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Assessment of physical and chemical pollution of urban agglomeration soils

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ABSTRACT

The article presents the results of tests performed on soil samples collected along the express road running across the city center with various types of land development. The purpose of this monitoring-oriented research paper was to analyze the sorption properties, the pH, the pollution with petroleum-derived compounds, and the content of heavy metals Cu, Pb, Zn, and Ni in the analyzed soil. In addition, it was assessed whether the area used by students as a research area does not pose a health risk. The granulometric composition was also discussed. The obtained test results indicate a comparable soil pH at the alkaline level with average organic carbon content in the range of 1.05%–2.36%. The studied soils are characterized by the largest percentage of coarse sand (0.63:2.0 mm) and medium sand (0.2:0.063 mm), the average iodine value indicates soils of average sorption. Infrared spectroscopic studies allowed us to assess the content of non-polar aliphatic hydrocarbons in the soil of the studied areas. These values are in the range of 8.34–42.05 mg/kg and were not exceeded in relation to the maximum values allowed in OJ.165.1359. The percentage of the analyzed heavy metals in relation to the binding maximum content specified in OJ.165.1359, was in the following order Pb > Cu > Ni > Zn.

Keywords: Non-polar aliphatic hydrocarbons; Urban soils; Organic carbon; Sorption; Heavy metals

1. Introduction

One of the most serious threats to environmental safety and human health is environmental pollution. It is the result of uncontrolled emissions from industrial systems, power plants, and communication routes. The condition of the soil environment in urbanized areas depends on climatic conditions, landform, development, and industrialization of a given area, and above all, on the intensity of car traffic. Communication routes are a source of toxic gases, dust, and aerosols containing also heavy metals [1]. The presence of these hazardous substances is connected with the processes of burning liquid fuels and abrasion of asphalt pavements or car tyres and also the wear and tear of the vehicle operational components. The problem of automotive soil contamination in the vicinity of busy arteries occurs mainly in large cities with a high level of population and dense transport network, where a very high number of cars within relatively small areas, and traffic congestion contributes to high emissions of exhaust fumes [2]. From year to year, the number of private passenger cars is increasing and transit traffic is intensifying, which in turn increases the volume of road traffic. The automotive contamination of the soil environment occurs in practically all cities. Soil contamination within the range of traffic arteries is very rarely visible, but is accountable for very dangerous, delayed in time, effects that have impact on the ecotoxicology of the environment. Adsorption and buffering properties of soils cause all pollutants to be accumulated in them. It is worth mentioning that in the water and soil environment they undergo very slow degradation chemically and biologically. This has a negative impact on the development of the plant world. Pollutants lower quality and quantity of harvested yields, disturbing the development of plants and reducing the aesthetic values of vegetation. They also cause corrosion of engineering structures and

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foundations of buildings. The contamination with petroleum derivatives (high frequency of occurrence) is highly hazardous. It has been assumed that in the case of failures and catastrophes resulting in soil contamination, about 40% of pollutants are petroleum derivatives [3,4].

Contaminants get into the soil, then into groundwater [5], through atmospheric precipitation, surface water overflow, together with sewage, dust, as well as with various waste or through failures in industrial plants and the transport of hazardous substances. Nowadays, chemicals are being used increasingly. Failures in warehouses of hazardous substances or during their transportation result in their penetration into the environment. Improper farming leads to soil contamination due to excessive use of fertilizers. Soils located in the area of roads and motorways are the most polluted ones, as they contain large amounts of heavy metals and petroleum-derived substances [6].

Heavy metals typically enter human and animal organisms through the food or inhalation route (e.g., by inhaling volatile compounds or as vapors of pure metal). In areas where gardens and public parks are exposed to significant levels of pollution, also soil dust is toxic by inhalation, especially by children and young people who are more susceptible to adverse environmental conditions. Health-related effects can be revealed after many years, because some metals accumulate in the body [7].

Hydrocarbons have the ability to penetrate and accumulate in living organisms. They can get through the skin, digestive system, and respiratory system. Due to their hydrophobicity, they easily dissolve in fats and enter the nervous system. Aliphatic hydrocarbons affect the nervous system, their metabolism occurs mainly in the liver and kidneys [8]. Contaminants deposited in soil undergo various processes, mainly of physicochemical nature. Petroleum substances and heavy metals can migrate from the soil surface to surface and underground waters, which entails degradation of the soil and water environment and violation of biological life [9,10]. The physicochemical properties of soil determine its quality, because adsorption, transport, and degradation processes depend on these properties [11,12].

Depending on the sorption capacity of soil and minerals, their resistance to degradation varies. The sorption capacity, that is, the binding of pollutants and detoxification of the environment largely depends on the amount of humus. Soils with a high content of humus or clay minerals have a high soil sorptive capacity, then the petroleum compounds are absorbed in them and can be more easily broken down, processed, and taken up by various microorganisms. Soil sorption and granulometric composition are mainly responsible for its water and air capacity. For this reason, for example, sands as soils with a large grain diameter of the granulometric fraction are more ventilated, which increases the activity and amount of microorganisms contained in them, and this translates into an increase in the possibility of removing petroleum hydrocarbons. However, in fertile or clay soils the biodegradation potential may be much smaller [13,14]. Loose and weakly loamy sand soils show the lowest resistance to degrading factors, while compact soils, such as rendzinas, muds, and black soils one manifest the highest [15].

The determination of the physicochemical properties of the soil (pH, organic substance, and sorption), heavy metal content and petroleum-derivative contamination will permit the selection of an appropriate test method to obtain accurate and reliable results.

2. Methodology of research

2.1. Characteristics of collection points

Soils of urban areas located at the communication route, separated from the road by a lane of trees and bushes, were examined and evaluated.

This route was tested over a length of 1,000 m and a width of up to 100 m on both sides of the route (Warszawska street). The soil was collected at five points marked numerically 1–5 (Table 1, Fig. 1). Soil collection points 1–3 are areas used by residents of neighboring buildings. These areas are decorative and recreational, whereas the area where points 4 and 5 are located belongs to the Kielce University of Technology. Student field activities take place in this area. It is a place particularly frequented due to the presence of walking paths in this area. These areas were selected to be the subject of research due the diversity of their land development and management over the last 50 y.

In the 70's and 80's of the last century, Warszawska street was a street marking the city limits. Currently, due to the dynamic expansion of the city of Kielce, this street is located in the center and is an important communication route, with a traffic of several thousand cars a day [16]. Currently around Warszawska street, there are residential buildings (single-family detached houses and multi-family buildings), a fuel station, and a 22 ha campus of the Kielce University of Technology (Fig. 1), which educates 6,000 students. The expansion of the campus of the Kielce University of Technology from two to six teaching buildings over 50 y required the preparation of sufficiently stable ground. The areas (collection points 4 and 5) for the construction of the campus were stabilized with anthropogenic soil with a granulometric composition of stony and gravel fractions, without modification with building materials [9]. Pursuant to the provisions on soil pollution [17], areas of this type are qualified as the IVC group – as transportation areas. On the other hand, the remaining areas around the transportation route (collection points 1–3) are characterized by compact housing, hence it is necessary to classify the studied soil as groups IA and IB [17]. During many years of use, the soil in points 1, 2, 3 (Table 1 and Fig. 1) was subjected to reclamation and adapted as necessary.

2.2. Research methodology

Temperature is a very important factor affecting biodegradation. It is assumed that the most effective degradation of petroleum compounds in soil occurs at a temperature of 30°C–40°C, because then the solubility of hydrocarbons increases, and thus their bioavailability increases [18]. The period March–May 2018 with air temperature from –2°C in March to +25°C in May was chosen for the study.

Samples for testing were taken from a depth of up to 30 cm in variable weather conditions. The level of sampling was adapted to the rate of accumulation of pollutants, penetration into the air, and migration to lower soil levels. Mixed, fresh, and air-dry samples were analyzed. The reference

Table 1
Location and point number, including the land use form of the soil samples collected

Sampling point	1	2	3	4	5
Sampling place	Warszawska St., multi-family building		Warszawska St., Lukoil fuel station	Warszawska St., ventilation air launcher	
Location in relation to the KUT campus	North		North	West	
Form of land use	Recreational and decorative		Utilized agricultural land, biodegradable waste area	Transitional-transportation routes, student field surveying area	

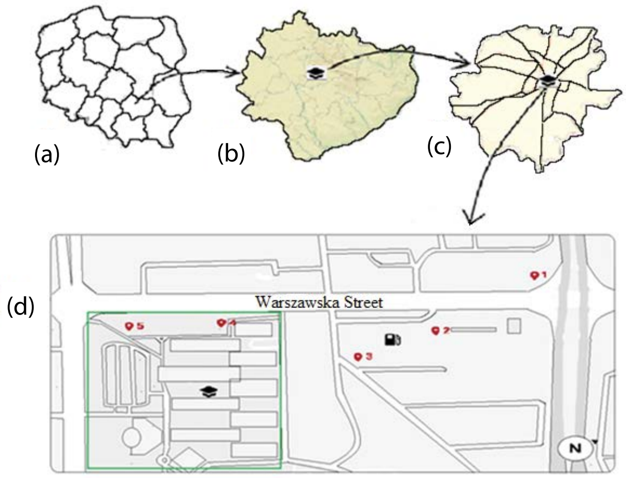

Fig. 1. Location of sampling points on the Kielce map; (a) Poland, (b) province Swietokrzyskie, (c) the city of Kielce, and (d) places of samples collection with the marked area of the Kielce University of Technology campus [27].

sample consisted of 25 basic samples taken in accordance with the standard [19,20].

The following determinations were carried out on the soil samples:

- granulometric composition by means of laser diffraction using a Mastersizer 3000 device.
- soil pH (potentiometric determination) in 1 MKCl – using a Mettler Toledo (Columbus, Ohio, USA) pH-meter [21],
- sorption capacity by determining the iodine number [22].

An innovative sorption study was used, using the simplified method, introduced by the research team of the Kielce University of Technology. This method determining the sorption capacity in soil involved the analytical measurement to define the iodine adsorption number on activated carbon [23]:

- organic carbon by the Tiurin method [24],
- content of non-polar aliphatic hydrocarbons by Fourier transform infrared spectroscopy. This method consists in extracting organic compounds from the analytical sample with carbon tetrachloride, separating polar compounds by adsorption on activated Al_2O_3 and determining the content of aliphatic hydrocarbons remaining in the extract by means of infrared spectrophotometric measurement at the wave number 2,926 cm^{-1} [25],
- content of total forms of selected heavy metals Cu, Pb, Zn, and Ni was determined by inductively coupled plasma atomic emission spectroscopy technique after mineralization of samples with aqua regia according to the standard [26].

The arithmetic mean, the median, and the standard deviation were calculated for the obtained results (non-polar aliphatic hydrocarbons and metals). Statistical analysis of the results was carried out in Microsoft Excel 2010 and Statistica 12.

3. Results and discussion

The studied soils are made of sand, from coarse to fine [28]. The largest percentage, 33%, is medium sand (0.2–0.63 mm), to a smaller extent 25% thick (0.63–2.0 mm), and 21% fine (0.063–0.2 mm). The dust fraction is in the range of 7% and the clay fraction <0.002 mm does not occur at all (Fig. 2). The dust fraction increases the sorption capacity of the soil. Sandy deposits are characterized by low retention capacity due to the high permeability, which is at the level of 15–25 L/m^3. High permeability can lead to the entry of pollutants into groundwater and cause their migration over considerable distances [29].

Soils, on both sides of the communication route, showed similar alkaline pH values (7.88–8.43) throughout the entire study area (Table 2). The highest pH was recorded on wasteland located behind the gas station (area 3), in May pH 8.39, 8.41, and 8.43, the lowest pH was recorded at the KUT – Kielce University of Technology campus (areas 4 and 5) and area 2 – with a similar manner of use, in March (Figs. 1 and 3). Alkaline soils are characterized by a low content of heavy metals [30].

The content of organic carbon in the samples tested varied depending on the manner of use, it ranges from 1.05% to 2.36%. The highest percentage of Corg content is found in samples from the recreational and garden areas of points 1 and 2 that residents care for (Table 2). This is due to the way land is used and the great care of the inhabitants for a place to relax. In point 3, residents collect biodegradable waste, therefore the organic carbon content is at the level of area 1 and 2. The lowest percentage of Corg is on the ordered area of the campus, used to conduct student field practices, points 4 and 5 (Table 2 and Fig. 3). The high correlation between organic carbon content and

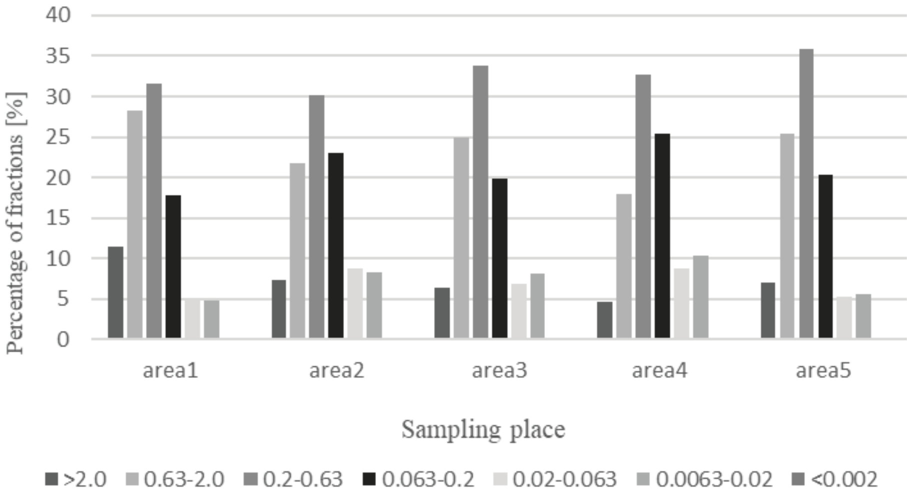

Fig. 2. Percentage of fraction with diameter (d) in [mm].

Table 2
Sampling location and average values for each point: pH, organic carbon, iodine number, and content of non-polar aliphatic hydrocarbons in samples of the tested soil in the period March–May 2018

Sample no.	pH [–]	Corg [%]	Iodine value (IV) [mg/g]	Non-polar aliphatic hydrocarbons [mg/kg]
1	8.19	2.08	92	28.02
2	8.07	1.95	90	30.80
3	8.26	2.02	94	25.12
4	8.08	1.57	48	17.97
5	8.14	1.19	49	19.62
Average	8.15	1.76	75	24.30

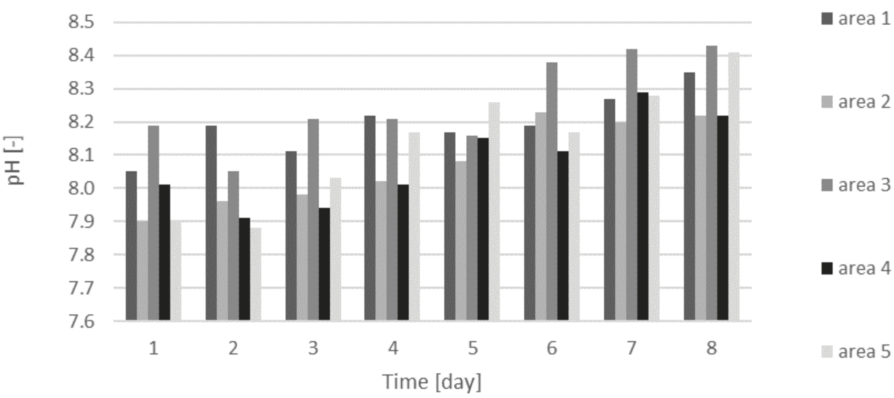

Fig. 3. pH of the soil during the sampling period (March–May 2018).

sorption determined by iodine number is shown in the vector configuration (Fig. 5). The percentage of organic carbon in the studied soils occurs at an average level of 1.76% (Table 2) [31], which indicates diligence of the inhabitants and their concern for the quality and development of the areas in a given location [32].

Iodine value (IV) for points 1, 2, 3 accounts for 93 mg/g on average, for areas with low Corg content (area 4 and 5), the average iodine value is 48 mg/g. Soils from areas taken care of by residents showed a high content of organic matter and were characterized by high sorption (Table 2 and Fig. 5).

The content of non-polar aliphatic hydrocarbons, for the studied areas, ranged from 17.97 to 30.80 mg/kg. The increased occurrence of non-polar aliphatic hydrocarbons in samples from test areas 1 and 2 may be caused by insufficient plant isolation from the transportation route (single trees planted along the route every few meters). In point 3, the increased hydrocarbon content, despite the high plant insulation, is caused by the nearby location of the fuel station. For areas 4 and 5, the content of non-polar aliphatic hydrocarbons in relation to points 1 and 2 is smaller by about 40% (Table 2 and Fig. 1), this is the result of dense planting of trees and shrubs with phytoremediation properties along the transportation route [12,33].

The activities of the inhabitants have no impact on traffic, but the effective bioremediation of the land, using the *in-situ* method, makes the place safer to use, also for recreational purposes. Performing process bioremediation through soil cultivation, bioventilation, planting reduces contamination, and isolates from the communication route [34,35].

The maximum content of non-polar aliphatic hydrocarbons specified in OJ.165.1359 has not been exceeded in the examined areas. But studies have shown that in areas 1, 2, 3 their maximum values (Table 3) constitute 80% of the permissible norm [17] and may pose a threat to human health especially in the summer months.

The average values and median values for non-polar aliphatic hydrocarbons are very similar. The analysis of statistical data clearly indicates that they are a good measure for environmental analyzes of the studied areas. A small dispersion of results around the mean value confirms the value of the standard deviation (Table 3).

The content of heavy metals lead (Pb), copper (Cu), nickel (Ni), and zinc (Zn) during the sampling period ranged from 3% to 37% of the maximum value specified in OJ.165.1359 [18] (Table 4).

The highest contents of tested heavy metals were recorded at the sampling points 1, 4, 5. These are areas located in the immediate vicinity of the very busy Warszawska street, despite the planting of trees and shrubs (Fig. 1). An additional factor conducive to metal accumulation in soil in the second half of April was favourable weather, elevated temperature, and atmospheric precipitation.

The tested soils are characterized by alkaline pH value and low content of heavy metals (Tables 2 and 4 and Fig. 4) [30].

In order to identify correlations between individual variables (IV, Corg, pH, organic carbon, NPA-non-polar aliphatic hydrocarbons, Pb, Cu, Ni, and Zn) determined for the period March–May 2018, analysis of the main components was performed. Due to incomparable analyzed variables (i.e., have different units), factor loadings for the first three components were determined. The values of the vectors of the analyzed variables and factor loadings relative to the main components are illustrated in Table 5 and Fig. 5.

The first two components together account for 53.89% of the total variance, while three components account for 69.80%. It is easy to see that IV, %C, NPA-non-polar aliphatic hydrocarbons and Zn are most strongly correlated

Table 3
Statistical parameters for the overall content of non-polar aliphatic hydrocarbons

Localization		Sample no.				
		1	2	3	4	5
Parameters		[mg/kg]				
Maximum		36.87	39.67	42.05	23.94	26.28
Minimum		21.79	20.82	18.61	13.49	8.34
Average		28.02	30.80	25.12	17.97	19.62
Median		26.11	31.39	22.74	17.97	23.10
Standard deviation (SD)		5.40	6.60	7.41	3.02	6.93
Total hydrocarbons C_{12}–C_{35}, ingredients oil fraction [17]	50 mg/kg					

Table 4
Statistical parameters for the overall content of selected metals in soils, March–May 2018

Parameters	Pb	Cu	Ni	Zn
	[mg/kg d.m.]			
Minimum	46	23	11	8
Maximum	103	49	29	26
Average	73	35	20	15
Median	73	34	21	16
Standard deviation	11	6	5	4
Permissible content of selected metals in the soil [17]	200	200	150	500
Average % of metal content in soil in relation to the maximum allowable amount given in the OJ.165.1359 [17]	37	18	14	3

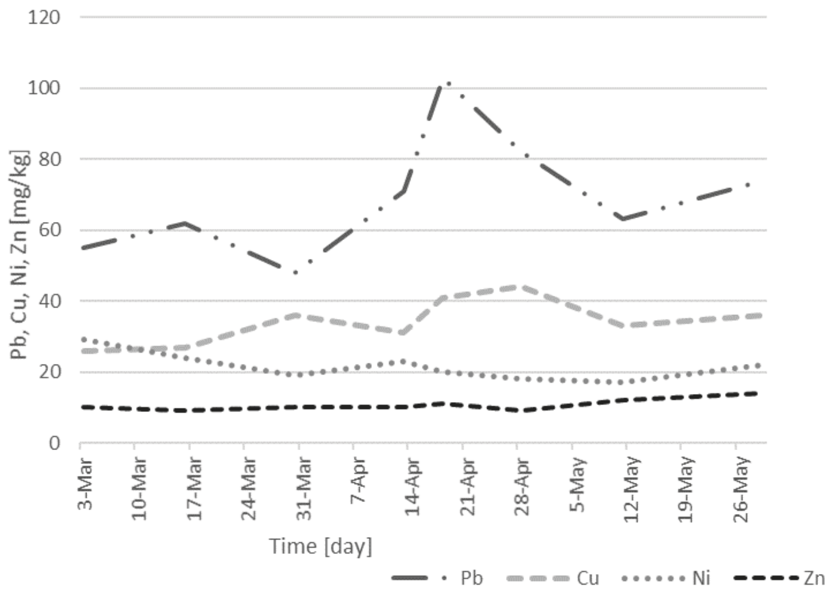

Fig. 4. Lead (Pb), copper (Cu), nickel (Ni), and zinc (Zn) content during the sampling period (March–May 2018).

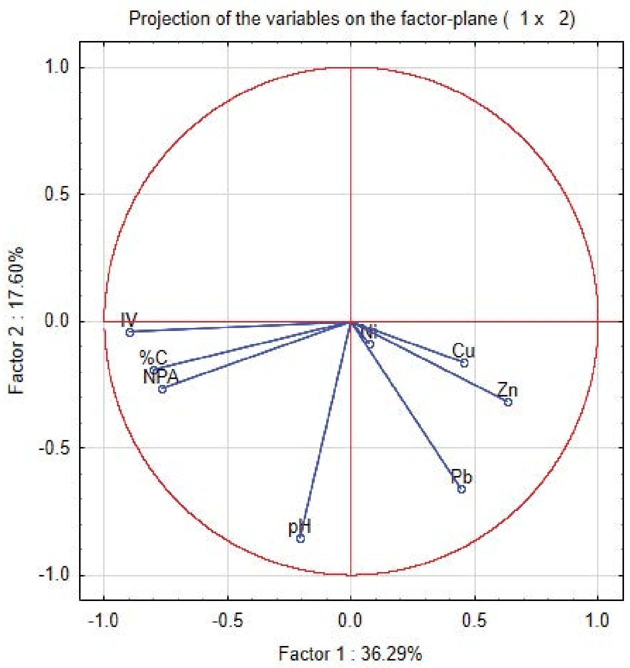

Fig. 5. Configuration of charge vectors of factors of the analyzed variables (%C, Pb, Cu, Ni, Zn, NPA, LJ, pH) and the first two main components (I and II).

with the first major component, Pb and pH with the second one (Fig. 5), Cu and Ni with the third oned (Table 5). The angles between the vectors illustrating the examined variables indicate a correlation of these variables, Zn and Cu, leads to a decrease in the iodine value. An increase in NPA results in an increase in % Corg. An increase in pH does not increase the iodine value. There is a relationship between % Corg and NPA-non-polar aliphatic hydrocarbons.

Table 5
Factor loadings for the first three components

Variables	Factor 1	Factor 2	Factor 3
Corg [%]	–0.802	–0.192	–0.329
Pb	0.443	–0.660	0.191
Cu	0.456	–0.164	–0.643
Ni	0.070	–0.087	–0.829
Zn	0.634	–0.318	0.090
NPA (non-polar aliphatic hydrocarbons)	–0.770	–0.266	0.111
IV (iodine value)	–0.901	–0.043	–0.051
pH	–0.208	–0.853	0.069

4. Conclusions

The scope of tests carried out taking into account pH, iodine number, organic carbon, content of non-polar aliphatic hydrocarbons, and selected heavy metals, as well as granulometric composition, indicates diverse pollution and a different degree of soil degradation.

- The studied soils are characterized by the largest percentage of coarse sand (0.63:2.0 mm) and medium sand (0.2:0.063 mm) fractions, the average iodine value indicates soils with average sorption.
- The content of organic carbon and iodine number used for the assessment of sorption capacity are closely correlated with each other and with the place of sampling for testing.
- In all the studied areas the soil has alkaline pH, which contributes to the lack of increased accumulation of heavy metals.
- The heavy metals selected for testing in the examined areas did not exceed the applicable maximum content specified in the Official Journal from 2016.

- Infrared spectroscopic studies allowed to assess the content of non-polar aliphatic hydrocarbons in the soil of the studied areas. These values are in the range of 8.34–42.05 mg/kg and were not exceeded in relation to the maximum values of the applicable standard OJ.165.1359.
- Due to the manner of use of the studied land, that is, as a recreational area and as a place of field work of students of surveying, there is no direct threat to the health and life of the users of the area covered by the study.
- Limitation of land use for the purposes of field work during periods of elevated temperature and rainfall, in order to eliminate the threat to student health.
- Reducing the risk of environmental threat by isolating the areas used from the transportation route by, for example, increased planting of shrubs and trees.
- It is recommended to further investigate the influence of phytoremediation on the reduction of contamination in the studied soil.

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