.13 \mu\text{g} \times \text{g}^{-1}$ - $22.76 \mu\text{g} \times \text{g}^{-1}$ (2–3 PAHs), $6.84 \mu\text{g} \times \text{g}^{-1}$ - $260.77 \mu\text{g} \times \text{g}^{-1}$ (4–6 PAHs), $0.01 \mu\text{g} \times \text{g}^{-1}$ - $0.49 \mu\text{g} \times \text{g}^{-1}$ (B(a)P) (Table 1). The standard deviation and coefficient of variation were higher for mean values of PAH at locations with operating kilns (1, 4 and 6). The standard deviation did not exceed twice the arithmetic mean, which indicates normal distribution of data (Table 1).

Table 1. Mean concentrations of the total PAH [$\mu\text{g} \times \text{g}^{-1}$] in soils from all sampling points in each sampling location (1–6, see Fig. 1) in the vicinity of charcoal kiln basis in the Bieszczady (for three sampling periods).

	Location no	n	Mean	Maximum	Minimum	Standard deviation	Coefficient of variation [%]
1-3 Sampling period							
Total PAH	1	12	111.46	709.84	2.36	206.34	183.48
	2	11	15.30	45.74	0.52	14.13	92.36
	3	12	8.95	26.31	0.25	8.17	91.27
	4	12	184.96	1072.92	1.45	313.39	169.44
	5	12	10.27	30.10	0.08	9.75	94.96
	6	8	283.53	835.92	8.76	363.06	128.05
2–3 PAH	1	12	18.96	116.38	0.04	35.03	184.74
	2	11	1.13	4.92	0.05	1.73.	153.50
	3	12	2.12	8.49	0.03	3.00	141.89
	4	12	17.29	80.22	0.54	25.68	148.57
	5	12	3.08	14.10	0.00	4.11	133.45
	6	8	22.76	97.02	0.16	36.71	161.30
4–6 PAH	1	12	93.49	650.80	2.29	183.34	196.10
	2	11	14.17	41.53	0.39	13.49	95.25
	3	12	6.84	19.51	0.09	5.70	83.30
	4	12	167.67	1025.43	0.64	297.32	177.32
	5	12	7.18	25.81	0.08	2.51	121.56
	6	8	260.77	738.90	6.72	331.57	127.14
B/a/P	1	12	0.09	0.50	0.00	0.15	180.00
	2	11	0.01	0.05	0.00	0.02	129.98
	3	12	0.02	0.13	0.00	0.04	160.47
	4	12	0.49	5.14	0.02	1.47	298.57
	5	12	0.01	0.07	0.00	8.73	168.48
	6	8	0.15	0.67	0.01	0.24	163.64
pH	1	12	5.12	6.86	3.57	1.15	21.41
	2	11	5.00	6.49	3.48	0.90	19.83
	3	12	7.22	7.49	6.33	0.40	9.46
	4	12	5.98	3.90	7.78	1.37	24.15
	5	12	5.24	7.64	3.42	1.69	32.52
	6	8	7.02	7.52	5.59	0.64	10.61

Two-factor ANOVA showed highly significant ($p \leq 0,001$) effect of time and place of samples collection on the total PAH and 4–6 ring PAH concentration in soil with no significant interaction between both factors. 2–3 ring PAH concentration was only slightly dependant on the location of sampling points ($p \leq 0.05$). Concentration of PAH in soil from different locations was related to the period of kilns activity and number of kilns. Concentration of PAH and 4–6 PAH (four-, five- and six ring polycyclic aromatic hydrocarbons) was significantly higher in soil samples from the locations with active kilns (1 and 4 location) comparing with other locations ($p \leq 0.001$), whereas concentration of 2–3 PAH (two- and three ring polycyclic aromatic hydrocarbons) was slightly higher at the 1st and the 4th location ($p \leq 0.05$). The highest concentrations of total PAH and their non-volatile fraction were determined at the 6th and the 4th location, while the highest concentrations of volatile hydrocarbons were at the 6th and the 1st location (Table 1).

The percentage of non-volatile hydrocarbons was 82% of identified hydrocarbons in examined soil samples, and indicated higher values at two operating locations – 1 and 4 (Fig. 2).

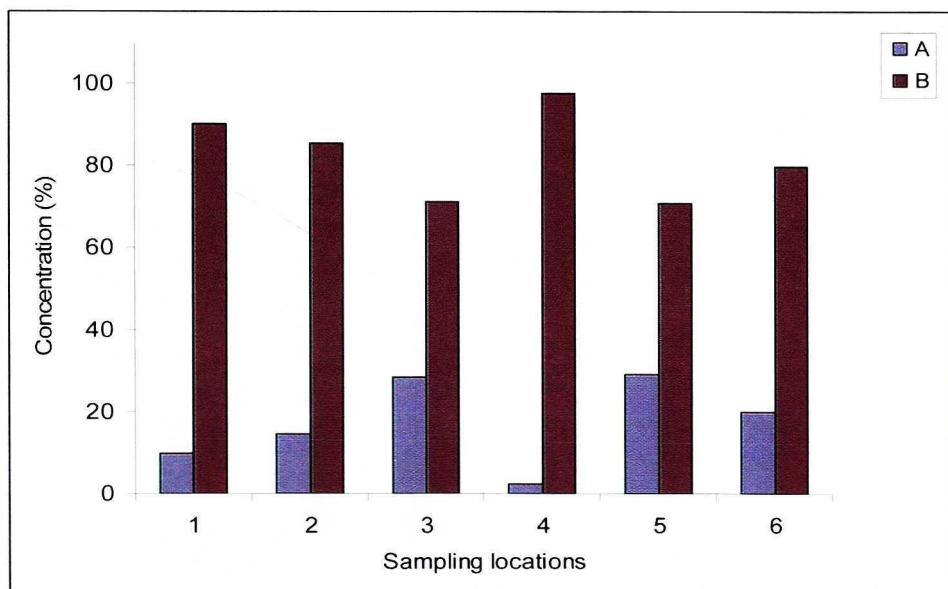


Fig. 2. The percentage of 2–3 ring PAH (A) and 4–6 ring PAH (B) fractions in soils at sampling locations (1–6, see Fig. 1) in the vicinity of charcoal kiln basis in the Bieszczady (for three sampling periods).

Concentrations of 16 individual polycyclic aromatic hydrocarbons from the six sampling locations are presented in Table 3 (for explanation of abbreviations see Annex). Among the identified PAHs the highest values were reached by dibenz/a,h/antracen – $194.23 \mu\text{g} \times \text{g}^{-1}$ and benzo/k/fluroanten – $168.95 \mu\text{g} \times \text{g}^{-1}$ (Table 2).

The analysis performed for samples taken from the soil profile showed that individual PAH concentrations generally decreased steadily with depth in soil profile. The mean concentrations of PAH in soil at a depth of 15 cm were about 1/3, and at a depth of 30 cm almost 2/3 lower than in the surface layer (Fig. 3).

Table 2. Mean concentrations of 16 PAHs [$\mu\text{g}\times\text{g}^{-1}$] in soils from 6 sampling locations (1–6, see Fig. 1) in the vicinity of charcoal kiln basis in the Bieszczady (for three sampling periods).

WWA*	1-3 Sampling period						SD	
	Mean							
	1	2	3	4	5	6		
Nap	0.12	0.34	0.07	4.30	1.46	3.18	5.37	
Acy	0.26	0.17	0.59	0.31	0.25	2.41	2.19	
Ace	0.34	0.11	0.04	5.25	0.10	2.73	6.91	
Fle	0.22	0.26	0.05	1.18	0.12	6.26	4.57	
Ph	0.26	0.07	0.14	0.37	0.34	3.91	2.58	
An	2.54	0.12	1.22	6.29	0.81	15.50	19.28	
Fla	3.44	1.17	0.07	0.42	0.06	13.77	8.06	
B/a/A	0.33	0.19	0.06	2.06	0.09	1.57	3.42	
Py	0.84	0.01	0.02	0.53	0.02	0.15	0.82	
B/a/P	0.09	0.02	0.03	0.27	0.03	0.65	0.44	
Chr	0.13	0.02	0.01	0.10	0.03	0.08	0.97	
B/b/F	0.08	0.01	0.01	0.05	0.01	0.07	0.10	
B/g,h,i/P	5.02	6.35	2.06	168.95	3.70	45.49	181.09	
B/k/F	1.45	0.21	0.04	0.04	0.02	2.02	1.46	
D/a,h/A	10.50	4.68	3.10	73.10	2.03	194.23	112.87	
Ind	5.61	0.69	1.44	5.90	1.20	2.73	5.32	

* Nap—Naphthalene, Acy—Acenaphthylene, Ace—Acenaphthene, Fle—Fluorene, Ph—Phenanthrene, An—Anthracene, Fla—Fluoranthene, Py—Pyrene, B/a/A—Benzo/a/anthracene, Chr—Chrysene, B/b/F—Benzo/b/fluoranthene, B/a/P—Benzo/a/pyrene, B/k/F—Benzo/k/fluorantene, Ind—Indeno/1,2,3-c,d/pyrene, D/a,h/A—Dibenz/a,h/anthracene, B/g,h,i/P—Benzo/g,h,i/perylene

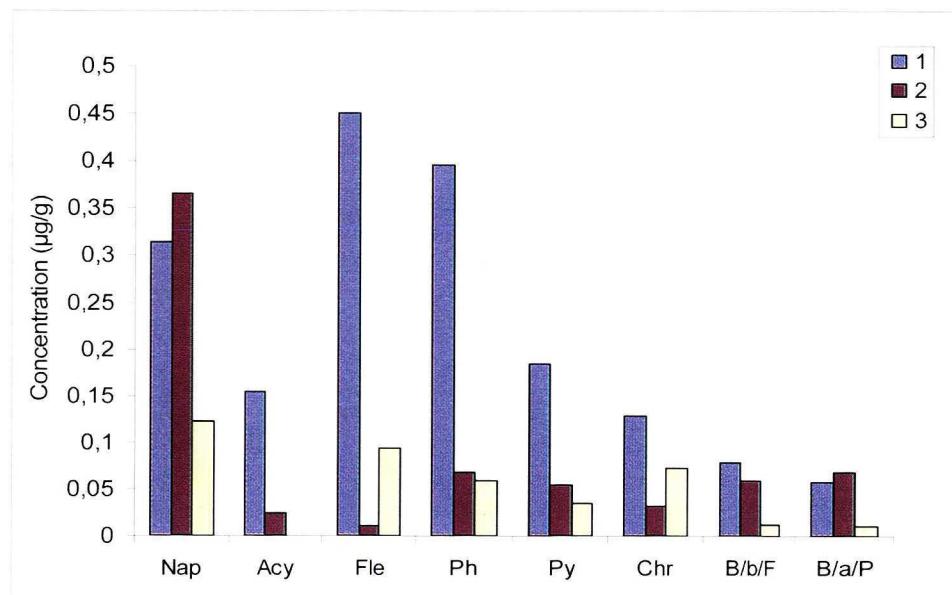


Fig. 3. Participation of individual PAHs in soil profile (1: 0–5cm; 2: 5–15cm; 3: 15–30cm); mean values for three locations (1, 4 and 5 see Fig. 1).

Concentrations of total PAH, 2–3 ring PAH, 4–6 ring PAH were significantly correlated with each other ($p < 0.01$; according to Bonferronii's correction $p < 0.0016$). Total PAHs were much more highly correlated with 4–6 ring PAHs ($= 0.99$) than with 2–3 ring PAHs (r values from 0.70 to 0.73).

Concentrations of PAH slightly correlated with soil pH values ($p < 0.01$; according to Bonferronii's correction $p < 0.0016$). The relationships between pH and total PAHs and 4–6 ring PAHs (r values from 0.40 to 0.41) were a little stronger than relationship pH/2–3 ring PAHs ($r = 0.38$).

The variation in the PAH concentrations during the growing season

The concentration of PAH and their non-volatile fractions in the soil showed large seasonal variations ($p \leq 0.001$), being significantly higher in soils collected in July ($p \leq 0.001$) and October ($p \leq 0.05$) (Fig. 4). In July the highest values of total PAH and 4–6 PAH were observed for location 1 and 4, while in October for location 6. 2–3 PAH concentration showed no significant seasonal variation (Fig. 4).

The effect of distance from source pollution on PAHs content in soil

One-factor ANOVA showed a significant effect of sampling points location within a single charcoal base on PAH concentration in soil. The effect was stronger ($p \leq 0.001$) in the case of 2-3 ring compounds than for total and 4–6 rings ($p \leq 0.05$). In each sampling location, the highest concentrations of PAH were found in the soils collected closest to kilns. Along with increasing distance from the burning point, PAH concentrations decreased (Fig. 5). The mean concentrations of 2–3 ring PAH in soils collected the farthest from the kilns (60 m) were significantly lower than at the other sampling points (1.5 m, 20 m and 40 m) ($p \leq 0.001$). The mean concentrations of total PAH and 4–6 PAH in soil samples collected the closest to the kilns (1.5 m) were significantly higher than means in the soils collected 40 and 60 meters away from the kilns ($p \leq 0.05$).

DISCUSSION

In the East Carpathian Biosphere Reserve, the absence of industrial activity and heavy traffic point to residential heating and charcoal kilns as the main sources of PAH emission. As a result of wood burning at homes larger quantities of some hydrocarbons (Ph, Fla, Py, B/a/P) are emitted to the atmosphere [11]. During the warm period, when the test was performed, home heating emission was significantly reduced, however, at the end of the spring, charcoal burning season began, which ended in the autumn, together with the increased precipitation [18].

According to Polish Regulation [25] the limit value for the content of 9 PAHs in the upper layer of soils from the protected areas under the Nature Conservation Act is $1 \mu\text{g} \times \text{g}^{-1}$, while the content of individual compounds should not exceed $0.01 \mu\text{g} \times \text{g}^{-1}$ (with exception of B/a/P with limit concentration of $0.02 \mu\text{g} \times \text{g}^{-1}$) [25]. In Poland, the mean content of PAH in uncontaminated soils varies within the limit of 0.3 – $0.6 \mu\text{g} \times \text{g}^{-1}$ [19, 33]. In highly contaminated areas (affected by industry or transport) PAHs concentrations may reach hundreds of $\mu\text{g} \times \text{g}^{-1}$ [2, 33].

Research conducted in the Bieszczady Mountains showed very high concentrations of polycyclic aromatic hydrocarbons. The mean concentrations of PAHs in soils at the

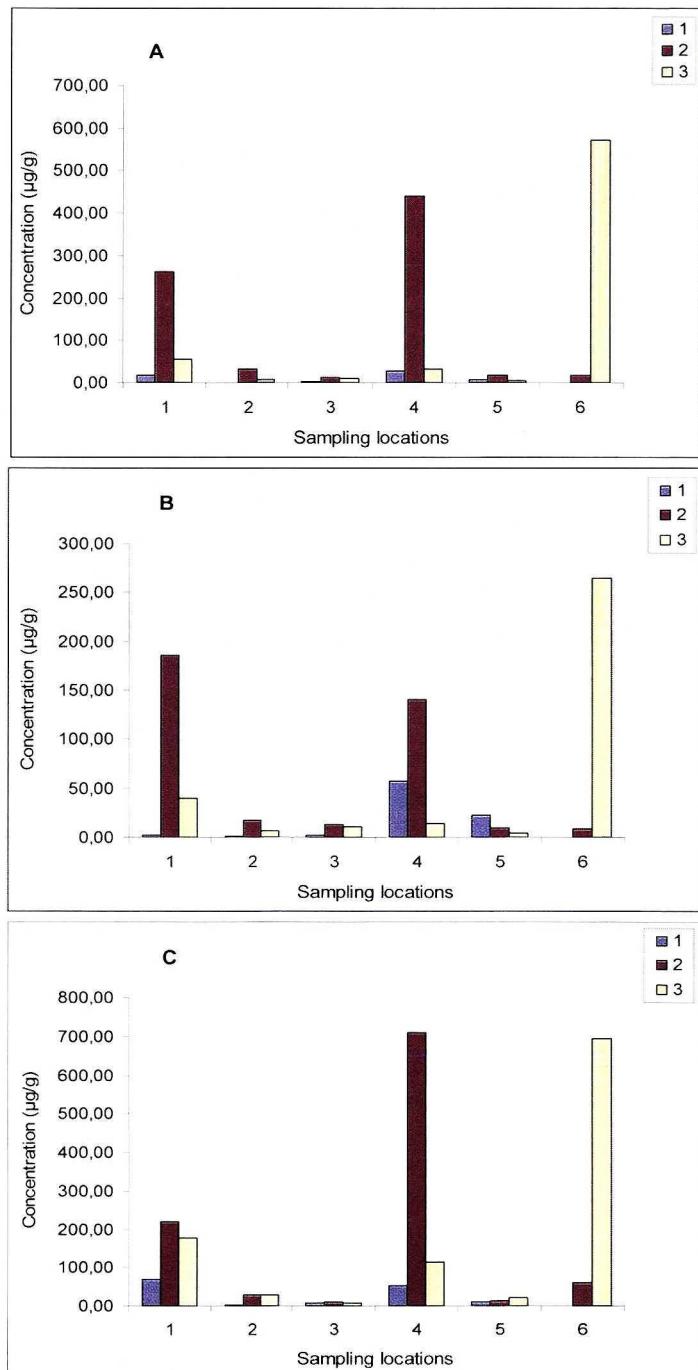


Fig. 4. Variability of total PAH (A), 2-3 PAH (B) and 4-6 PAH (C) [$\mu\text{g} \times \text{g}^{-1}$] concentration in soils from 6 sampling locations (1-6, see Fig. 1) in the vicinity of charcoal kiln basis in the Bieszczady (for three sampling periods).

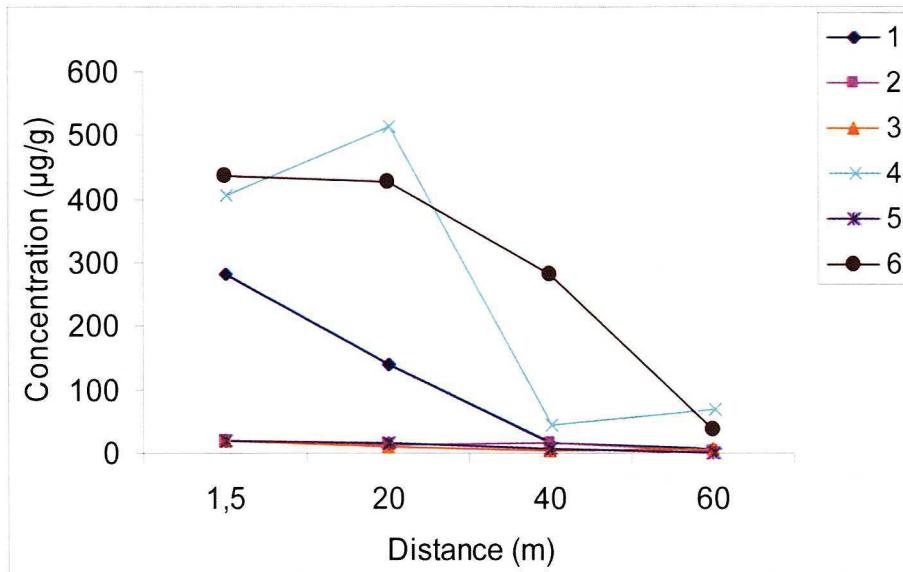


Fig. 5. Variations in concentration of the total PAHs [$\mu\text{g}\times\text{g}^{-1}$] in soils collected from 1.5 to 60 m from the kilns located in the vicinity of charcoal kiln basis in the Bieszczady (means for three sampling periods).

different sampling locations varied from $8.95 \mu\text{g}\times\text{g}^{-1}$ (location 3) to $294.79 \mu\text{g}\times\text{g}^{-1}$ (location 6), and at individual points they even reached the value of $1500 \mu\text{g}\times\text{g}^{-1}$ in soil. PAH concentration from different locations was dependent on the length of each charcoal base activity, number of kilns and burning intensity. At the locations with active kilns (1, 4, 6), these values were from a few to several times higher than those from inactive locations (3, 5). The highest mean concentrations of PAH were determined at the 6th location, where there were 2 active kilns. These values were higher than in other active charcoal bases with more kilns (location 1 and 4), what may be due to an imposition of pollutants from other, close existing charcoal bases. A similar trend was observed for the volatile and non-volatile fraction, and B/a/P.

As a result of wood combustion more non-volatile PAHs are emitted into the atmosphere comparing emission from coal and fuel burning process. Coal-burning on an industrial scale (e.g., coke furnace) may emit up to 90% of individual volatile compounds, e.g. naphthalene, while the wood burning at homes emits about 10% of this hydrocarbon, and the percentage of non-volatile fraction increases several times (Fla, Py, B/a/P B/g,h,i/P) [11]. The process of wood burning at a reduced amount of oxygen can also increase the amount of emitted 4–6 PAHs up to 80% [37]. The prevailing percentage of non-volatile PAH fractions in relation to volatile fractions was found throughout the whole research area. This proportion varied slightly between closed and active charcoal bases, where the participation of 4–6 PAHs was even greater. The reason of the difference was probably more intensive 4–6 PAHs emission than 2–3 PAHs emission. Part of emitted PAH volatile fractions might undergo photochemical oxidation process [21], reducing their concentration in precipitation. In addition, during the vegetative season, green plants contribute significantly to the retention of pollutants and can remove up to 44% ambient air pollutants [26].

Processes, which PAHs undergo in the soil, depend on both the physicochemical properties of soil, and individual compounds, whose properties presented by Maliszewska-Kordybach [17] have a greater impact on PAH transformations. High PAH concentrations in soils rich in organic matter may be related to high accumulation and slow desorption processes. PAH binding in soil depends on the amount of organic matter, especially its lipophilic organic fraction. Soils with a high content of organic matter contain usually more PAHs than soils with low humus content [17]. Acid brown soils are typical of Bieszczady Mountains and the average organic-C content ranges from 4 to 5% [35]. Studies on charcoal kilns emission showed a higher carbon content in soils near the kilns and, therefore, high levels of PAH was the result of both their binding intensity in soil and continuous, intense emission [31, 34, 36]. Besides, 4–6 ring PAHs show a greater sorption capacity for organic matter than the volatile fractions, which can easier evaporate from the soil surface [22, 26].

Creating bonds between PAHs and humus is also dependent on the presence of catalysts (chemicals, enzymes), and sustainability of these bonds may increase with increasing hydrolytic acidity value of the soil [34]. Researches conducted in charcoal kiln bases, relic charcoal hearths and surrounding sites indicated higher pH values in soil [10, 31, 36]. The studied soils were characterized mostly as slightly acidic, which had additional effect on PAH binding by organic matter (Tab. 1) and creation of unfavorable environment for soil microorganisms, which could contribute to PAH biodegradation [13, 23].

Soil physical factors such as humidity and temperature, have a direct effect on PAH metabolism in soils. Favorable soil humidity enhances biodegradation of these compounds by soil microorganisms [36]. However, high soil humidity inhibits PAH adsorption by organic matter and mineral fractions, due to PAH interaction with water molecules [23]. Low temperature favors the sorption of PAH by soil colloids and influences reduction of solubility, decreasing the activity of soil microorganisms [23]. High soil temperature causes evaporation of PAH volatile fractions from soil, even adsorbed permanently on soil particles [23]. The highest PAH concentration in soil from two active charcoal bases (location 1 and 4) was found in the second period (July), and the lowest in the first period (June). These differences are likely due to burning intensity, and PAHs accumulation during the following months. Due to heavy rainfall occurring in the middle of the season, they can contribute significantly to the PAHs migration into the soil profile, where these compounds may be permanently bound, thus increasing their concentration in the soil. High temperatures in the beginning of the season may have contributed to PAH evaporation from the soil, and intense sunshine induced photochemical oxidation process, what confirmed the lower value of volatile fractions in this period.

The PAH concentrations in soil at the depth of 30 cm were more than twice lower than in the surface layer (Fig. 3). However, these values were still high, posing a threat to plants and surface waters. PAH accumulation occurs mainly in the surface soil layer up to 20 cm, although some quantities are also present at the depth of 2 m (e.g., Ph) [28]. This is related to the presence of organic matter (PAH binding) in the surface soil layer and the low solubility of PAH in water, which significantly slows down the movement into the soil profile. Some PAHs may migrate to deeper soil layers and the process depends on the presence of carriers in the soil, such as: soluble organic matter, inorganic colloidal particles (clays, iron oxides), soil microorganisms [23].

As a result of PAH emissions into the atmosphere, some of them can be transported for up to several hundred meters away [1]. PAHs with low molecular weight can be

transported for long distances, unlike five- and higher ring PAHs, which deposit close to the source of emissions. This may explain high concentrations of those compounds in studied soils (Fig. 2). Humidity decreases the amount of PAH in the atmosphere; rain and snow cause their removal from the atmosphere to ground [18]. In the studied soils, PAH concentration decreases with increasing distance from the source of emission, but a significant decrease was visible at the distance of 40 m. At a distance of 60 m the concentration of PAH was almost ten times lower than at the sampling point closest to the kilns. Unfortunately, all along the transect PAH concentrations were very high in comparison to unpolluted areas. In all locations the concentrations of PAHs were at least 10 times higher than the Polish guide values [25] and in some of the sampling points they exceeded the limit values of over two orders of magnitude.

Research conducted in the area of relic charcoal hearths existing in the 19th and 20th centuries showed minimal lasting effect on soil properties (higher pH, carbon and calcium content). Forest density and biodiversity differ on hearths comparing adjacent area [13, 36]. Studies on existing kilns reveal significant alterations in forest soil chemistry (higher pH, carbon and calcium content, cation exchange capacity with lower P content) pointed to local soil and air pollution, changes in local vegetation (lower density, plants degradation), threat of leaking into groundwater [10, 31]. Although high carbon content reduces PAH biotoxicity in soil, extremely high PAH concentrations, comparable with those in studied soils, may have toxic effect on earthworms and most of the soil micro-organisms [8, 34].

CONCLUSIONS

The results of the study pointed to very high PAH concentrations in soil in the vicinity of charcoal kiln bases in the Bieszczady area. This may create a serious ecological risk to East Carpathian Biosphere Reserve. Concentrations differed significantly between the sampling locations and reached higher values at locations with the longest and the most intense burning activity. PAH concentrations gradually decreased along with increasing distance from the kilns. Analysis of the data from three sampling periods (June-August) pointed to a higher PAH concentration in samples collected in the middle of the burning season.

REFERENCES

- [1] Aamot E., E. Steinnes, R. Schmid: *Polycyclic aromatic hydrocarbons in Norwegian forest soils: Impact of long-range atmospheric transport*, Environ. Pollut., **92**, 275-280 (1996).
- [2] Adamczewska M., J. Siepak, H. Gramowska: *Studies of levels of polycyclic aromatic hydrocarbons in soils subjected to anthropopressure in the city of Poznań*, Pol. J. Environ. Studies, **9**(4), 305-321 (2000a).
- [3] Application Note 313, DIONEX: Extraction of PAHs from environmental samples by Accelerated Solvent Extraction (ASE), 1997.
- [4] Bartulewicz J., J. Gawłowski, E. Bartulewicz: *Pobieranie i przygotowanie prób do oznaczania związków organicznych metodami chromatografii*, Państwowa Inspekcja Ochrony Środowiska Biblioteka Monitoringu Środowiska, Warszawa 1997, 13-27.
- [5] Biosphere Reserve Information. Poland-Slovakia-Ukraine East Carpathian. The MAB programme, www.unesco.org, 26.02.2007.
- [6] Bojakowska I., G. Sokołowska: *Polycyclic aromatic hydrocarbons in materials of burned peatlands*, Pol. J. Environ. Studies, **12**, 401-408 (2003).
- [7] Borkowska M., A. Dutkiewicz, A. Strusiński: *Wpływ transportu samochodowego na zawartość benzeno/pirenu w glebie i roślinach*, Roczniki PZH, T. XXXIII, **4**, 297-302 (1982).

- [8] Brandys J.: *Wielopierścieniowe węglowodory aromatyczne (WWA). Chemiczne substancje toksyczne w środowisku*. Komisja Nauk Medycznych – Oddz. PAN w Krakowie, 163–176 (1990).
- [9] Bytnarowicz A., B. Godzik, W. Frączek, K. Grodzińska, M. Krywult, O. Badea, P. Barančok, O. Blum, M. Černy, S. Godzik, B. Mankovská, W. Manning, P. Moravčík, R. Musselman, J. Oszlányi, D. Postelnicu, J. Szczęsny, M. Varšavová, M. Zota: *Distribution of ozone and other air pollutants in forests of the Carpathian Mountains in central Europe*, Environ. Pollut., **116**, 3-25 (2002).
- [10] Fisher Z., P. Bieńkowski: *Some remarks about the effect of smoke from charcoal kilns on soil degradation*, Environ. Monitoring & Assessment, **58**(3), 349-358 (1999).
- [11] Gawlik M.B., M. Bilek: *Możliwości obniżenia emisji wielopierścieniowych węglowodorów aromatycznych ze źródeł antropogenicznych*, Medycyna Środowiskowa, **9**(1), 79-82 (2006).
- [12] Główny Urząd Statystyczny. Ochrona Środowiska 2009. Informacje i opracowania statystyczne. Wersja elektroniczna. Warszawa 2009.
- [13] Hart J.L., S.L. Van de Gevel, D.F. Mann, W.K. Clatterbuck: *Legacy of charcoaling in a Western Highland Rim Forest in Tennessee*, The American Midland Naturalist, **159**(1), 238-250 (2008).
- [14] Kluska M.: *Soil contamination with the polycyclic aromatic hydrocarbons in the vicinity of the Ring Road in Siedlce City*, Pol. J. Environ. Studies, **12**(3), 309-313 (2003).
- [15] Laurow Z.: *Pozyskiwanie drewna i podstawowe wiadomości o jego przerobie*, Wyd. SGGW, Warszawa 1999.
- [16] Magnus F.: *Toxic substances in environment*, Environ. Sci. Technol., [in:] A. Wiley: *Interscience Series of Texts and Monographs*, 279-281 (1994).
- [17] Maliszewska-Kordybach B.: *Zależność między właściwościami gleb i zawartością w nich WWA; na przykładzie gleb z terenów użytków rolnych w województwie lubelskim*, Archiwum Ochrony Środowiska, **24** (3), 79-91 (1998b).
- [18] Maliszewska-Kordybach B.: *Sources, concentrations, fate and effect of polycyclic aromatic hydrocarbons (PAHs) in the Environment. Part A: PAHs in air*, Pol. J. Environ. Studies, **8**, 131-136 (1999).
- [19] Maliszewska-Kordybach B., B. Smreczek, A. Klimowicz-Pawlak: *Concentrations, sources, and spatial distribution of individual polycyclic aromatic hydrocarbons (PAHs) in agricultural soils in the Eastern part of the EU. Poland as a case study*, Sci. Total Environ., **104**(12), 3746-3753 (2009).
- [20] Michalik S.: *Karpaty Wschodnie. Miedzynarodowy Rezerwat Przyrody*, Wyd. 2 – Olszanica, BOSZ, 10-14, 1997.
- [21] Niu J., J. Chen, D. Martens, X. Quan, F. Yang, A. Kettrup, K. W. Schramm: *Photolysis of polycyclic aromatic hydrocarbons absorbed on spruce [Picea abies (L.) Karst.] needles under sunlight irradiation*, Environ. Pollut., **123**, 39-45 (2003).
- [22] Nelson A.H. (ed.): *PAHs and related compounds*, The Handbook of Environ. Chem., **3**, Part I, Springer-Verlag Berlin Heidelberg, 56-65 (1998).
- [23] Oleśczuk P.: *Zanieczyszczenia organiczne w glebach użyźnianych osadami ściekowymi. Część II. Losy zanieczyszczeń w glebie*, Ecological Chemistry and Engineering, **14**(S2), 185-198 (2007).
- [24] Reid B.J., K.C. Jones, K.T. Sample: *Bioavailability of persistent organic pollutants in soils and sediments - a perspective of mechanisms, consequences and assessment*, Environ. Pollut., **108**, 103-112 (2000).
- [25] Rozporządzenie Ministra Środowiska z 9 września w sprawie standardów jakości gleby oraz standardów jakości ziemi (Dz.U. rok 2002, nr 165, poz. 1359).
- [26] Simonich S.L., R.A. Hites: *Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere*, Nature, **370**, 49-51 (1994a).
- [27] Sims R.C., M.R. Overcash: *Fate of polynuclear aromatic compounds (PNAs) in soil-plant system*, Residue Rev., **88**, 1-68 (1983).
- [28] Stanković D., B. Krstić, N. Nikolić: *Effect of traffic on the soil contamination with polycyclic aromatic hydrocarbons (PAHs)*, Biotechnol. & Biotechnol., **22**(2), 736-741 (2008).
- [29] Steiner C., K.C. Das, M. Garcia, B. Förster, W. Zech: *Charcoal and smoke extract stimulate the soil microbiological community in a highly weathered xanthic Ferralsol*, Pedobiologia, **51**(5-6), 359-366 (2008).
- [30] Technical Note 208, DIONEX: Methods optimization in Accelerated Solvent Extraction (AEE), 1997.
- [31] Uvarov A.V.: *Effect of smoke emission from a charcoal kiln on the functioning of forest soil system: A microcosm study*, Environ. Monitoring & Assessment, **60**(3), 337-357 (2000).
- [32] Van Jaarsveld J.A., W.A.J. Van Pul, F.A. De Leeuw: *Modeling transport and deposition of persistent organic pollutants in the European region*, Atmos. Environ., **31**, 1011 (1997).
- [33] Weisło E.: *Soil contamination with polycyclic aromatic hydrocarbons (PAHs) in Poland – a Review*, Pol. J. Environ. Studies, **7**(5), 267-272 (1998).
- [34] Weissenfels W.D., H.J. Klewer, J. Langhoff: *Adsorption of polycyclic aromatic hydrocarbons (PAHs) by soil particles: Influence on biodegradability and biotoxicity*, Applied Microbiology and Biotechnology, **36**(7), 689-696 (1992).

- [35] Woźniak L., S. Dziedzic: *Organic matter and some element contents in soil profile of meadows in the mountain region of Bieszczady – Poland*. “Organic matter and element interactions, Austrian – Polish Workshop, ALVA Mitteilungen Heft 3(2005).
- [36] Young M.J., J.E. Johnson, M.D. Abrams: *Vegetative and edaphic characteristics on relic charcoal hearths in the Appalachian mountains*, Plant Ecology, **125**(1), 43-50 (1996).
- [37] Zou L.Y., W. Zhang, S. Atkinson: *The characterization of polycyclic aromatic hydrocarbons emissions from burning of different firewood species in Australia*, Environ. Pollut., **124**, 283–289 (2003).

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STĘŻENIA WWA W GLEBIE W SĄSIEDZTWIE WYPALARNI WĘGŁA DRZEWNEGO W BIESZCZADACH

W niniejszej pracy zostały przedstawione dane dotyczące zanieczyszczenia gleb przez wielopierścieniowe węglowodory aromatyczne (WWA) w okolicy wypalarni węgla drzewnego, usytuowanych na terenie Rezerwatu Biosfery Karpaty Wschodnie. Celem badań była ocena stopnia zanieczyszczenia gleb przez WWA oraz zasięgu emisji zanieczyszczeń z poszczególnych wypalarni. Stężenia WWA w glebach pochodzących z poszczególnych stanowisk badawczych wskazywały na silne lub bardzo silne zanieczyszczenie ekosystemu tymi związkami ($8,95 \mu\text{g} \cdot \text{g}^{-1}$ – $283,53 \mu\text{g} \cdot \text{g}^{-1}$).

Stężenia WWA w glebie różniły się istotnie pomiędzy badanymi stanowiskami. Analiza próbek pochodzących z warstw gruntowych (do 30 cm) wskazywała na zagrożenie przedostawania się części z tych zanieczyszczeń do wód gruntowych. Najwyższe stężenia WWA pochodziły z próbek gleby pobranych najbliżej wypalarni (1,5 m) i mieściły się w przedziale $17,81 \mu\text{g} \cdot \text{g}^{-1}$ – $435,54 \mu\text{g} \cdot \text{g}^{-1}$. Zawartość WWA w glebie maleała stopniowo wraz z odległością od retort (do 60 m), osiągając jednak nadal wysokie wartości dla dwóch najintensywniej działających wypalani (4 i 6): $0,44 \mu\text{g} \cdot \text{g}^{-1}$ – $69,3 \mu\text{g} \cdot \text{g}^{-1}$. Analiza danych z trzech polorów (czerwiec – październik) wskazuje na wyższe stężenia WWA w glebie w środku sezonu wypałowego, co wynika prawdopodobnie z najintensywniejszej ich emisji oraz stosunkowo małej ilości opadów atmosferycznych.