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Quality of the soil and water environment in the immediate vicinity of the Barania Gora Forest Reserve

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ABSTRACT

The aim of the study was to determine the content of selected fractions of bioavailable trace elements (Cd, Cr, Ni, Cu, Pb, Zn), the content of non-polar aliphatic hydrocarbons (NPA) in agricultural soils and the quality of drinking water from the Strawczyn intake. The tested soils had a neutral pH, the organic carbon content ranged from 0.92% to 1.02%. The bioavailable forms of the examined elements were characterized by a different percentage content between individual samples. In all the tested soils, the fractions that accounted for the highest percentage were the fraction with organic matter in the range of 9.1%–27.4% and the residual fraction in the range of 50.3%–75.2%, in which the immobilized metals accumulate in the residue insoluble in concentrated acids. The pH values of the tested soil from all the areas were in the range of pH 6.6–7.5, and the content of NPA was on average 26.74 mg/kg in all areas. The quality of drinking water from the deep water intake in Strawczyn is at the level of drinking water from the Zagnansk, it is low-mineralized, low-fluoride water, containing a large group of microelements beneficial for health.

Keywords: Sequential extraction; Heavy metals; Mobility of heavy metals; Drinking water

1. Introduction

This research paper determined the pollutants of arable lands located around the Barania Gora Reserve in terms of the total content and the fractions of heavy metals, and with regard to the impact of these pollutants on the quality of groundwater located within the Strawczyn water intake area.

The objective of the research paper was to determine the content of heavy metals in the arable soils repeatedly cultivated with agricultural machines in the areas adjacent to the nature reserve, and the impact of the pollutants found in the soil on the quality of the drinking water from the Strawczyn intake as compared with the drinking water from the Zagnansk intake. Kielce dwellers enjoy a very good quality water provided from the Zagnansk intake.

Being one of the environment constituents with a direct or indirect impact on human health and life, soil has the ability to accumulate various types of pollutants, including heavy metals.

The transmission of pollutants accumulated in soil to the human digestive system can take place through potable water and food of plant and animal origin. The highest emission of this type of pollutants results, for example, from industrial coal combustion, mining, metallurgical processing of metals and from other industries. Pollutants

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emitted into the atmosphere (e.g., from industry and households) are transported over long distances and ultimately most of them accumulate in the soil.

The emission of pollutants from industrial plants, including coking plants, has a significant impact on the soil and the vegetation covering it, the conducted research confirms that it is a source of excessive pollution [1].

The chemical industry, offering a wide range of products used in agricultural production, whose application is an important condition for improving the efficiency of farming, largely contributes to anthropogenic pollution [2]. Plant protection products and fertilizers used in agricultural production can contribute to increased bioavailability of selected heavy metals for plants. Therefore, the environmental risk assessment requires determining the shares of individual forms and fractions that make up the total content of a given metal [3].

The presence of hazardous substances in the soil is also associated with burning liquid fuels, abrasion of asphalt surfaces or car tyres and the wear of vehicle parts. Soil contamination due to pollution from motor vehicles in the vicinity of busy motorways occurs mainly in large cities with a high population density and a dense transportation network, but it is also to be found in relatively small areas with a large number of cars and other motor vehicles with high exhaust emissions.

Contamination with petroleum compounds is very dangerous (high frequency of occurrence). It has been assumed that in the case of accidents and catastrophes polluting the soil, about 40% of pollutants are oil derivatives [4].

Due to the adsorptive and buffering properties of soils, all pollutants are accumulated in it. In the water and soil environment, they undergo very slow chemical and biological degradation. This has a negative effect on plants. Pollutants cause lower quality of crops and yield reduction and hinder plant development [5].

In the case of forest soils, the greatest amount of pollutants is accumulated at the level of forest floor, while in arable land the greatest accumulation occurs up to the plowing depth [6]. Depending on the type of soil, the type of contamination and its concentration, the pollutants move deeper into the soil profile, posing a threat to groundwater. The use of integrated solutions in water quality analysis helps in taking strategic decisions, prioritizing remedial actions and assessing the phenomenon in a more accurate manner [7,8].

Water is one of the most important human resources, being a key factor in domestic, agricultural, industrial and recreational applications. Altering water quality through its deterioration may endanger human and animal health. In order to prevent the deterioration of water quality, it is necessary to conduct monitoring and collect reliable data in order to make appropriate decisions promptly. Main causes of the presence of heavy metals in water may be pollutants flowing from agricultural areas, high concentrations of chemicals, fertilization or the application of plant protection products.

Determining the concentration of heavy metals in water is of particular importance taking into account their toxicity during long-term exceeding of certain standards [9].

Water pollution threatens the sustainability of river ecosystems, therefore, it is necessary to control the quality of water in order to bring it to the optimum level so as to protect its ecology [10].

2. Research methodology

The research was conducted on agricultural soils around the Barania Gora Reserve, with an area of 81.6 ha (Figs. 1a and b) in the municipality of Strawczyn in the Swietokrzyskie Voivodeship. The study sites were located on the northern, southern, eastern and western sides of the reserve (Fig. 1b).

From the north, south, east and west, the sources of agricultural soils contamination include access roads to arable lands. Moreover, the Kielce – Czestochowa voivodeship road, performing the function of a local road for the inhabitants of the municipality, is a further source of contamination from the south. Since the arable lands are small-sized, there is an increased traffic of agricultural machinery during agrotechnical operations, spring sowing and autumn harvesting.

In the studied area, the arable land is divided into several small 2–3 ha farms, each with a different owner cultivating the land, which results in several times higher number of agricultural machines working in the area than in the case of ten times bigger farms.

In Strawczyn, about 4 km from the reserve, there is a drinking water intake for the local community.

The main sources of pollution are, first, the anthropogenic ones from road traffic, and then urban anthropogenic ones. Therefore the examination covered the soil of the cultivated lands and the water, which seeps from the surface of arable fields into groundwater and then feeds the intake in Strawczyn.

The water samples were collected from the area supplying the Strawczyn and Zagnansk intakes. The Zagnansk water intake for the city of Kielce was selected for comparative purposes, the water from this intake being "the highest quality product" [11].

The studies were conducted in the period July 2019 – January 2021. Depending on the conducted analysis, fresh or air-dry soil samples were examined. The reference sample consisted of 25 basic samples collected in accordance with the standard [12,13] with Egner's stick from a depth of 30 cm [14]. The water samples were collected from the watercourse supplying water to the intakes in Strawczyn and Zagnansk, in accordance with the instructions of water sample collection [15].

The following parameters were determined in the collected samples:

- granulometric composition (grain size structure) by laser diffraction using the Mastersizer 3000 in the soil [16],
- pH of the soil and the water (potentiometric determination) using a FiveEasy Plus pH meter FP20 (Mettler-Toledo, Warsaw, Poland), soil pH in 1 M KCl [17],
- organic carbon in soil using the Tiurin method [18],
- content of non-polar aliphatic hydrocarbons by spectroscopy in infrared with Fourier transform [19],
- the content of total forms and fractions of selected heavy metals Cd, Cr, Ni, Cu, Pb and Zn in the soil was

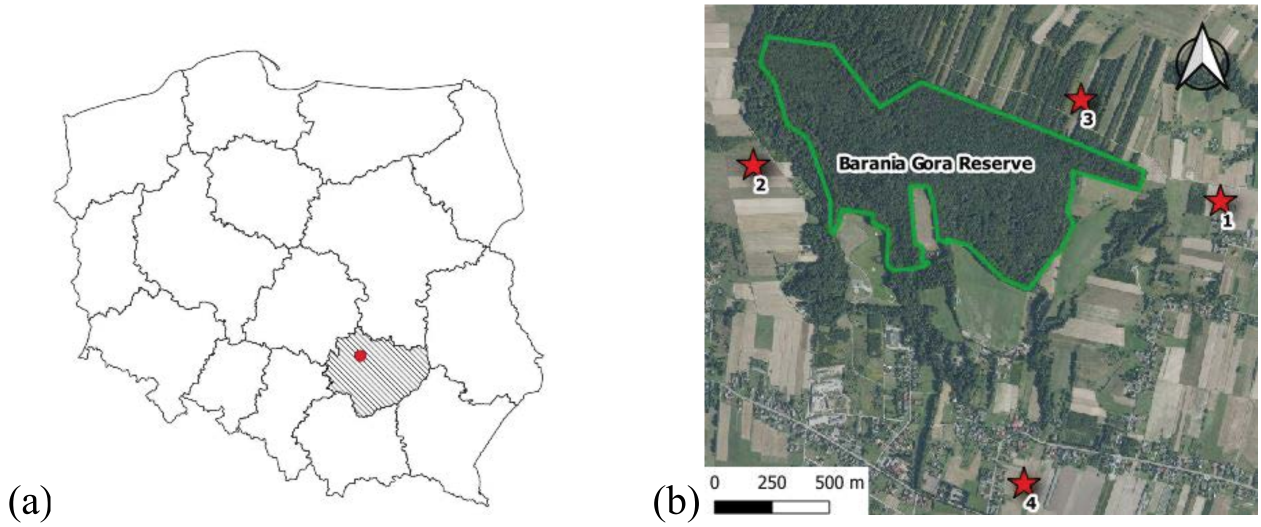

Fig. 1. Location of sampling points: (a) Poland, the Swietokrzyskie Voivodeship, •Nature Reserve Barania Gora, (b) Nature Reserve Barania Gora, sampling points *1,2,3,4 (Source: Authors' own study).

determined using the ICP-AES technique after mineralizing the samples with royal water in accordance with the EN-13346: 2000 standard] [20],
- total organic carbon (TOC) in water samples [21],
- total water hardness [22],
- determination of chloride ions in water with the application of Mohr's method and specific conductivity [23].

The obtained results provided the basis for calculating the arithmetic mean and determining the linear relationship between the parameters of the dust fraction and organic carbon. The results were performed in Microsoft Excel 2010.

The following parameters were determined: the soil pH and the particle size fractions, organic carbon content and non-polar aliphatic hydrocarbons (NPA) content. The sequential analysis of the heavy metals (Cd, Cu, Cr, Ni, Pb, Zn) was performed. The pH, metal content, chlorides, TOC and total hardness were determined in the water.

3. Results and discussion

3.1. Soil

The total content of heavy metals (Cd, Cr, Ni, Pb, Zn) in all research areas did not exceed 27% of the permissible amount specified in the Act [24], with the exception of cadmium (Cd), the content of which amounted to 63%.

In the entire study area, the following elements: lead, zinc and cadmium were those whose percentage was the highest (Table 1, Fig. 2).

Lead is included among the elements that are most toxic to living organisms. In agricultural soils, the lead content is strongly related to the granulometric composition and the organic matter. The acidic reaction of the soil, low humus content, and poor sorption capacity contribute to the process of lead uptake by plants. The source of soil contamination is industry and the use of vehicles [25]. The presence of lead in the surface layers of soils is related to the effect of anthropogenic factors. It is assumed that the natural content of this element is about 20 mg/kg, the Polish average being 18 mg/kg [26]. The total lead content in the study areas varied in the range of 17.72–54.77 mg/kg, with the average being 29.93 mg/kg (Table 1, Fig. 2).

Zinc is an element that is to be found in nature in the form of easily soluble compounds, especially in an acidic environment. It forms permanent connections with an organic substance, accumulates in the surface layers of the soil, and in the roots and leaves of plants. The total zinc content in soils is 10–200 mg/kg, with the average concentration

Table 1
Total heavy metal content in the soil in the research areas around the Barania Gora Reserve, the Swietokrzyskie Voivodeship

Sampling points	mg/kg					
	Cu	Cr	Ni	Pb	Zn	Cd
East	10.50	8.07	4.40	54.77	68.79	1.73
West	9.27	9.88	6.77	24.34	66.66	1.11
North	9.54	11.65	6.09	22.91	96.94	1.31
South	8.68	7.88	4.77	17.72	58.41	0.89
Average content from four study areas	9.49	9.37	5.50	29.93	72.7	1.26
Limit value of selected metals in soil [22]	200	200	150	200	500	2

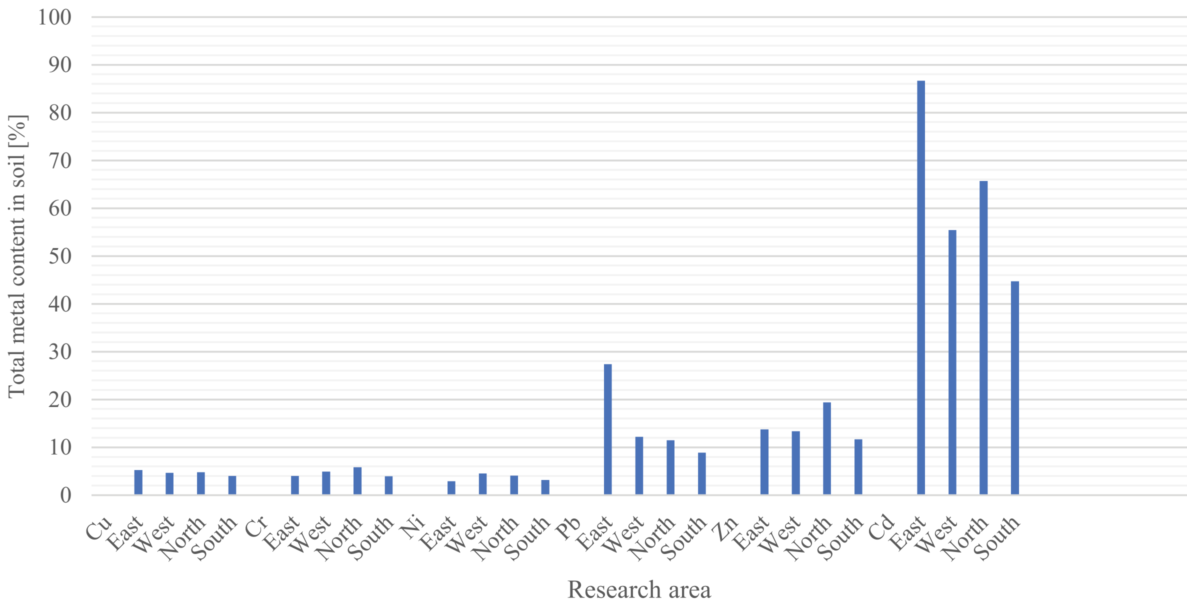

Fig. 2. Percentages of the total content of metals (Cu, Cr, Ni, Pb, Zn, Cd) in the soil at the testing grounds of the Barania Gora Reserve, the Swietokrzyskie Voivodeship.

of zinc in soils in Poland being 40 mg/kg [26]. The content of total zinc in the study areas ranged from 58.41 to 96.94 mg/kg, with the average of 72.70 mg/kg (Table 1, Fig. 2).

Cadmium is classified as one of the elements with the strongest toxic effect on the biosphere. Its average content in the earth's crust is estimated at 0.1–0.2 mg/kg, values of this order are usually found in light soils not exposed to anthropogenic threats. When soils are exposed to industrial or transportation pollution, they may contain much higher amounts in the range of 0.3–5.0 mg/kg. Cadmium is characterized by great ease of incorporating into the food chain, and its uptake by plants depends to a large extent on the pH. In acidic soils, its concentration is relatively high, but when the pH increases, cadmium becomes immobilized, it precipitates in the form of carbonates, sparingly soluble hydroxides, and its adsorption on soil colloids increases [25,26]. The total cadmium content in the study areas ranged from 0.89 to 1.73 mg/kg, the average was 1.26 mg/kg (Table 1, Fig. 2)

The copper content in soils varies and is in the concentration range of 1–140 mg/kg, with an average of 10.32 mg/kg. The content in the tested soils was 8.68–10.50 mg/kg, the average was 9.49 mg/kg (Table 1, Fig. 2) [26–28].

The presence of chromium in soils is generally low, it is related to the content in soil parent materials, where the concentration ranges from 7 to 150 mg/kg, 30 mg/kg being the average amount. The content in the tested soils was 7.88–11.65 mg/kg, the average was 9.37 mg/kg (Table 1, Fig. 2) [26,29].

The natural content of nickel in Polish soils at the surface levels falls within the range of 4–50 mg/kg, with the average of 7.4 mg/kg. The content in the tested soils was 4.40–6.77 mg/kg, the average was 5.50 mg/kg (Table 1, Fig. 2) [26,30].

The content of total forms of the studied elements Cu, Cr, Ni, Pb, Zn, and Cd was below the permissible content specified by the Standard [21], Cu, Pb, Zn, and Cd were above the average content in Polish soils [23] While analysing the mean value of exceeding the cadmium content, the Authors referred to the value of 0.3 mg/kg, because the studied soils are affected by the transportation-related pollution only.

Fraction one (F1) – the carbonate – sensitive to pH changes, contains the highest percentage share of cadmium and is identical in the three research areas: west, north and south Cd > Zn > Ni > Cu > Pb > Cr, the average percentage shares were 25.8 > 17.8 > 7.1 > 4.8 > 2.0 > 0.9, in the eastern area lead represents the lowest percentage share – 0.6% (Table 2, Fig. 3). Fraction two (F2) – metals absorbed on the surface of iron and magnesium oxides – in the west, north and south contain the highest percentage share of lead Pb > Cd > Cu > Ni > Zn > Cr, the average percentage shares of metals were: 26.6 > 12.2 > 9.6 > 7.2 > 6.8 > 0.3, in the eastern area nickel accounts for the highest share – 15.8%. Fraction three (F3) – metals absorbed on the organic surface – the average percentage share of elements in all areas is diversified. Fraction four (F4) – metals embedded in the crystal lattice of minerals – contains the highest percentage share of chromium also for the three research areas Cr > Ni > Cu > Zn > Cd > Pb, a differentiation in the eastern area and a high average percentage shares 80.2 > 75.0 > 63.5 > 56.0 > 33.8 > 15.5 are observed. The lead content in the samples collected from the east was dominant in Fraction four (90.4%), as opposed to the other samples, where the highest accumulation of lead was recorded in Fraction three in the samples collected in the west, north and south. For all the investigated areas, the highest average concentrations of metals were recorded in the F4 fraction.

Metals found in water-soluble compounds and metals bound to carbonates, which showed an average percentage content of 7.2%, except for cadmium (Cd) at the level of 24.3% (Fig. 3), are regarded as the most mobile ones.

Table 2
Classification of metals according to their percentage fraction content in soil on research plots around the Barania Gora reserve, Swietokrzyskie voivodeship

Percentage of metals in the fractions (%)			
Fraction one F1	Fraction two F2	Fraction three F3	Fraction four F4
East			
Cd > Zn > Ni > Cu > Cr > Pb	Ni > Cd > Zn > Cu > Pb > Cr	Cr > Ni > Cu > Zn > Cd > Pb	Pb > Cu > Cr > Zn > Cd > Ni
West			
Cd > Zn > Ni > Cu > Pb > Cr	Pb > Cd > Cu > Ni > Zn > Cr	Pb > Cd > Cu > Ni > Zn > Cr	Cr > Ni > Cu > Zn > Cd > Pb
North			
Cd > Zn > Ni > Cu > Pb > Cr	Pb > Cd > Cu > Ni > Zn > Cr	Pb > Cu > Cd > Cr > Zn > Ni	Cr > Ni > Cu > Zn > Cd > Pb
South			
Cd > Zn > Ni > Cu > Pb > Cr	Pb > Cd > Cu > Ni > Zn > Cr	Pb > Cd > Zn > Cu > Cr > Ni	Cr > Ni > Cu > Zn > Cd > Pb

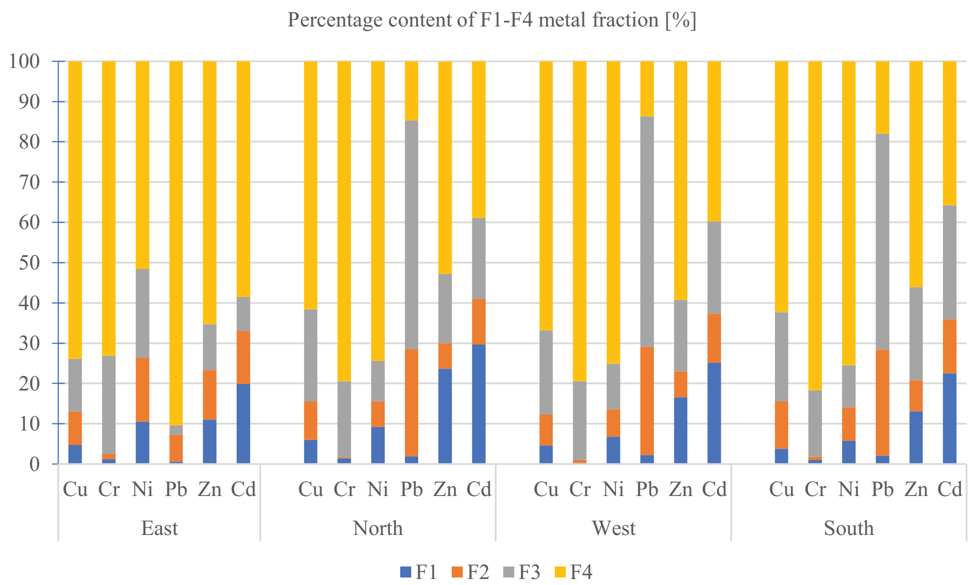

Fig. 3. Relation between the percentages [%] of the FI – FIV fractions of copper, chromium, nickel, lead, zinc and cadmium (Cu, Cr, Ni, Pb, Zn, Cd) and the place where the soil samples were collected during the research period.

The metals bound to the iron and manganese oxides are released into the environment much more slowly. Those metals, which form permanent bonds with organic matter or are present in the form of sulphides [31] are regarded as temporarily immobile. Unavailable metals are believed to be those bound to aluminosilicates.

Soil pH is a feature that determines the course of many processes in the soil environment. It has a considerable effect on the development and colonization of soils by microorganisms, soil sorption capacity, nutrient digestibility, bioavailability and phytotoxicity of heavy metals, plant development, etc. The optimum range of soil pH for most plants is between 6.0 and 7.0 [32]. In all the research areas, the pH of the tested soils fell within the optimum range of pH 6.6–7.5 (Table 3).

Organic matter is one of the most important components of the solid phase of soils, it is subject to mineralization and humification. Organic substances in the substrate undergo continuous quantitative and qualitative changes [33], by binding heavy metals into compounds that are insoluble or sparingly soluble in water, which limits their desorption to the soil solution, and thus their mobility in the soil [34].

The average content of organic carbon in soils in Poland is 0.9%–2.33%, whereas in the Swietokrzyskie Voivodeship it amounts to 0.94% (Table 3) [26].

Bioavailability of heavy metals depends on their form of occurrence. The determination of metal content in fractions allows to conclude on the possibility of migration in soil–plant and soil–groundwater systems. Most metals occur mainly in the non-mobile F4 fraction, however, metals such as Cd, Cu and Pb often show high percentages in mobile fractions [35].

In the studied soils, there is an increased content of very fine sand fraction at the average level of 18% and dust fraction at the level of 35%. The remaining fine, medium, coarse and very coarse sand fractions are at a comparable level (Table 3). The relation between the percentage share of the dust fraction and the content of organic carbon

Table 3
Average value of pH, dust fraction, organic carbon (Corg) and non-polar aliphatic hydrocarbons (NPA) in the examined soil around the Barania Gora Reserve, the Swietokrzyskie Voivodeship

Location	(-)	(%)		(mg/kg)	(%)
	pH	Dust (2–50 μm)	Corg	NPA	
East	7.4	26.6	0.92	24.9	49.8
West	6.6	46.0	1.02	23.9	47.9
North	7.0	31.2	0.94	26.5	52.9
South	7.5	35.6	0.98	31.7	63.3
Total hydrocarbons C_{12}-C_{35}, ingredients oil fraction [22]				50 mg/kg	[22]

results from the analysis of numerical data. The highest percentage share of the dust fraction (West) corresponds to the highest percentage of organic carbon content, the lowest percentage share of the dust fraction (East) contains the lowest percentage of Corg content (Table 3). Such a relation is not confirmed by the R-square determination coefficients for the dust fraction $R^2 = 0.0361$ and for Corg $R^2 = 0.0847$. Too large discrepancies were observed in the content of the dust fraction in the examined soil between the eastern and western areas (Fig. 4).

Contaminants deposited in soil undergo various processes, mainly of a physicochemical nature. Petroleum derivatives and heavy metals may migrate from the soil surface to surface and ground waters, which results in the deterioration of the soil and water environment and the disturbance of biological life [36,37]. The physicochemical properties of soil determine its quality, because the processes of adsorption, transportation and degradation of pollutants depend on them [38,39].

The maximum content of non-polar aliphatic hydrocarbons specified in the Act [22] was not exceeded in the researched areas. The increased content of NPA in the studied soil was found only in the southern section of the research area No. 4 (Table 3, Fig. 5) and amounted to 31.7 mg/kg, which is approximately 63% of the limit value. In this part runs the voivodeship road Kielce – Czestochowa, with increased intensity of local, tourism-related and general transportation use of vehicles. Studies have shown that in areas 1, 2, 3 their maximum NPA values (Table 3) account for approximately 50% of the limit value [22] and may pose a threat to human health, especially in the summer months. Hydrocarbons have the ability to penetrate into living organisms and accumulate in them. They can enter through the skin, digestive and respiratory systems [40].

3.2. Water

Surface waters may contain natural and anthropogenic pollutants that determine its quality.

Among the pollutants resulting from human activity, we can distinguish those connected with physical properties (causing turbidity, taste, smell and colour of water), as well as chemical and biological properties. The latter are a group of compounds and substances dissolved in water [41]. Water intended for human consumption must be of the appropriate quality and thus have physicochemical parameters specified in the Regulation of the Minister of Health [42], Council Directive 98/83/EC [43] and WHO Guidelines [44]. The laboratory analysis of the characteristics of water from the Strawczyn and Zagnansk water intakes and the physicochemical characteristics of raw

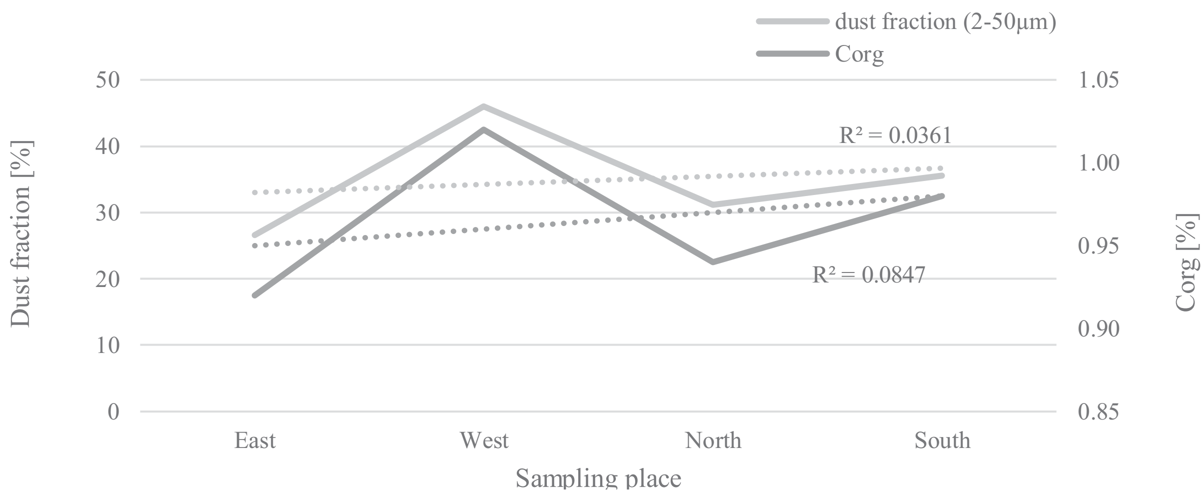

Fig. 4. Relation between organic carbon content and the dust fraction in the investigated soils.

water provided basis for comparative analysis. The following features which determine the chemical composition of the analysed water were identified: the pH, chloride content, total organic carbon (TOC), total hardness and electrical conductivity. The obtained results permitted calculating the average values for the duration of study (Table 5).

Waters from the area of the Barania Gora Reserve and the adjacent agricultural fields supply the drinking water intake for Strawczyn. The groundwater intakes Strawczyn and Zagnansk, used in the studies, are located in accordance with the direction of the watercourses, which for the analysed areas run from North to South East (Figs. 1a and 6a–c).

The city of Kielce is supplied with drinking water from several intakes; however, the water from the Zagnansk deep intake located 12 km from Kielce (Figs. 6a and c) is regarded as the best. Water in Kielce is of high health value, characterized by high nutrition and taste qualities, it is low-mineralized and low-fluoride, containing a large group of health sustaining minerals.

The mineral substances found in the Kielce water are present in an appropriate amount, making it beneficial for health [11].

The comparison of the chemical compositions of water from Strawczyn and Zagnansk shows differences in the case of Mg^{2+}, Cl^{-} and NO_3^- ions (Table 4). The remaining values are comparable and within the standard range [42,43].

The assessment of water quality before the treatment process was performed on the basis of the Regulation of the Minister of Health [42] on the quality of water intended for human consumption, the Regulation of the Minister of Maritime Economy [46] and the Regulation of the Minister of the Environment [43] on the criteria and methods of assessing the state of water bodies underground.

In the duration of the studies, the analysed water samples from the catchments supplying water for the Strawczyn and Zagnansk intakes were neutral and slightly alkaline. The mean pH values ranged from 6.25 to 7.47 (Table 5).

The amount of organic matter is an important parameter determining the degree of contamination of natural

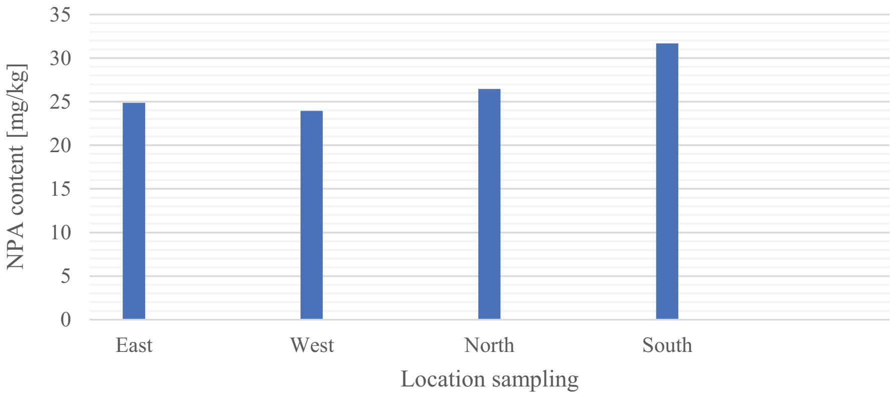

Fig. 5. Relation between the content of non-polar aliphatic hydrocarbons (NPA) and the place of soil samples collection.

Table 4
Parameters of drinking water from the intakes in Strawczyn and Zagnansk [11,45]

Chemical composition					
Mineral substance	Symbol	Average content (mg/kg)		Limit value (mg/kg)	
		Strawczyn	Zagnansk	Poland	European Union
pH	pH (-)	7.30	7.42	6.5–9.5	
Calcium	Ca^{2+}	91.0	62.20	n.n	n.n
Sodium	Na^{+}	9.5	5.0	200	175
Magnesium	Mg^{2+}	7.0	12.20	50	50
Iron total	Fe	0.04	0.04	0.2	0.2
Chlorides	Cl^{-}	38.9	15.4	250	200
Sulphates	SO_4^{2-}	25.60	45.3	150	150
Nitrates	NO_3^-	34.0	43.0	50	50
Fluorides	F^{-}	<0.10	<0.10	1.5	1.5
		Average content (mg/dm³)		D20172294 [42]	
General hardness	$CaCO_3$	229.0	202.0	60–500	

n.n - not normalized.

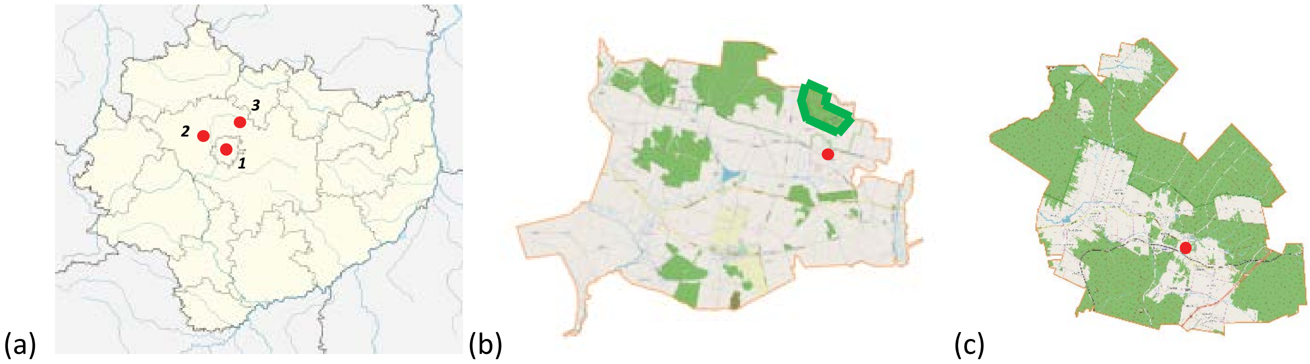

Fig. 6. Location of the sampling points: (a) Swietokrzyskie voivodeship, 1. Kielce, 2. Strawczyn, 3. Zagnansk, (b) the sampling point for water feeding the Strawczyn intake and (c) the sampling point for water feeding the Zagnansk intake (Source: Authors' own study).

waters. The TOC is a well-defined indicator identifying the total of all organic pollutants. Average TOC values in the range of 4.30–5.33 mg/dm^3 rank the tested waters in the 1st purity class (Table 5) [40]. Water conductivity can be regarded as an indicator of salt content. The obtained conductivity values did not exceed 1,000 Scm and the water can be considered as fresh and belongs to the 1st purity class (Table 5).

The concentration of dissolved magnesium and calcium ions in water (in the form of carbonates, bicarbonates, chlorides, sulphates and nitrates) is called the total water hardness. The total water hardness is also an important parameter of active aquatic ecosystems. On the basis of the average values in the range of 168.0–231.84 mg $CaCO_3$/dm^3 found in the analysed water, it can be classified as medium hard (Table 5).

Chlorides are essential compounds for living organisms, including humans. They are one of the components with the highest percentage share in water. They are not harmful to health, but their excess is manifested by an increased corrosive effect of water on metallic materials, which may lead to an increase in the metal content. Chlorides rarely enter groundwater, it happens in the case of specific substrate and intense anthropogenic activity. The chloride content in the analyzed waters of Strawczyn and Zagnansk is approximately 7.0% in relation to the applicable Polish standard (Table 5) [42].

In the soil samples collected in the entire research area the highest percentages were recorded for lead, zinc and cadmium (Fig. 2). For water, on the other hand, it was nickel, lead and cadmium (Table 6). All the heavy metals, with the exception of lead and cadmium, did not exceed the concentration limits provided by WHO (Table 6) [44]. The increased lead content in water may result from of the presence of lead, largely in mobile fractions (FI and FII), at the sampling area. Lead in mobile fractions has the ability to migrate from the soil, it can get into the groundwater, resulting in its increased content there. There is a strong relation between the content of heavy metals in the FI + FII fractions in the soil and the total content of metals in water (Fig. 7).

4. Conclusions

The specific feature of the studied area is small-sized farms with several hectares of land. The conducted research has shown that the level of pollutant emissions from the agricultural machinery, the intensity of fertilization and the frequent use of vehicles on the way to arable fields cause pollution with heavy metals and NPA. The studied soils have a neutral pH, slightly exceeding pH 7.2. A detailed analysis of the content of individual granulometric fractions indicates a high presence of the dust fraction (35%) and fine sand (18%), which provides favourable conditions for agricultural crops, but a low content of organic matter (0.94%) requires intensive cultivation.

The contamination with heavy metals: cadmium, chromium, nickel, lead, zinc did not exceed 27% of the limit value specified in DU20161395, in the case of cadmium the contamination amounted to 63% of the value. Bioavailability and related heavy metals digestibility by plants depend on the chemical form of the metal and the ways in which it is present in the environment. The metals

Table 5
Parameters of the underground water supplying the drinking water intakes in Strawczyn and Zagnansk

Parameter	Unit	Average values	
		Strawczyn	Zagnansk
pH	(-)	7.47	6.25
Total organic carbon	(mg/dm^3)	5.33	4.30
Chlorides	(mg/dm^3)	17.7	18.0
Total hardness	(mg$CaCO_3$/dm^3)	231.84	168.0
Conductivity	(µS/cm)	578	339

Table 6
Heavy metal contents of carbonate fraction F1 and oxide fraction F2 in soil (mg/kg) and in waters from intakes in Strawczyn and Zagnansk (mg/L)

Metal	Average content (FI + FII) in the soil (mg/kg)	Metal content in the water from the Strawczyn intake (mg/L)	Metal content in the water from the Zagnansk intake (mg/L)	Limit value for the content of the examined metals in the water (mg/L) [41]
Cu	1.33	0.006	0.030	2.00
Cr	0.16	0.001	0.001	0.05
Ni	0.92	0.010	0.015	0.02
Pb	5.67	0.016	0.076	0.01
Zn	18.16	0.035	0.190	3.00
Cd	0.46	0.001	0.020	0.003

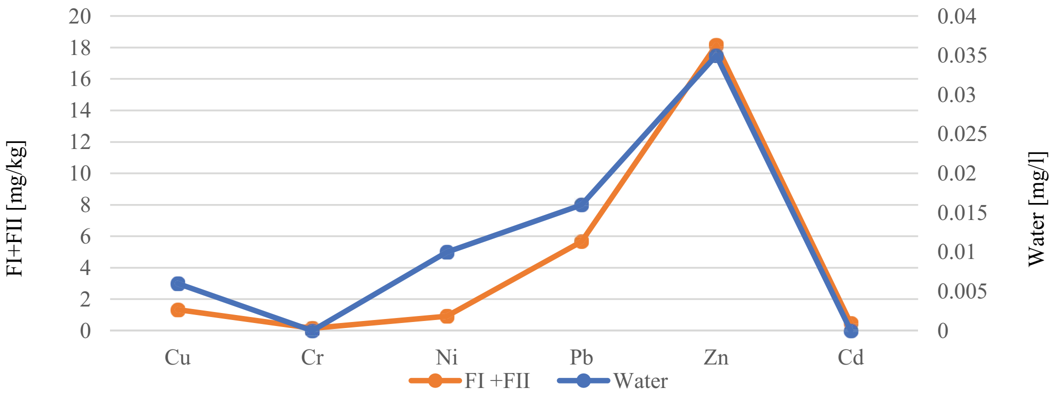

Fig. 7. Heavy metal content in the tested water and in the FI + FII fractions in the soil.

found in water-soluble compounds and metals bound to carbonates are considered to be the most mobile ones. As far as Fraction 1 is concerned, the highest percentage share was recorded for cadmium with 24.3%, on the surface of Fraction 2 (F2) the highest percentage share was recorded for lead that accounted for 22.3%. Also, non-polar aliphatic hydrocarbons cause soil contamination to the degree of 50% of the standard value, a slight exceedance occurred in the southern region along an additional road route.

Substances contaminating the studied soil from the area of the Barania Gora Reserve do not pose a threat to the drinking water intake in Strawczyn. The groundwater collected from the deep intake supplying water to the Strawczyn intake is characterized by very good physicochemical parameters, which permit it to be classified as the water of the 1st class of purity. The slightly exceeded limit for lead in the studied water is the result of an increased lead content in the mobile fractions.

Using a comparative analysis of the examined groundwater and referring to the parameters of drinking water from the intakes for Strawczyn and Kielce, we can conclude that the inhabitants drink good quality water, and the studied area is not contaminated with the analysed metals.

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