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THE HYDROCARBON IMPURITY OF MINERAL WATERS AND SOILS IN IWONICZ-ZDRÓJ

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Abstract:
The commune of Iwonicz-Zdrój is a spa commune. The co-occurrence of springs of mineral water with sources of hydrocarbon substances is characteristic of the commune. The natural emissions of hydrocarbons poses a risk of their continuous or pulsed entering into soil and water.
The zone A of the health resort protection is to meet the specific requirements of environmental protection. In this zone, samples of soil and underground water were taken for laboratory tests. Substances exceeding the standards of environmental quality were fixed.

Key words: *soil, water, mineral water springs, the analysis of physico-chemical*

INTRODUCTION

Places of natural emissions of hydrocarbons is a potential source of contamination [4, 5]. The hydrocarbon substances are difficult to remove. This means that they are stable in the hydrogeological environment. This pollution degrades the natural condition of the subsoil. The ground becomes the focuse of toxiticity.

The commune of Iwonicz-Zdrój have the status of the spa and must meet specific legal requirements on environmental protection zones of the health resort [13].

The zone A of the health resort in the commune of Iwonicz-Zdrój is an area of 155 ha. There are located devices and spa treatment facilities and other facilities that serve health resorts treatment activities, support the patient and the tourist. The green areas represent 89 % of surface area of the zone A of the health resort.

In the paper are given some of the results of physic-chemical properties of soil and underground water that are made by an accredited laboratory.

METHODS

The general area of study determines net 14 points that the coordinates of the situation and elevation were determined by GPS, Fig. 1 and 2. It defines the area of field research conducted in the zone A of the health resort to the commune of Iwonicz-Zdrój. Environmental samples were collected at points 1, 2 and 3 net (by [9, 10]).

Research position no. 1 – assesment of physic-chemical

Results of laboratory tests of soil samples, taken at well (Fig. 3 and 4) did not indicate the presence of hydrocarbon indicators expressed the sum total of gasoline and mineral oils, Table 1. In terms of monocyclic aromatic hydrocarbons all samples meet the quality requirements for type "A" areas to be protected. Polynuclear aromatic hydrocarbons in some cases appear in measurable amounts, but only in one case and only the concentration of phenanthrene exceeded the standard value for soil type "A". It is recorgnized that there shuld be an additional samples is taken from this place to confirm the significance of this excess.

The next soil samples (Table 3, code 247.2/1) showed very high concentrations of polynuclear aromatic hydrocarbons, with the exception of anthracene, benzo(g,h, i) perylene and benzo(a)fluoranthene. The results of samples from the lower depths is not show elevanted levels of these substances. It was recorgnized that very high concentrations of PAHs may be a natural result of the occurrence of domestic heavy hydrocarbons to shallower soil layers. Accordingly, theses spiky and large depth of occurance of elevated contents should be verified whether it actually exceeded the reference values are characteristic for the site and examined in depth. Generic compositon of PAHs could be an important parameter of comparison.

Found to exceed the maximum content of nickel in all samples and exceedances of barium, chromium and copper in several cases (Table 1). No clear trends observed concentrations explaning their source. For this reason it is considered that it would be desirable also to make additional studies on the content of these metals into the area, particulary in areas that may be regarded as a natural geochemical background of groundwater.

Grandwoter extracted from the well from a depth of 1,80 m below the surface meets the content of heavy metals and polycyclic aromatic hydrocarbons of class I [8]. The values of all the indicators examined are located on the hydrogeochemical background levels, Table 2.

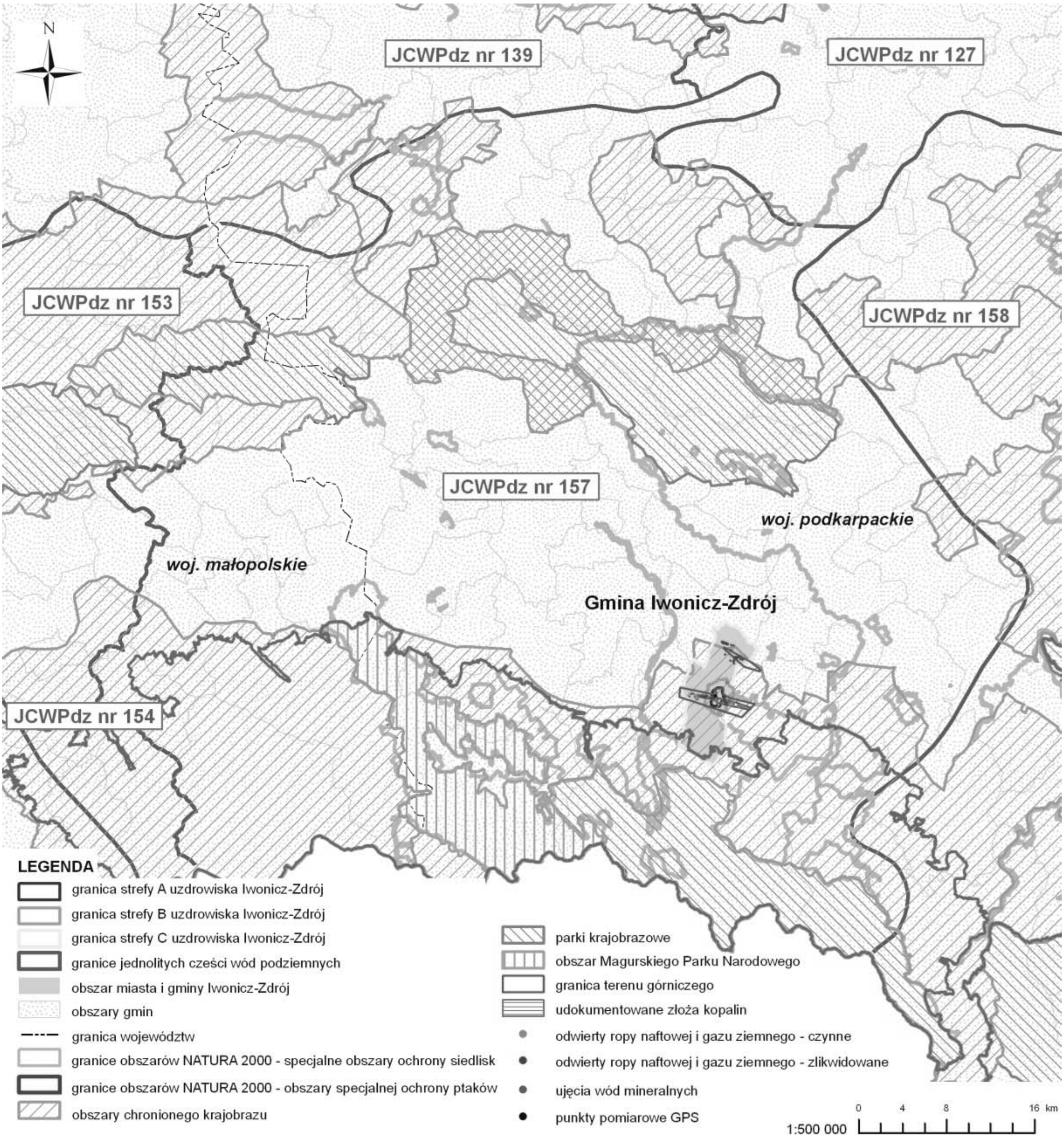

Fig. 1. Location of the commune of Iwonicz-Zdrój against the body of groundwater No. 157 and natural protected areas; Subcarpathian voivodeship, 2012 (author's study Lipińska E. J. and Rybak T. on [1, 2, 3, 6, 7, 12, 14, 15])

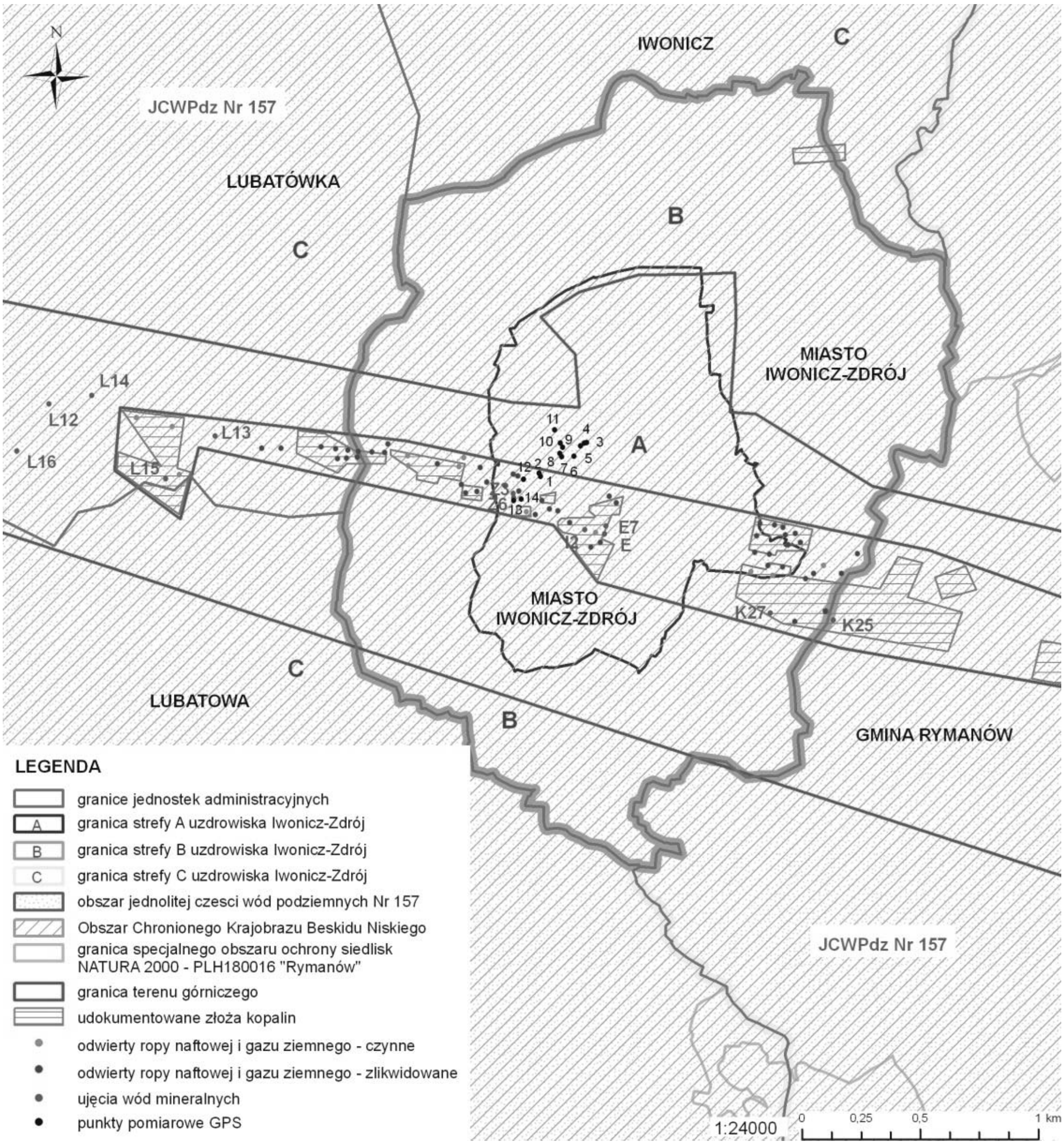

Fig. 2. Location of 14 study points. Zones A, B and C of the health resort in the commune Iwonicz-Zdrój spa protection against groundwater body No. 157 and natural protected areas. Proven natural medicinal resources: K27-Klimkówka 27, I II-Iwonicz II, E-Emma, E7-Elin 7, L12-Lubatówka 12, L14-Lubatówka 14, Z6-Zofia 6; Subcarpathian voivodeship, 2012 (author's study Lipińska E. J. and Rybak T. on [1, 2, 3, 6, 7, 12, 14, 15])

Fig. 3. Research Position No. 3. The well covered with a concrete slab – emissions from inside the well; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011 (photo by Lipińska E. J.)

Fig. 4. Research Position No. 3. The well has wooden casing preserved; see the section of pipe casing; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011 (photo by Lipińska E. J.)

Table 1

Research Position No. 1. The results of soil tests – range of heavy metals; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011

Index	Unit	The results of measurement							Admissible value for type „A" of the area by [11]
		Sample code							
		247.1/1	247.1/2	247.1/3	247.1/4	247.1/5	247.1/6	247.1/7	
		Deph							
		0,10 m	0,50 m	1,0 m	2,0 m	3,0 m	5,0 m	6,5 m	
Barium	mg/kg dry s.	121	70	**320**	138	158	176	**202**	200
Kadmium	mg/kg dry s.	0,64	0,57	0,30	<0,4	<0,4	<0,4	<0,4	1
Chromium	mg/kg dry s.	50	25,8	**60**	**51**	**59**	50	**57**	**50**
Copper	mg/kg dry s.	**33,8**	10,5	**47**	**31,3**	24,9	25,9	27,3	**30**
Nickel	mg/kg dry s.	**64**	**38,0**	**135**	**37,0**	**36,8**	**35,4**	**36,8**	**35**
Lead	mg/kg dry s.	16,8	11,2	11,8	7,1	12,3	6,7	6,9	50
Mercury	mg/kg dry s.	0,128	0,054	0,117	<0,05	<0,05	<0,05	0,210	0,5
Fenanthren	mg/kg dry s.	0,026	<0,02	<0,02	<0,02	<0,02	0,100	**0,133**	0,1

Table 2

Research Position No. 1. The results of underground water; I-values that fall below the concentrations of the sample; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011

Index	Unit	The results	Hydrogeochemical background	Admissible value for underground water of quality classes by [8]				
		247.4/2		I	II	III	IV	V
Barium	mg/l	**0,058 ± 0,006**	0,01 – 0,3	**0,3**	0,5	0,7	3	>3
Chromium	mg/l	**<0,0005**	0,0001 – 0,010	**0,01**	0,05	0,05	0,1	>0,1
Copper	mg/l	**<0,001**	0,001 – 0,020	**0,01**	0,05	0,2	0,5	>0,5
Nickel	mg/l	**0,0063 ± 0,0006**	0,001 – 0,005	**0,005**	0,01	0,02	0,1	>0,1
Lead	mg/l	**<0,005**	0,001– 0,010	**0,01**	0,025	0,1	0,1	>0,1
Mercury	mg/l	**<0,000005**	0,00005 – 0,001	**0,001**	0,001	0,001	0,005	>0,005
Dibenzeno(ah)anthracene	mg/l	**<0,000001**	–	–	–	–	–	–
Benzo(a)piren	mg/l	**<0,000001**	0,000001 – 0,00001	**0,00001**	0,00002	0,00003	0,00005	>0,00005
Benzo(b)fluoranthene	mg/l	**<0,000001**	–	–	–	–	–	–
Benzo(k)fluoranthene	mg/l	**<0,000001**	–	–	–	–	–	–
Benzo(g,h,i)perylene	mg/l	<0,000001	–	–	–	–	–	–
Indeno(1,2,3-cd)pirene	mg/l	<0,000002	–	–	–	–	–	–
Sum PAHs	mg/l	<0,000002	0,00001 – 0,0001	**0,0001**	0,0002	0,0003	0,0005	>0,0005

Research position no. 2 – assesment of physic-chemical

The test of oil simples with codes 247.2/2-4, Table 3, the content of polynuclear aromatic hydrocarbons showed no significant exceedances expect for phenanthrene and beno (a)anthracene with a total PAHs content is located in the limit values.

In terms of heavy metals was a slight over-concentration of copper and the like crossing the bar, Table 4. In the one simple showed a large oversize nickel content. In another the sample of metal concentrations exceeded the limit values. The concentrations of barium, chromium and copper to a small extent while the nickel content significantly exceeded the limit values for type "A" protected area is also exceeded the permitted level laid down for the "B" sites [11].

Table 3
Research Position No. 2. The results of soil tests – range of PAHs; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011

Index	**Unit**	**The results of measurement**				**Admissible value for type „A" of the area by [11]**
		Sample code				
		247.2/1	**247.2/2**	**247.3/3**	**247.2/4**	
		Deph				
		7,5 m	**0,10 m**	**1,0 m**	**7,5 m**	
Sum monocyclic aromat ic hydrocarbons	mg/kg dry s.	-	-	-	-	0,1
Naphthalene	mg/kg dry s.	**3,64 ± 2,18**	<0,02	<0,02	0,037 ± 0,022	0,1
Phenanthrene	mg/kg dry s.	**1,80 ± 0,90**	<0,02	<0,02	**0,70 ± 0,35**	0,1
Anthracene	mg/kg dry s.	<0,01	<0,01	<0,01	<0,01	0,1
Fluoranthene	mg/kg dry s.	0,023 ± 0,012	<0,01	<0,01	<0,01	0,1
Benzo(a)anthracene	mg/kg dry s.	**0,62 ± 0,25**	<0,01	<0,01	**0,15 ± 0,06**	0,1
Chrysen	mg/kg dry s.	**0,19 ± 0,06**	<0,01	0,011 ± 0,003	0,059 ± 0,018	0,1
Benzo(a)fluoranthene	mg/kg dry s.	<0,01	<0,01	<0,01	<0,01	0,1
Benzo(a)pirene	mg/kg dry s.	**0,082 ± 0,058**	<0,01	<0,01	0,013 ± 0,009	0,02
Benzo(g,h,i)perylene	mg/kg dry s.	0,047 ± 0,033	<0,01	<0,01	<0,01	0,1
Sum PAHs	mg/kg dry s.	**6,40 ± 2,37**	<0,01	0,011 ± 0,003	0,96 ± 0,36	1

Table 4
Research Position No. 2. The results of soil tests – range of heavy metals; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011

Index	**Unit**	**The results of measurement**				**Admissible value for type „A" of the area by [11]**
		Sample code				
		247.2/1	**247.2/2**	**247.2/3**	**247.2/4**	
		Deph				
		7,5 m	**0,10 m**	**1,0 m**	**7,5 m**	
Barium	mg/kg dry s.	--	161 ± 24	**226 ± 34**	**208 ± 31**	200
Cadmium	mg/kg dry s.	-	-	-	-	1
Chromium	mg/kg dry s.	-	40,4 ± 10,1	38,2 ± 9,6	**64,4 ± 16,1**	50
Copper	mg/kg dry s.	-	**30,9 ± 7,7**	26,8 ± 6,7	**37,8 ± 9,4**	30
Nickel	mg/kg dry s.	-	**139 ± 28**	20,5 ± 4,1	**143 ± 29**	35
Lead	mg/kg dry s.	-	-	-	-	50
Mercury	mg/kg dry s.	-	-	-	-	0,5

Research position no. 3 – assesment of physic-chemical

The research position No. 3 was determined in the vicinity of the source "Bełkotka" – a monument of nature, Fig. 5. Research on polynuclear aromatic hydrocarbons in soil suggest a slight excess: naphthalene, phenanthrene and chrysene, Table 5. It shuld be noted that the total PAHs content is error-level analysis of the acceptable values.

In terms of heavy metals was a slight over-concentration of chromium, nickel and copper, Table 6.

Fig. 5. The sources of "Bełkotka"; surface is covered with autumn, fallen leaves – interference waves created by the emission of natural gas arranged them in circles; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011 (photo by Lipińska E.J., 2011)

Table 5
Research Position No. 3. The results of soil tests – range of PAHS; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011

Index	Unit	The results of measurement – Sample code 247.3/1, Deph 0,30 m	247.3/2, 1,0 m	247.3/3, 7,5 m	Admissible value for type „A" of the area by [11]
Sum monocyclic aromat ic hydrocarbons	mg/kg dry s.	-	-	-	0,1
Naphtalene	mg/kg dry s.	**0,24 ± 0,14**	<0,02	0,078 ± 0,047	**0,1**
Fenanthrene	mg/kg dry s.	**0,52 ± 0,20**	<0,02	**0,41 ± 0,20**	**0,1**
Anthracene	mg/kg dry s.	<0,01	<0,01	0,012 ± 0,006	0,1
Fluoranten	mg/kg dry s.	0,040 ± 0,020	<0,01	0,037 ± 0,018	0,1
Benzo(a)anthracene	mg/kg dry s.	0,044 ± 0,022	<0,01	0,032 ± 0,016	0,1
Chrysen	mg/kg dry s.	**0,18 ± 0,05**	<0,01	**0,26 ± 0,08**	**0,1**
Benzo(a)fluoranthene	mg/kg dry s.	0,014 ± 0,008	<0,01	0,013 ± 0,008	0,1
Benzo(a)pirene	mg/kg dry s.	0,014 ± 0,010	<0,01	0,063 ± 0,044	0,02
Benzo(g,h,i)perylene	mg/kg dry s.	<0,01	<0,01	<0,01	0,1
Sum PAHs	mg/kg dry s.	**1,05 ± 0,30**	<0,01	0,90 ± 0,23	**1**

Table 6
Research Position No 3. The results of soil tests – range of heavy metals; the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011

Index	Unit	The results of measurement – Sample code 247.3/1, Deph 0,30 m	247.3/2, 1,0 m	247.3/3, 7,5 m	Admissible value for type „A" of the area by [11]
Barium	mg/kg dry	-91 ± 14	73 ± 11	180 ± 27	200
Kadmium	mg/kg dry	-	-	-	1
Chromium	mg/kg dry	**54 ± 14**	42 ± 10	**76 ± 19**	50
Copper	mg/kg dry	25 ± 6	30 ± 8	**85 ± 21**	30
Nickel	mg/kg dry	23 ± 5	**40 ± 8**	**41 ± 8**	35
Lead	mg/kg dry	-	-	-	50
Mercury	mg/kg dry	-	-	-	0,5

Table 7
Research Position No. 3 – Bełkotka. *The results of underground water – range of heavy metals;* ***the commune of Iwonicz-Zdrój, Subcarpathian voivodeship, 2011***

Index	Unit	The results – Code 247.3/4, Deph 0,70 m ppt	Hydrogeochemical background	Admissible value for underground water of quality classes by [8] – I	II	III	IV	V
Barium	mg/l	0,061 ± 0,006	**0,01 – 0,3**	0,3	0,5	0,7	3	>3
Chromium	mg/l	0,0106 ± 0,0011	0,0001 – 0,010	**0,01**	**0,05**	0,05	0,1	>0,1
Copper	mg/l	0,0266 ± 0,0027	0,001 – 0,020	0,01	**0,05**	0,2	0,5	>0,5
Nickel	mg/l	0,0146 ± 0,0015	0,001 – 0,005	0,005	0,01	**0,02**	0,1	>0,1

When reached aquifer investigated whether groundwater is a mixture of hydrocarbon substances. Study using a thickness gauge hydrocarbons ruled their presence. The physic-chemical analysis indicated that the groundwater meets the requirements on the heavy metal content of a least of class III, Table 7. This means that one of the "waters of satisfactory quality where the physic-chemical elements are increased as a result of natural process occurring in groundwater or a weak impact of human activity" [8]. The decisive factor is the increased concentration of nickel in a sample of underground water. The concentrations of other metals are at the level of water quality and the barium content in the range of hydrogeochemical background.

CONCLUSIONS

1. These exmples confirm the desirability of physico-chemical properties in zone A of the healt resort in the commune of Iwonicz-Zdrój that is the spa commune.
2. Physoco-chemical analysis of soil samples showed that tere exceeded environmental quality standards for such substances hydrocarbons: phenanthrene, naphthalene, benzo(a)anthracene, chryzene, benzo(a)pirene, the total of PAHs.
3. Physico-chemical analusis of soil samples showed that tere exceeded environmental quality standards for such heavy metals: barium, chromium, copper, nickel.
4. Physico-chemical analusis of groundwater samples showed that there were exceeded in the case of nickel.
5. The described methodology for the determination of hydrocarbon contaminants and heavy metals in soil and underground water creates the possibility of full control of environmental quality standards in the zone A of the health resort.
6. Continued monitoring shuld allow to investigate the changes of hydrocarbon impurities during the course of their natural biodegradation or to determine corrective actions by identifying changes in the values of the parameters.
7. Those activities are designed protect groundwater form hydrocarbons emissions from old mine worgings.

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