AGH DRILLING, OIL, GAS • Vol. 33 • No. 1 • 2016

http://dx.doi.org/10.7494/drill.2016.33.1.39

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MONITORING OF PETROLEUM SUBSTANCES IN THE NEIGHBORHOOD OF DRINKING WATER INTAKE**

1. INTRODUCTION

Area of groundwater quality monitoring is located in the area belonging to the shopping center parking consisting of 865 parking spaces and internal passageways. Parking is located in the underground water intake, so it is necessary to monitor the impact of car parking on groundwater. Car parking, belonging to the shopping centre, is located in the protection zone established in 1998, Decision of the Governor of Krakow, for the water intake Mistrzejowice. That decision was taken in accordance with applicable when the Minister of the Environment, Natural Resources and Forestry on the framework for establishing protection zones sources and groundwater intakes [13]. Protective zone for the intake was upheld by Regional Water Management in Krakow at 24 June 2013 on the establishment of a protection zone of underground water intake Mistrzejowice [17].

The existing provisions of the Regulation of the Minister of the Environment, Natural Resources and Forestry [15] were among the group of car parks or parking lots for more than 500 cars. For this reason, geological documentation for the location of the shopping center area was carried out in 2002, setting out in accordance with the then applicable law Geological and Mining Law [14], the hydrogeology of the area of the shopping center parking lots. This documentation showed the necessity of monitoring existing water intake, designed to supply the population with drinking water. Therefore, was created a network of monitoring holes documented in [9]. Network of holes and quarterly monitoring of groundwater samples creates a system of constant monitoring of quantitative and qualitative changes in groundwater monitoring in accordance with the idea of shielding in the protection zone approach, presented in the literature [7].

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** Work performed within the statutory research program of AGH UST 11.11.190.555

2. GEOLOGICAL AND HYDROGEOLOGICAL CONDITIONS IN THE RESEARCH AREA

Car parking is located within a large geological unit – Carpathian Foredeep. It is built of a tertiary layer of considerable thickness – Miocene, developed in the form of clays and shales with interbeds of fine sand and gypsum. The top of these layers is eroded by the Vistula River and its tributaries. In the holes located at area of parking lot, the top of clays was found at a depth of 19.5 to 24.8 m below ground level, at altitudes from 193.05 to 189.62 meters above sea level (wells 19 and 19a). Over arrears Quaternary – Pleistocene, forming accumulation terraces, built in the bottom of land sand – gravel, and the top of the sandy soil and alluvial loess. The thickness of the latter was defined in the monitoring hole M6 and is 12.3 m below the ground. There are clays, sandy clays, dust clays, sands with different grain size, gravel and boulders and occasionally silts and peats (well 19a). These works are characterized by significant variability in both the vertical and horizontal spread.

Groundwater in the area of research, occur within the Quaternary. The study area is located within the major groundwater basin, (MGB 450) – Valley of the river Vistula. Characteristic parameters of MGB are as follows: Estimated disposable resources – 20 000 m^3/day, the average depth of shots – 15 to 30 m, the type of center-porous surface MGB – 95 km^2 [5].

Usable aquifer is a complex gravel-sand 8.7–12.5 m thick, impermeable clays tertiary. Over the complex was found groundwater, where host rocks are water-bearing sandy land with different granulation of very many small interbeds of clayey soils. Power of quaternary groundwater in this area is carried out by infiltration of rainwater. Underground water table does not form in this case, a continuous film. Water is provided directly by the infiltration of rain water. During periods of prolonged droughts water can be lost, as evidenced by the course of the monitoring study.

3. PROCEDURE FOR STUDIES OF WATER TABLE CHANGES

In some holes periodically there was no presence of water or its amount did not provide a representative collection of samples for laboratory tests. Periodic interruptions in water monitoring holes endearing suspended groundwater indicate that there is a hydraulic connection between the water and the utility, located below the aquifer. Suspended water was found in monitoring holes M1–M5, and M6 hole in the suspended water did not succeed and the hole goes directly to the aquifer.

Changes of the position of underground water table in each measurement series with a reference to all the monitoring holes are shown in Figure 1. It shows that the underground water table in the study fluctuates in each monitoring hole. Position of water table in monitoring hole M5 shows periods without water. These are time series 11-13 and 18-22. Water dropouts in the hole M5 made it necessary to deepen. The reconstruction of this hole was carried out in 2005 [9]. M5 hole after reconstruction is used to monitoring the other aquifer.

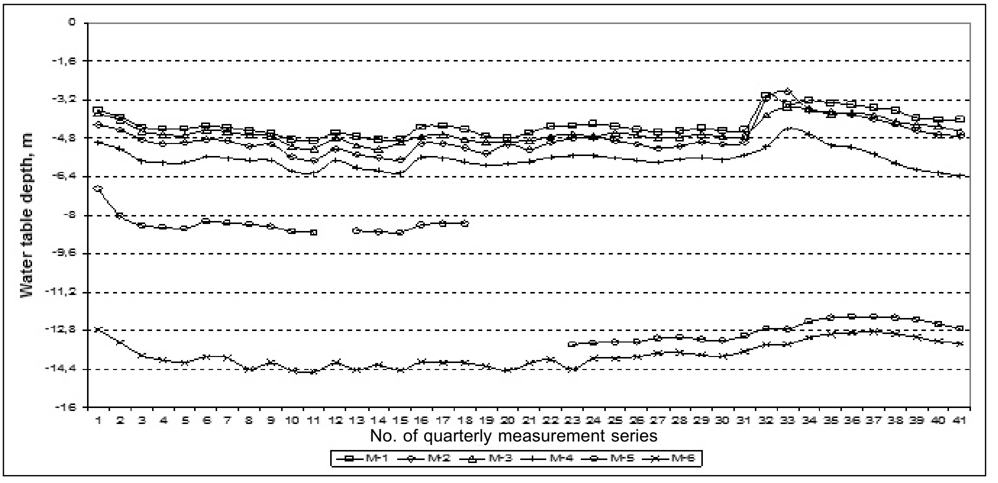

Fig. 1. Changes of groundwater table in monitoring wells

4. THE PROCEDURE FOR MONITORING OF WATER QUALITY

Holes for monitoring the quality of water that may contain oil pollution having a density less than the density of water, have been designed in accordance with the principles contained in the literature [7]. Consequently, the perforated part of the filter includes a predicted maximum level of the water table in the hole, which allows the supply of any liquid hydrocarbon phase to monitoring hole and collecting a representative sample to test. Representative sample taken from the monitoring hole with a special probe is used to measure the thickness of residual hydrocarbon at the water table. The quarterly results of the field studies of the presence of oil in the form of free petroleum product at the groundwater table was performed by a special probe of liquid hydrocarbon phase, that is the product of the Dutch company – Eijkelkamp Agrisearch Equipment. New original probe of liquid hydrocarbon phase has been tested, which is the copyright solution that has been registered in the Patent Office [11]. Field studies in each hole gave zero result, so there is no need for further analysis of the results of field studies. Also underground water samples from each hole to the laboratory test are taken. Quarterly frequency of testing was determined in the geological documentation [8]. As part of the monitoring of underground water intake, the range of the laboratory tests for substances of petroleum hydrocarbon comprises the sum of hydrocarbon with the division to aliphatic and aromatic hydrocarbons.

During laboratory tests were performed quarterly determination and quantitative analysis of petroleum substances in the groundwater. The laboratory methodology used Fourier infrared spectroscopy. The apparatus used a spectrometer FTS 165 Bio-Rad Digilab Analytical Instruments using a research methodology based on the PN-C-04565-01:1982. This methodology ensures that the low-boiling hydrocarbon components present in eg. gaso-line.

It involves extraction of hydrocarbon fractions, the purification of the water and trace amounts of polar hydrocarbon, and then subjecting them to infrared radiation [2].

For quantitative determination of it the absorption is used in conjunction with the measurement of the intensity of the bands derived from the individual groups of valence vibrations of aliphatic and aromatic hydrocarbons. The combined determination of the concentration of petroleum compounds (TPH) is carried out by measuring the absorption of IR radiation, wherein is necessary to extract the sample of soil or water by using the extractant, which does not contain the CH connections similar to the compounds contained in the sample. The IR methodology can separate concentrations of petroleum (TPH) only to aliphatic and aromatic hydrocarbons. For the quantitative determination measurement of absorbance of the sample in the range 3200–2800 cm^{-1} is used in combination with the measurement of the intensity of the bands derived from the characteristic vibrations of CH_2 groups (range 2925–2939 cm^{-1}) CH_3 (range 2958 cm^{-1}) and vibration CH – aromatic rings (3330 cm^{-1} band).

5. ANALYSIS OF THE LABORATORY RESULTS

Absorption spectrum of the extract is the graphical effect of research. It is separated from the water samples, plotted with precise indications fraction content of the dominant aliphatic and aromatic character. The absorbance on the axis of ordinate is a physical quantity and the amount of radiation absorbed depending on the wave number shown on the abscissa as 1/λ, where λ is the wavelength. Examples of the absorption spectra of the extracts of hydrocarbon separated from the sample of water from the M1 hole is shown in Figure 2.

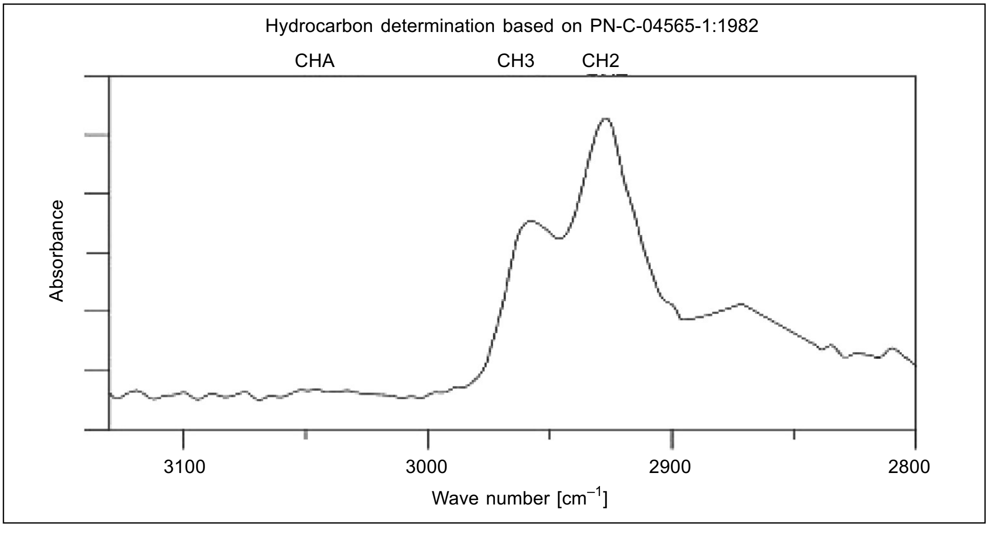

Fig. 2. Absorption spectrum of hydrocarbon extract isolated from a water sample

Quarterly results of laboratory testing of petroleum substances dissolved in water samples collected from monitoring holes M1-M6 are shown in the chart – Figure 3. The ordinate axis in this graph indicates the hydrocarbon content in each sample of water, and the *x*-axis indicated the number of quarterly series. The broken line shows the arithmetic mean of the individual measurement series.

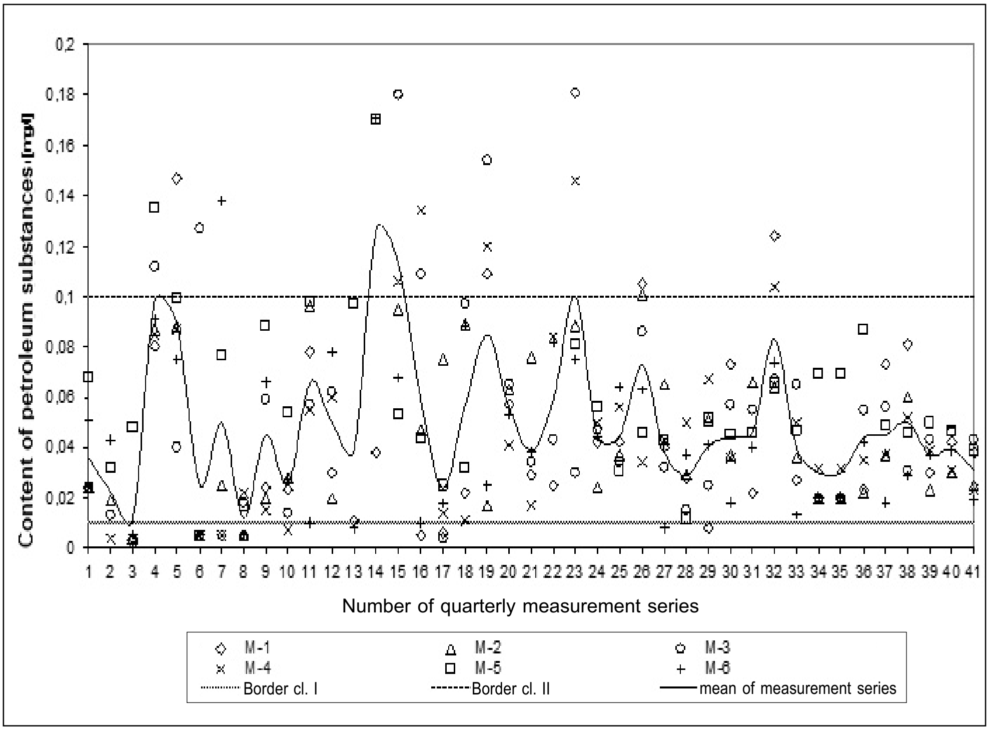

Fig. 3. Summary results of petroleum substances content

6. QUALITY OF GROUNDWATER NEAR INTAKE

Regulation of the Minister of Environment of 23 July 2008 on the criteria and methods of evaluation of groundwater [16] establishes five classes of groundwater quality. Classification results of water quality monitoring holes taken from M1-M6, in relation to the hydrocarbon, are shown in Table 1. In Figure 3, the graph provided two horizontal lines – a lower level of 0.01 mg/l and the upper level of 0.1 mg/l. These are the limits for Classes I and II. Limit value for class III does not exist in the drawing, because it goes beyond the scope of the picture, and any hydrocarbon content obtained is not close to the border of class III, established at 0.3 mg/l.

Table 1

Grades of groundwater quality in the studied area

No. of hole	Count of results	Quality classes of water in monitoring holes				
		I	II	III	IV	V
M1	40	7	27	6	0	0
M2	38	3	34	1	0	0
M3	38	2	31	5	0	0
M4	38	5	28	5	0	0
M5	36	1	33	2	0	0
M6	41	5	33	2	0	0
Sum	231	24	186	21	0	0

In the case of the analyzed water samples collected from monitoring holes located in a shopping center car park, qualified, due to the presence of oil derivatives, are classified to the Class II (81%). In this class, in accordance to the Regulation, the water has good quality, and the value of some physico-chemical elements are elevated as a result of natural processes occurring in groundwater and do not indicate the impact of human activity or influence is very weak. The second group of water samples in terms of frequencies are those that qualify because of the content of petroleum to the Class I (10%), where the water has good quality, in which the values of some physico-chemical elements are elevated as a result of natural processes occurring in groundwater and show the impact of human activity or influence is very weak. The third group of water samples in terms of frequencies are those that qualify because of the content of petroleum to the Class III (9%), where the water has satisfactory quality, and the physico-chemical elements are elevated as a result of natural processes occurring in groundwater or low-impact of human activities. There were no water samples in Class IV, which are classified as unsatisfactory water quality, and examined the physico-chemical elements are elevated as a result of natural processes occurring in groundwater and the clear impact of human activities. There were not also water samples in class V, which are classified as poor water quality, in which the physico-chemical elements confirm a significant impact of human activities.

7. STATISTICAL ANALYSIS OF THE RESULTS

As is shown in the graph in Figure 3, the quarterly laboratory testing of petroleum substances in the tested water samples showed the variable content. These results require statistical analysis [6, 12]. Table 2 shows the results of statistical analysis, which is the basis for the structure and of control cards and further conclusions. It concerns the results of 41 quarterly measurement series, except that for certain number of holes the number of results is less due to the periodic absence of water in an amount necessary to take a representative sample for laboratory analysis.

Table 2

Statistical analysis results of measured data

No. of hole	Count of results	Max value	Min value	Arithmetic mean	Median	Range	Standard deviation
	N	C_{max} [ppm]	C_{min} [ppm]	X_{sr} [ppm]	Me [ppm]	R [ppm]	σ [ppm]
M1	40	0,181	0,003	0,048125	0,0295	0,178	0,046473
M2	38	0,101	0,004	0,045211	0,0365	0,097	0,029346
M3	38	0,18	0,003	0,053737	0,0445	0,177	0,040034
M4	38	0,146	0,002	0,047737	0,038	0,144	0,037132
M5	36	0,17	0,005	0,058994	0,0495	0,165	0,032959
M6	41	0,171	0,005	0,04529	0,039	0,166	0,035942

The Table 2 shows that the hole M1 has the most and M2 hole has the least diverse results (the highest and lowest value of the coefficient of variation). For the analysis of the results of laboratory tests was also used Shewhart Control Chart [3]. Control card switched on Figure 4 was constructed in a such way that at the average height of all the results of the measured parameter center line CL = 0.050 was plotted, and above the central line of the upper control line UCL = 0.164 at the limit of the value of the parameter 3 σ from the arithmetic mean (probability P = 0.998) was placed. Under the upper control limit the upper warning line UWL = 0.128 was placed, which determines its value equal to 2 σ from the arithmetic mean (probability P = 0.95). Parameter σ is the standard deviation.

In the control card 147 results are under center line CL, 77 in the interval between the center line CL and the upper warning line UWL, 7 in the interval between the upper warning line UWL and the upper control line UCL, and 5 results are above the upper control line UCL. The last five results were treated as thick errors in the measurement results (according to the idea of a control card). Another five results, which are in the range between the auxiliary control line (CL 2 σ) and the upper control line (CL 3 σ), were treated as warning signs.

For the results which exceed upper control line, further tests of water samples were carried out, which gave similar results It excluded an error in the sampling, transport and laboratory tests of water samples. Further researches of the causes of high oil content in the water samples were carried out by identifying, analyzing and eliminating events that could have an impact on the results of laboratory tests. This led to finding the causes of water pollution monitoring in the test holes. The direct cause of the deterioration of groundwater quality was improper use of car parking in the winter season, which consists of collecting piles of snow in the vicinity of the monitoring holes, coming from snow removals in car parking and internal traffic routes. After removing the cause the groundwater quality has significantly improved, as can be seen in Figure 3, where the average of the results of measurements in the final measurement series has been significantly reduced, and the content of oil in the next series of samples of water decreases.

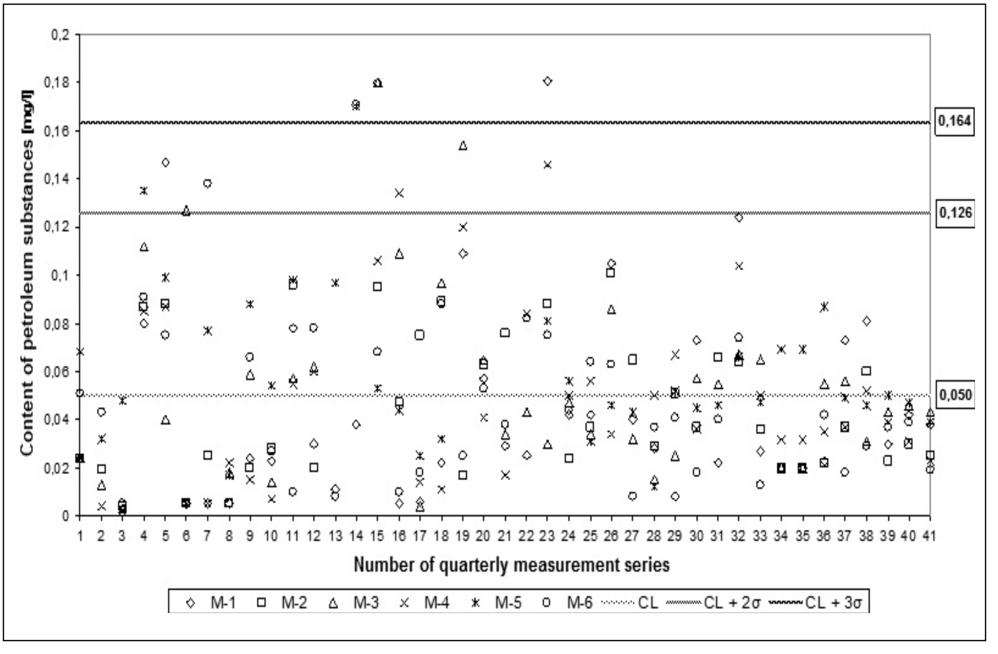

Fig. 4. Control card of hydrocarbon content test results

8. CONCLUSIONS

1. Results of laboratory analysis of groundwater quality in the monitoring holes, located in the car parking, showed cyclical changes in hydrocarbon content in groundwater samples.
2. During the monitoring was found that the increase of petroleum substances in groundwater samples appears after the winter season.
3. It was found that the direct cause of the increase of hydrocarbon content in the tested water samples is infiltration of irrigation water coming from polluted snow collected in the car parking.

4. Cessation of storage piles of snow in the parking lot, in areas exposed to the infiltration of irrigation water has led to a permanent reduction of hydrocarbon content in the tested water samples in subsequent measurement series.
5. Case study indicates that locating the large surface car parking in the protection zone (aquifer), is loaded with a significant risk of deterioration of water quality parameters.

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