Petroleum-Contaminated Soil and Water Analysis and Biodegradation

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Abstract

Our paper looks at an area near the town of Międzychód that is heavily contaminated by petroleum substances. Due to a pipeline failure in 1996, 70 tons of petrol were dumped into groundwater and soil. Initially, contamination occurred solely near storage base No. 71, and over the next few years it expanded beyond the area of the base. At present, more than 3,000 m[2] of land is considered to be contaminated. In spite of the reclamation efforts, the analyses of water and soil samples continue to indicate their heavy contamination and presence of above-average petrol and oil concentration. Furthermore, the hydrogeological conditions of Międzychód are favorable for the contaminants to migrate from the surface into the groundwater. Therefore, subsequent and extensive reclamation works are still to be strongly recommended.

Introduction

The Area Contaminated by Petroleum Substances

The area where the contamination by petroleum substances was found [1-4] initially comprised the petrol station (storage base No. 17) situated in the north-eastern part of the town of Międzychód (in the Międzychód-Bielsko district) on Przemysłowa Street, 1 km north from the Międzychód-Sieraków-Wronki national road (Fig. 1).

Petroleum substances are contaminants that most frequently occur in the water-soil environment [5-8]. Despite improvements to the technical conditions of sites involved in the production, storage, and distribution of liquid fuels, the threat to the environment posed by petroleum substances is still very real [9]. The contamination of water

and soil by petroleum substances negatively affects plant production, and puts health of people and animals at risk as most of the substances are toxic for living organisms [10].

In the studied area, contamination by petroleum-derived substances was initially found in the northern part of the station, and more specifically, in the area around the pumping station (Fig. 2).

The study area of the processes of fuel bailing along with the depression of the groundwater table comprised approximately 2,500 m[2]. The undertaken remediation works aimed at the possibly fastest bailing of fuel deposited in ground and on the surface of groundwater. This was aimed at stabilizing the "patch." In spite of the fact that the petroleum-derived substance kept migrating, its accumulation took place only in the area of the warehouse base.

However, a large number of erosion structures occurring in the area of the discussed gas station and their spatial arrangement caused the hydrocarbon migration to take

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place in the form of periodic spillages from one structure to another – such a situation occurred during the disastrous flood in 1997 [1-2]. Until today, the contamination has spread beyond the base area toward Lake Gorzelec, which is situated to the northeast, about 250 m from the station (with an area of 3,177 m^2). Petroleum-derived substances also were found in the water body about 600 m west of the warehouse base, which also indicates the contamination of groundwater and soil in the area.

The generally discussed site of fuel storage is situated in an area disadvantageous in terms of hydrogeological conditions that are favorable for the infiltration of contaminants from the area surface to groundwater (the predominance of sand forms in the aeration zone, deep deposition of the top layer of weakly permeable forms).

The Study of the Degree of Water and Soil Contamination

Storage base No. 71 in Międzychód was constructed in 1954. To the north, west, and east, it is surrounded by forests. According to the resolution of the Council of Ministers of 24 September 2002 on defining the types of undertakings that might significantly affect the environment (Polish Journal of Laws No. 179(1490)), the base is regarded as an undetaking that might significantly affect the environment.

In spite of the fact that the contamination of soil-water environment in the area of base No. 17 proceeded systematically as a result of leaks of petroleum-derived substances in the area of distribution and loading devices, and also as

a result of the failure and leaks related to long-term operation of the railway side track, the first study of the area and its sozological and hydrogeological conditions (the assessment of water permeability, porosity, and adsorption properties of particular ground layers) was conducted in March and April 1994.

A net monitoring groundwater was developed then, involving the drilling of 8 investigation holes 4-6.5 m under ground level, evenly arranged in the area of the base. Chromatographic studies of water and soil, as well as atmogeochemical probing, were conducted. Only two water analyses from two holes indicated trace signals of groundwater contamination, and soil contamination was found as a result of atmogeochemical analysis in the area of the railway side track the beginning of the track and in the area of the pumping station. (Fig. 2).

In 1996 the pipeline failure took place, resulting in over 70 tons of petrol getting into the soil. Measurements and hydrogeological observations were begun immediately, as well as the measurements of gas thickness in the exploitation holes and laboratory control checks of soil and water samples.

The size of the area contaminated by petrol needed to be assessed. In order to do that, it was necessary to make additional observation-investigation holes (piezometers). Their task was to determine the migration of petroleum substances, especially the ones situated below the zone of periodical changes of the groundwater table. Hydrogeological measurements in piezometres were taken once a week. The analysis of the results aimed at indicating the directions of the groundwater flow in the study area.
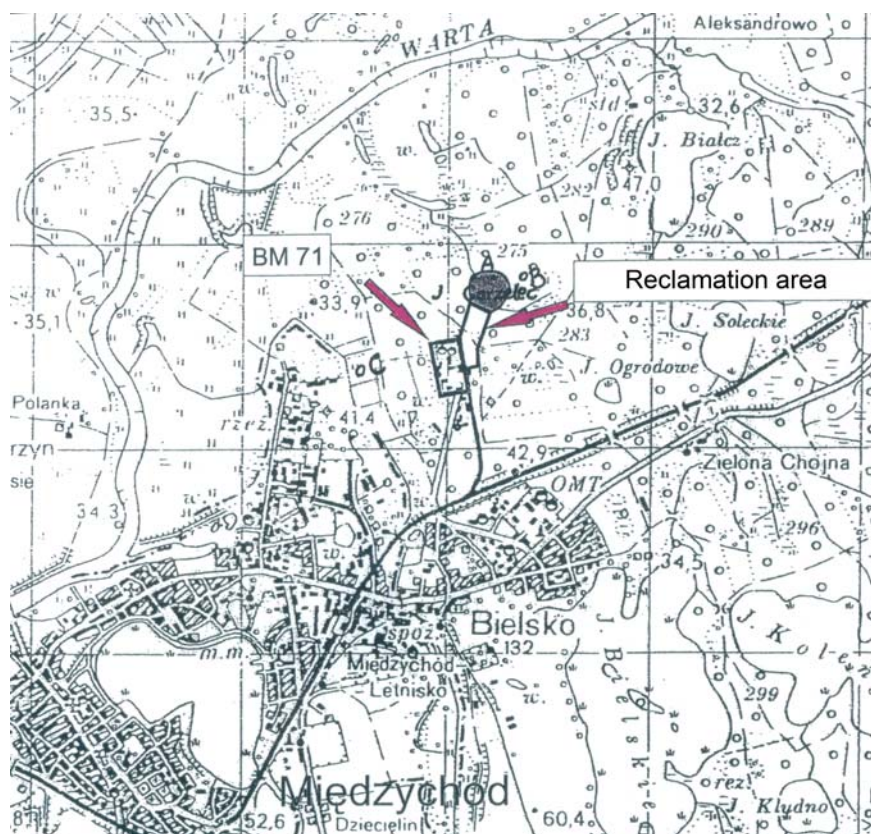

Fig. 1. Map of the research area.

After determining the range of contamination, organoleptic examination of water was done, which confirmed the presence of the investigated substances. Soil samples were then collected for laboratory analyses. The samples were collected from the most contaminated hole, which did not, however, suggest the occurrence of the petroleum-derived products, in sterile, tightly shut, containers. Soil samples were examined in terms of determining the concentrations of the following petroleum substances: petrol, oil and BTEX. Groundwater samples were also collected, after pumping each of the holes three times.

The trial run and pumping of the selected exploitation holes were conducted in order to define the hydrogeological conditions. After activating the technological system, hydrogeological and sozological surveillance was conducted within the scope necessary for the appropriate functioning of the system and for controlling the "patch" of petroleum-derived substances. It involved periodic measurements of gas thickness in holes, control over the depression of groundwater table, and the amount of the pumped water. The obtained results helped in making corrections of particular elements of the system so that the best effect in the form of gas recovery could be reached. Twice a month, the measurements of the height of groundwater table were taken in all piezometres, and once a month the measurements of the bailed gas were conducted.

Materials and Methods

The currently binding Polish Norms (ISO-EU) do not include explicit regulations defining the methodological aspect of the determinations of contamination of water, sewage, and soil by petroleum-derived substances. For this reason, in order to determine the degree and type of contamination, more than one method was used [9-10].

In the study of water and soil, the methodology involving the determination of total content of organic matter extracted with organic solvents was adapted.

Petroleum substances were determined using gas chromatography (GC) from water and soil samples subjected to extraction (at 20ºC without condensation). The chromatographic analyses were performed using capillary columns (Dexil 300 and SP 2100, 30 m) with FID detector.

The products (petroleum fractions) were identified based on the model fraction (diesel oil), to which the results of quantitative determinations also are referred.

In order to conduct the determinations, it is necessary to separate the product from water already in the hole and extract it onto the surface. This excludes the need to apply the ground separation of phases and water treatment. A selective fuel-water pumping system is used for this purpose. The process of bailing the petroleum product from exploitation holes is based on the system of groundwater depression (Fig. 3).
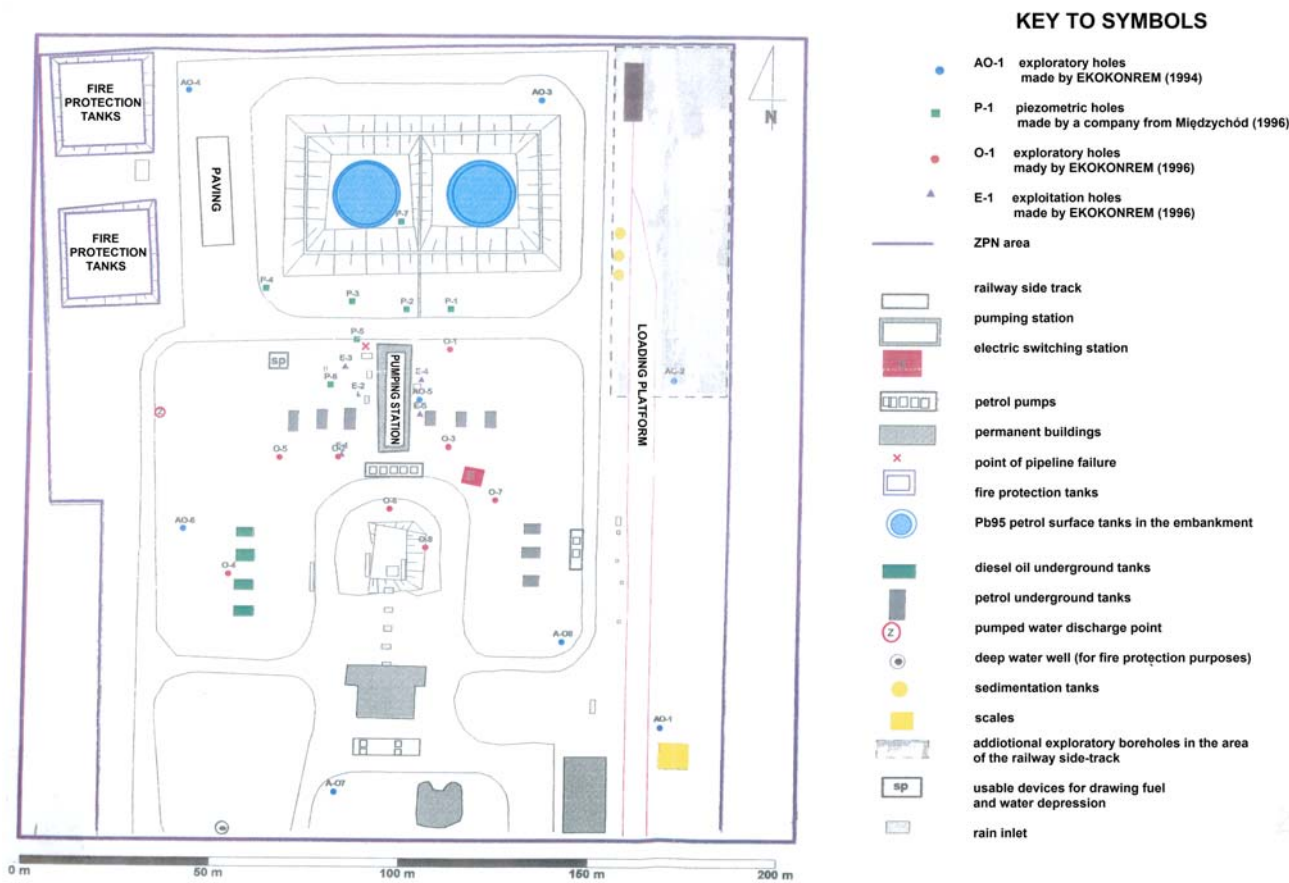

Fig. 2. Map of storage base 71 area.

Table 1. Daily and monthly average gas yield (L) (1999).

Month	Litre	Total yield	Average daily yield
May	140	140.0	4.52
June	141	281.0	4.70
July	120	401.0	3.87
August	67	468.0	2.16
September	76	544.0	2.53
October	184	728.0	7.08
November	327	1055.0	10.90
December	169	1224.0	5.63

Bailing petroleum substances from two pairs of holes at the simultaneous depression of groundwater table proved to be the optimal solution. For this reason, observation-exploitation holes were selected depending on the determined gas thickness. The assessment of the contamination degree of areas connected with the leaks of petroleum products and designing the systems of soil and groundwater treatment can be performed using the SpillCad computer program. Its basic element is the data base that allows for the identification of points (monitoring wells, drilling wells, etc.) on the map, as well as conducting the quantitative and qualitative analyses of soil and water contamination.

This program allows for the analysis of a series of data collected at different time intervals. Moreover, the program is equipped with analytical modules connected with the data base that enable the estimation of the size of the leak, contaminated ground, and the amount of petroleum-derived substances [1].

In May 1999, before the groundwater pumping system was installed, the measurements of gas thickness in the holes were taken. This allowed for estimating the geometry of the "patch" of petroleum product lying in the ground. The presence of petroleum-derived substances was found in holes P-6 (17 cm), E-1 (11 cm), E-2 (0.5 cm), E-3 (trace), E-4 (45 cm), and E-5 (0.5 cm).

The location of the holes has been presented in Fig. 4.

The pumping works began next and the measurements of petroleum-derived product were taken every day in all holes.

The daily yield of gas bailed from the holes also was recorded. The amount of gas in the holes changed depending on the conducted pumping supported by the groundwater depression.

Generally, the gas thickness at that time, in the defined area (gas station base), ranged from 2 cm to 90 cm. In order to provide the graphic illustration of the process of gas bailing, daily and monthly average gas yield was calculated (Table 1).

The decrease in the amount of bailed gas in August and September was caused by the slow process of gas flow and the clearing of its flow zones to the depression areas, as well as by the atmospheric influence (small amount of precipitation causing the slower rinsing of the aeration zone contaminated with petroleum products). On the other hand, a significant increase in gas recovery in October was mainly connected with several gas "patches" merging into one, accumulated in the centre of the pumping station, mainly as a result of the depression conducted in this area (Fig. 4). In the whole exploitation period (from May to December 1999) 1,224 litres of gas were bailed. The average daily yield ranged from 2.16 to 10.9 litres.

In the same period (1999), chromatographic analyses of water samples for the content of petroleum-derived sub-
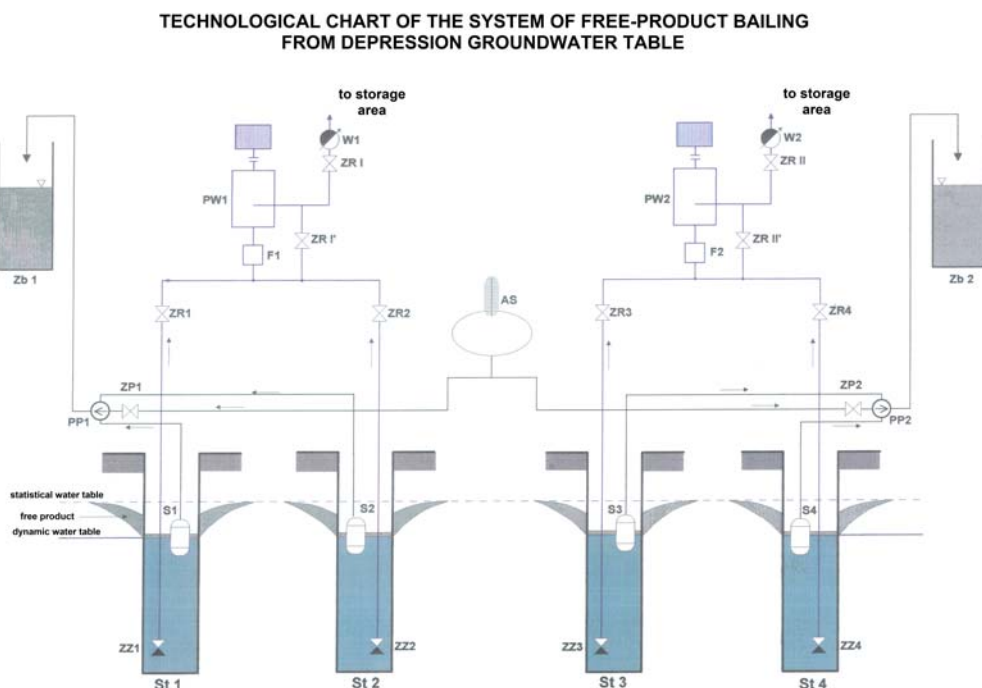

Fig. 3. Technological scheme of petroleum-derived substances bailing from depressed underground water table.

stances were conducted. Water samples were collected in accordance with the PN-88/C-06420.03 norm. The samples were collected in order to determine, using gas chromatography, the qualitative and quantitative characteristics of petroleum-derived hydrocarbons that the samples contained.

The water samples were collected in 1-liter glass bottles. A total of 10 water samples were collected (from holes P-4, P-7 – two samples in three series, from hole P-3 – also 3 samples and one additional sample from hole P-5). Each sample collection was preceded by clearance pumping. In samples, P-4 and P-7, signals were observed in the range of retention of hydrocarbons of gas fraction components and their residues (from 0.16 to 1.89 mg/dm³). On the other hand, in water samples collected from holes P-3 and P-5, very intensive signals in the range of retention of light gas components (petrol and diesel oil) were found. The determined concentrations of petroleum-derived substances ranged from 421.2 to 625.3 mg/dm³. Chromatographic analyses of water samples collected from holes P-4 and P-7 confirmed that the patch of product did not spread beyond the pumping station area to the west and north.

Following the completion of field works and laboratory analysis, the obtained results of gas thickness were analyzed using the SpillCad computer program. This allowed for drawing the maps of the thickness and calculating the surface area occupied by petroleum-derived product, the total amount of gas lying on the groundwater surface, and the amount of fuel in the aeration and saturation zones.

Based on maps presenting the thickness (Fig. 4), it was observed that the amount of petroleum product lying on the surface of ground water varied depending on the hydrogeological and soziological conditions, as well as on the configuration of the pumping system. The range of the gas "patch" changed during the hole study period (May-December 1999) as a result of its disintegration and merging at different time intervals.

The research was continued over the next few years. Although at the end of 1999 the control over the petroleum-derived product "patch" was finally gained, which was important for the soil-water environment, it did not prevent the product from dispersion and migration toward the groundwater flow in the following years. In March 2004 investigations of the area surrounding the base in the north and northeast began. Based on the results defining the contamination of the soil-water environment, the presence of contamination outside the base area was stated (71), from the northeastern base borderline (71) to the shore of Lake Gorzelec, covering 3,177 m². According to the cadastral map, the area of the contamination belongs to the Międzychód Forest Inspectorate. It is an afforested area that does not serve as a usable area [6].

As a result of petroleum-derived substances spreading beyond the base area (71), and the persistent high concentrations of the product, research is still being conducted.

For the purpose of our research, additional exploitation and observation holes were drilled. The area that is subjected to the process of remediation was also enlarged (the area
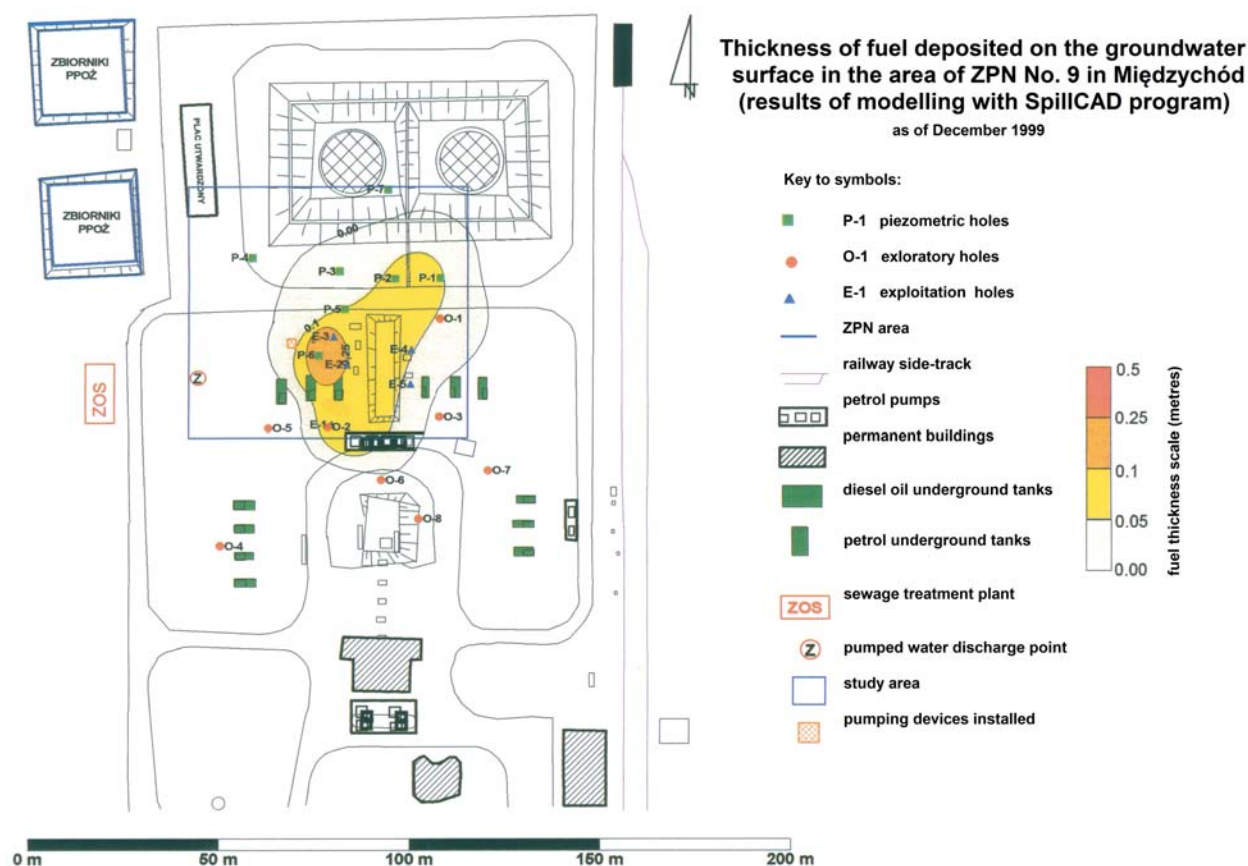

Fig. 4. Map of gas thickness lying on the underground water surface within storage base 71 in Międzychód.

Table 2. Laboratory analysis of water samples (June 2008).

No. Area	Unit	Pz12 B	Pz13 C	Pz14 C	Pz16 B	Pz17 B	Pz19 B	Pz20 B	Pz22 B	Pz23 B	Pz28 B	Pz29 B	EP1 B	EP2 B	EP3 B	EP4 C	EP5 B	EP6 B	Sewage discharge B	Min	Max	NDS B	NDS C
petrol	ug/dm^3	130	690	500	190	6,090	9,360	2,610	4,880	170	2,400	190	1,660	11,030	980	3,270	1,100	450	25	25	11,030	40	150
oil	ug/dm^3	50	20	0	30	400	990	190	170	10	50	0	140	320	40	50	0	0	30	0	990	200	600
Sum	ug/dm^3	180	710	500	220	6,490	10,350	2,800	5,050	180	2,450	190	1,800	11,350	1,020	3,320	1,100	450	55	55	11,350	-	-
benzene	ug/dm^3	0	0	0	0	200	23	12	342	0	8	0	120	623	8	50	79	11	0	0	623	1	5
toluene	ug/dm^3	0	30	40	0	780	230	80	180	0	150	20	310	2370	90	1,190	180	10	40	0	2370	15	50
ethylbenzene	ug/dm^3	0	0	0	0	40	200	0	120	0	20	0	10	150	0	40	0	0	12	0	200	20	60
xylenes	ug/dm^3	20	120	80	40	1,230	2,220	230	1,140	50	480	40	250	1,880	220	450	210	120	2	2	2,220	20	60
Sum	ug/dm^3	20	150	120	40	2,250	2,673	322	1,782	50	658	60	690	5,023	318	1,730	469	141	18	18	5,023	30	100

B – ecological area comprising the western foreground of the old pumping station of the storage base
C – ecological area comprising the western and northern foreground of the new pumping station

between the northwestern boundary of storage base No. 71 and the south-western boundary of Lake Gorzelec shoreline (Fig. 5). Areas A, B, C, and D (Fig. 5), which require remediation, were determined in the study area. The analyses of the degree of contamination of underground water and soil were conducted on a quarterly basis.

Groundwater is mainly contaminated with petrol fractions, sometimes oil fraction is predominating, and sometimes the contamination is of a combined nature with the predominance of petrol. In June 2008, groundwater samples were collected during one measuring series from the following holes: Pz9, Pz12, Pz13, Pz14, Pz16, Pz17, Pz19, Pz20, Pz22, Pz23, Pz27, Pz28, Pz29, EP1, EP2, EP4, EP5, and EP6 (Fig. 5). Additionally, one water sample was collected from the water treatment system (drop behind the absorber). The samples were collected after pumping each of the holes three times.

Also, the physicochemical analyses of groundwater were conducted. In all the samples, the analyses of pH, total phosphorus, total nitrogen and total organic carbon were conducted. The analyses aimed to assess the conditions of ground environment for the growth of microorganisms necessary in the process of bioremediation. It is assumed that optimal conditions for the bacteria growth occur at the pH range of 6.5-8.0, and when the proportion of carbon to nitrogen and phosphorus amounts to 10:1:0.1 [2].

In order to assess the qualitative and quantitative analysis of microorganisms involved in the process of bioremediation in the studied area, bacteriological analyses of groundwater were also conducted. The water samples were collected during one measurement series (June 2008) in the following holes: Pz13, Pz16, Pz17, Pz28, EP1, EP4, EP5, and EP6 (Fig. 5). The samples were collected in 1.5 dm^3 containers after pumping each hole three times. The following water parameters were then analyzed: total amount of bacteria in 1 ml of water, the titre of bacteria-decomposing petroleum products, and oxygen absorption by microorganisms. The bacteria involved in the process of bioremediation are *Pseudomonas* sp. and *Bacillus* sp. [9-10].

Groundwater also was subjected to control analyses in April and June 2010. The samples were collected in virtually all the observation and exploitation holes in the studied area. Similarly to the year 2008, chromatographic analyses determining the content of petroleum-derived products were performed. The physicochemical analysis of groundwater in holes Pz13, Pz17, Pz22, EP1, EP2, EP4, EP5, and EP6 also was conducted (Fig. 5). The samples were collected in 1.0 dm^3 glass bottles.

On the other hand, the bacteriological analyses were conducted during one measurement series in April 2010, in the same holes from which samples were collected for physicochemical analysis. The samples were collected in 1.5 dm^3 bottles. The following water parameters were analyzed: the total amount of bacteria in 1 cm^3 of water by the method of deep sowing on nutritious agar, and the titre of bacteria-decomposing petroleum products by the method of sowing on the mineral base with the addition of petroleum product [4].

Soil was also subjected to laboratory analyses for the content of petroleum-derived substances. The analyses

Table 3. Laboratory analysis of water – biotechnological and physicochemical research (June 2008).

No.	Parameter	Unit	Date of measurement VI 2008		
EP1	TBA	units/ml	850,000		
	HDB titre	ml	0.001		
	Oxygen consumption	mg O_2/1h/l			
	pH		6.8		
	P_2O_5	mg/dm^3	0.17		
	N_{org}	mg/dm^3	0.44		
	C_{org}	mg/dm^3	33		
	C:N:P proportion		75	1	0.39
EP4	TBA	units/ml	1100		
	HDB titre	ml	0.1		
	Oxygen consumption	mg O_2/1h/l			
	pH		6.5		
	P_2O_5	mg/dm^3	0.06		
	N_{org}	mg/dm^3	0.41		
	C_{org}	mg/dm^3	28.8		
	C:N:P proportion		70.2	1	0.1
EP6	TBA	units/ml	40,000		
	HDB titre	ml	0.1		
	Oxygen consumption	mg O_2/1h/l			
	pH		6.7		
	P_2O_5	mg/dm^3	0.09		
	N_{org}	mg/dm^3	0.22		
	C_{org}	mg/dm^3	6.5		
	C:N:P proportion		29.5	1	0.4
Pz13	TBA	units/ml	70,000		
	HDB titre	ml	0.01		
	Oxygen consumption	mg O_2/1h/l			
	pH		6.5		
	P_2O_5	mg/dm^3	0.07		
	N_{org}	mg/dm^3	0.44		
	C_{org}	mg/dm^3	25.4		
	C:N:P proportion		57.7	1	0.2
Pz16	TBA	units/ml	680,000		
	HDB titre	ml	0.001		
	Oxygen consumption	mg O_2/1h/l			
	pH		6.9		
	P_2O_5	mg/dm^3	0.62		
	N_{org}	mg/dm^3	3.38		
	C_{org}	mg/dm^3	7.1		
	C:N:P proportion		2.1	1	0.2

Table 3. Continued.

No.	Parameter	Unit	Date of measurement VI 2008		
Pz17	TBA	units/ml	1,840,000		
	HDB titre	ml	0.0001		
	Oxygen consumption	mg O_2/1h/l			
	pH		7.4		
	P_2O_5	mg/dm^3	0.14		
	N_{org}	mg/dm^3	0.92		
	C_{org}	mg/dm^3	4.22		
	C:N:P proportion		4.6	1	0.2
Pz28	TBA	units/ml	80,000		
	HDB titre	ml	0.1		
	Oxygen consumption	mg O_2/1h/l			
	pH		6.3		
	P_2O_5	mg/dm^3	0.09		
	N_{org}	mg/dm^3	0.32		
	C_{org}	mg/dm^3	39.5		
	C:N:P proportion		123	1	0.3
EP5	TBA	units/ml	49,600		
	HDB titre	ml	0.1		
	Oxygen consumption	mg O_2/1h/l			
	pH		6.8		
	P_2O_5	mg/dm^3	0.04		
	N_{org}	mg/dm^3	0.25		
	C_{org}	mg/dm^3	10.8		
	C:N:P proportion		43.2	1	0.2

HDB – hydrocarbons decomposing bacteria
TBA – total bacteria amount

were started on 28-29 August 2007. 12 study holes were drilled (Br1 – Br-12) (Fig. 5).

Based on the organoleptic test, in holes Br3, Br4, Br5, Br8, Br9, Br10, and Br11 the presence of petroleum substances was found and a decision was made to collect soil samples for laboratory analyses. The samples were collected in tightly closed sterile plastic containers from the most contaminated hole which did not, however, suggest the presence of the petroleum-derived substances. Soil samples were analyzed in terms of determining the concentrations of the following petroleum-derived substances: petrol, oil, BTEX. The samples were collected above the water table, and the methodology of sample collection complied with the norm PN-C-04620.03 [9].

Subsequent control sampling of soil was conducted in May and August 2009. Soil samples were analyzed in terms of: the content of petroleum-derived hydrocarbons – the sum of petrol and oil, the content of nitrogen, phosphorus, total organic carbon, total amount of bacteria and bacteria-

Table 4. Results of research on the content of petroleum-derived substances (Augus 2007).

No.	Sample marking	Depth [mppt]	Concentration of petroleum-derived substances PN-C-04643 and EN ISO 9377-2:2003 [mg/dm³]			Concentration of aromatic compounds (BTEX) PN-89/C04641 [mg/dm³]				
			Sum of hydro-carbons (TPH)	Petrol C6-C12	Oil>C12	Benzene	Toluene	Ethylobenzene	Xylenes	BTEX sum
1	Br3	3.8-4.0	<1.0	<1.0	<1.0	<0.1	<0.1	<0.1	<0.1	<0.1
2	Br4	3.9-4.1	1082.4	536.80	545.6	0.2	0.8	0.1	11.7	12.8
3	Br5	2.6-3.0	258.4	6.60	251.8	<0.1	<0.1	<0.1	<0.1	<0.1
4	Br8	4.0-4.2	2227.6	2188.1	39.5	22.0	13.9	38.3	282.9	357.1
5	Br9	4.8-4.9	50.0	39.70	10.3	0.3	0.3	0.4	2.5	3.5
6	Br10	6.3-6.5	2.8	<1.0	2.80	<0.1	<0.1	<0.1	<0.1	<0.1
7	Br10	7.3-7.6	1783	1746.5	36.5	2.7	11	1.40	232.1	247.2
8	Br11	4.4-4.6	1.5	<1.0	1.5	<0.1	<0.1	<0.1	<0.1	<0.1

Table 5. Results of research on the content of petroleum-derived substances in soil (May 2009).

No.	Sample marking	Depth [mppt]	Concentration of petroleum-derived substances (CHG) PN-C04643 and EN ISO 9377-2:2003 [mg/dm³]		
			Hydrocarbons sum (TPH)	Petrol C6-C12	Oil C12-C35
1	OP1	4.8-5.0	2,817.5	2,717.9	99.6
2	OP2	4.8-5.0	3,092.5	2,993.8	98.7
3	OP3	4.8-5.0	1,872.6	1,344.9	527.7
4	OP4	4.8-5.0	367.7	256.7	111
5	OP5	4.8-5.0	108.1	40.3	67.8

Table 6. Results of research on the content of petroleum-derived substances in soil (August 2009).

No.	Sample marking	Depth [mppt]	Concentration of petroleum-derived substances (CHG) PN-C04643 and EN ISO 9377-2:2003 [mg/dm³]		
			Sum of hydrocarbons (TPH)	Petrol C6-C12	Oil C12-C35
1	OP1	4.9-5.0	2,022	1,491.7	530.3
2	OP2	4.9-5.0	3,766.9	2,732	1,034.9
3	OP3	4.9-5.0	1,705.5	884.3	821.2
4	OP4	4.9-5.0	1,699.8	450.5	1,249.3
5	OP5	4.9-5.0	29.9	8.5	21.4

decomposing petroleum-derived substances. Five points were selected for the control sampling for the content of petroleum-derived substances in soil samples: OP1 – next to hole NP22, OP2 – between holes E6 and OD36, OP3 – next to hole E7, OP4 – next to hole OD36, OP5 – between holes P5 and E10 [1] (Fig. 6).

In each measurement series, one soil sample was collected from each hole. In most cases the samples were collected from a depth of 4.8-5.0 m (directly above the water table). The methodology of sample collection was compliant with the norm PN-88/C-04620.03. Collecting samples in order to conduct physicochemical analyses was conducted at control points OP1 and OP2 in two measurement series. The analysis concerned the same soil parameters that were studied in 2008 in the case of groundwater analysis.

For bacteriological analyses, the samples were collected in control points PO1 and OP5, also in two measurement series. The analysis concerned the following parameters of soil: total amount of bacteria in 1 gram of soil and the titre of bacteria-decomposing petroleum products.

Table 7. Physicochemical and bacteriological analyses of soil (may and August 2009).

No.	Parameter	Unit	Date of measurement					
			V 2009			VIII 2009		
OP1	TBA/g		2,310,000			38,000,000		
	HDB titre	g	0.001			0.00001		
	Oxygen consumption	mg O_2/1h/kg sm.						
	DHA	ug/TF/1 g sm.						
	pH		6.7			6.5		
	P_2O_5	g/kg	0.03			0.005		
	N_{org}	g/kg	0.1			0.36		
	C_{org}	g/kg	0.36			0.64		
	C:N:P proportion		3.7	1	0.3	1.8	1	0.01
	moisture	%	19.3			14		
OP2	TBA/g		1,090,000			95,000,000		
	HDB titre	g	0.001			0.00001		
	Oxygen consumption	mg O_2/1h/kg sm.						
	DHA	ug/TF/1 g sm.						
	pH		6.6			7.3		
	P_2O_5	g/kg	0.05			0.005		
	N_{org}	g/kg	0.07			0.16		
	C_{org}	g/kg	0.18			0.86		
	C:N:P proportion		2.6	1	0.8	5.4	1	0.03
	moisture	%	16.4			16		
OP3	TBA/g		510,000			13,000,000		
	HDB titre	g	0.0001			0.00001		
	Oxygen consumption	mg O_2/1h/kg sm.						
	DHA	ug/TF/1 g sm.						
	pH		7.4			6.4		
	P_2O_5	g/kg	0.023			0.005		
	N_{org}	g/kg	0.014			0.44		
	C_{org}	g/kg	0.38			0.48		
	C:N:P proportion		27	1	1.6	1.1	1	0.01
	moisture	%	15.8			16		
OP4	TBA/g		210,000			390,000,000		
	HDB titre	g	0.0001			0.00001		
	Oxygen consumption	mg O_2/1h/kg sm.						
	DHA	ug/TF/1 g sm.						
	pH		6.8			6.4		
	P_2O_5	g/kg	0.05			0.005		
	N_{org}	g/kg	0.098			0.28		
	C_{org}	g/kg	0.38			0.63		
	C:N:P proportion		3.9	1	0.5	2.3	1	0.02
	moisture	%	17.6			20		

Table 7. Continued.

No.	Parameter	Unit	Date of measurement					
			V 2009			VIII 2009		
OP5	TBA/g		160000			92000000		
	HDB titre	g	0.0001			0.00001		
	Oxygen consumption	mg O_2/1h/kg sm.						
	DHA	ug/TF/1 g sm.						
	pH		7.8			7.2		
	P_2O_5	g/kg	0.02			0.005		
	N_{org}	g/kg	0.056			0.13		
	C_{org}	g/kg	0.26			0.13		
	C:N:P proportion		4.6	1	0.4	1	1	0.04
	moisture	%	20.2			25		

TBA – total bacteria amount
HDB – hydrocarbons decomposing bacteria
DHA – dehydrogenase activity

In April 2010, in order to assess the development of remediation works, another eight soil samples were collected for analysis of the content of petroleum-derived substances (petrol, oil, BTEX). The depth of sample collection was defined based on the organoleptic test (color and smell of soil indicating the presence of petroleum-derived substances). The samples were collected from the most contaminated hole that did not suggest the presence of petroleum-derived substances, in sterile, tightly closed glass containers. The samples were collected above the water table. The methodology of sample collection was compliant with the norm PN-C-04620.03. The results of laboratory analyses were compared with the allowable values of petroleum-derived substances defined in the resolution of the Minister of the Environment of 9 September 2002 on soil quality standards, including the nature of land use.

Results and Discussion

The analyses of groundwater conducted in June 2008 revealed the exceeded highest allowable concentrations for petrol and aromatic hydrocarbons in all the studied samples (both in area B and C). In three holes, the exceeded highest allowable concentrations of oil were also found (Table 2).

The physicochemical analyses did not find the presence of pH values highly unfavourable for the development of bacteria in the soil samples, in the studied period. The pH of water ranged from 6.3 in hole Pz28 to 7.4 in hole Pz17. The other parameters of groundwater were not studied earlier in this area and for this reason they were assumed as initial (Table 3).

Bacteriological analyses of water samples showed the presence of bacteria (*Pseudomonas* sp. and *Bacillus* sp.) able to biodegrade petroleum products. The amount and activity of bacteria differentiated. In most of the samples, relatively high content of organic carbon in relation to the other nutritive components is worth mentioning (Table 3).

In the year 2010 (April and June) the analysis of 19 groundwater samples was conducted. In April, in the water from hole EP2 (Fig. 5) the presence of free phase was found at the film level.

In 15 out of 19 soil samples the allowable concentration of petroleum-derived substances (both for the sozological level B and C) was found to be exceeded.

The content of petrol ranged from 20 ug/dm³ (Pz23, April 2010) to 198,080 ug/dm³ (Pz9, June 2010). For oil, values ranging from 10 ug/dm³ to 8,280 ug/dm³ (Pz9, April 2010) were obtained. The BTEX sum ranged from 6 ug/dm³ (Pz12, April 2010) to 114,200 ug/dm³ (Pz9, June 2010).

Petroleum-derived substances were not observed in groundwater in the base area in holes Pz1 and Pz2. Moreover, the presence of petroleum-derived substances in the shoreline zone of Lake Gorzelec, in holes Pz23 and Pz29, was not observed (Fig. 5).

Physicochemical analyses of groundwater conducted in the same period of time (2010) found the reaction of water environment favourable for bacterial growth. In five soil samples (EP1, EP4, EP5, Pz13, Pz17, and Pz22) the lack of phosphorus compounds was observed, and small amounts of this element were found in holes EP6 – 0.03 mg/dm³ and EP2 – 0.11 mg/dm³.

Contamination by petroleum-derived substances results in the increased inflow of carbon source (substratum), whose bidegradation causes the increase of the microorganisms' demand for nitrogen and phosphorus in comparison with their natural content in the soil-ground environment. The C:N:P ratio shows the deficiency of nitrogen and phosphorus. The development of microorganisms requires

Table 8. Results of research on the content of petroleum-derived substances in soil (November 2010).

Place of sample collection	pH	Sum of hydrocarbons	petrol C6-C12	oil
		mg/kg d.w.	mg/kg d.w.	mg/kg d.w.
100 m from J. Gorzelec	6.8	1.5	<1.0	<0.1
100 m from Karpników	6.2	<1.0	<0.5	<0.05
100 m from Glinianki	6.0	<0.5	<0.1	<0.01

d.w. – dry weight

the process biostimulation in the form of delivering biogene substances (solutions of mineral fertilizers) in order to supplement the deficiency of nitrogen and phosphorus, which are essential elements for the microorganisms, apart from carbon, to perform life functions.

Bacteriological analyses of water samples (in 2010) revealed the presence of bacteria in all the samples. These were mainly bacteria that decomposed hydrocarbons – the selected strains of *Pseudomonas* sp. and *Bacillus* sp., which was indicated by the titre of bacteria decomposing hydro-carbons, correlating with bacteria amount [11-12]. The smallest amount of bacteria was found in sample EP2 (Fig. 5), which may suggest the ending of the biodegradation process of contaminants and their elimination, or the lack of biogene substances (N, P).

In the remaining samples the amount of bacteria was high, which indicated the intensive processes of organic matter decomposition [13-15].

Soil analyses conducted in August 2007 revealed the content of sum of petrol in the range from <1 mg/kg (Br3,
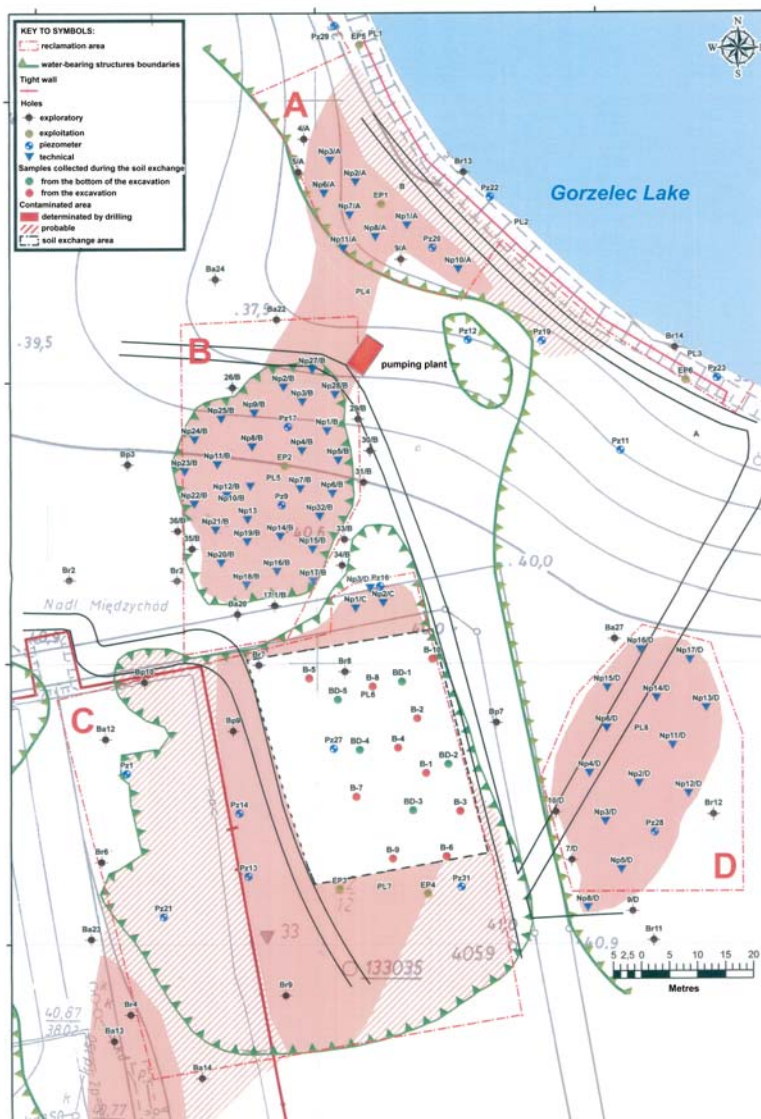

Fig. 5. Location of underground water and oil sample collection points for analysis purposes.

Table 9. Results of pH, insolation, and soil moisture measurements (July 2011).

No.	pH	moisture	insolation
		pF	J/m² × s
Pz17	7.3	1.1	200
Pz14	7.5	1	150
EP3	7.2	4	720
Pz28	7.5	1.5	190
Pz26	7.5	1	190
Pz11	7.5	2	180
Pz23	7.2	7	180
EP5	7.5	2.1	200
EP1	7.4	1.9	400
Pz12	7.5	1.3	550

Br11) to 2,188.1 mg/kg (Br8). The sum of oil ranged from <1mg/kg (Br3) to 545.6 mg/kg (Br4). The sum of BTEX ranged from <0.1 mg/kg (Br3, Br5, Br10) to 357 mg/kg (Br8) (Table 4).

The analyses of soil conducted in May and August 2009 (Tables 5 and 6) revealed the variable content of petrol sum in all samples in the range from 8.5 mg/kg (OP5, August 2009) to 2993.8 mg/kg (OP2, May 2009). The sum of oil ranged between 21.4 mg/kg (OP5, August 2009) and 1,249.3 mg/kg (OP4, August 2009). In the analyzed samples the content of petrol was predominant.

The results presented in the above table suggest that the sum of petrol in May 2009 at point OP1 was exceeded 54.4 times, and in point OP2, 59.9 times.

In physicochemical analyses of soil from the year 2009 (Table 7), the optimal pH for bacteria growth was observed, whose reaction in the collected samples ranged from 6.4 in holes OP3 and OP4 (August 2009) to 7.8 in hole OP5 (May 2009). As regards nutritious substances, in all the holes the differentiated, unfavorable proportion of organic carbon, organic nitrogen, and assimilable phosphorus, different from the recommended proportion was found. The defi-
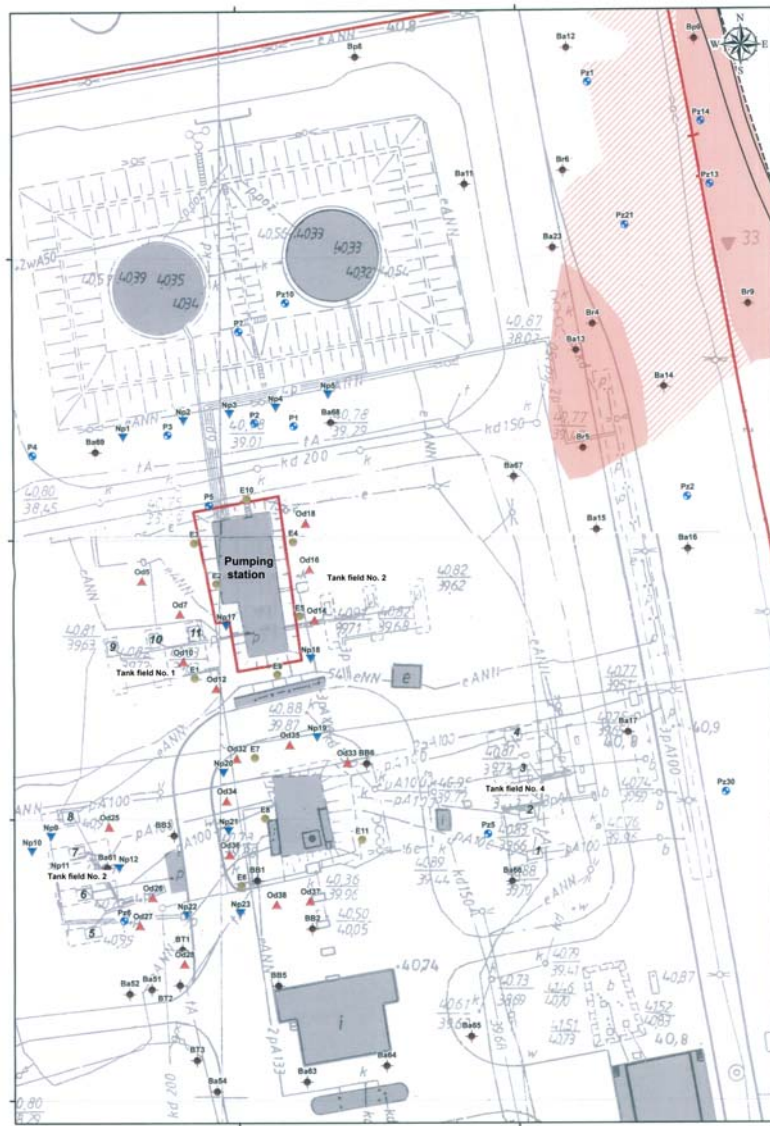

Fig. 6. Location of sample collection points for control sampling.

ciency of total organic carbon was observed, and in August 2009 a nearly total lack of phosphorus content was recorded.

Bacteriological analyses of soil in August 2009 revealed an increase in total amount of bacteria after conducting the inoculation of soil using biopreparation. Also, the increase in the amount of bacteria decomposing petroleum-derived substances was observed. Bacteriological analyses were conducted in terms of: total amount of bacteria in 1g of soil by the method of deep sowing on nutritious agar, the titre of bacteria decomposing petroleum product by the method of sowing on mineral base with the addition of petroleum product, dehydrogenase activity determined by the TTC testing method for soil according to Casidy, and using the reduction reaction of triphenyl-tetra-zolium chloride to colored TF by living soil microorganisms [14-15].

The study revealed that the microflora of the investigated soil was marked by relatively high respiratory and enzymatic activity. This means that the improvement of conditions of biodegradation process enabling the growth of microorganisms or introduction of biopreparation may efficiently advance the process of soil treatment [3].

In November 2010, soil samples were collected for the analysis of the content of petroleum-derived substances. The samples were collected near water bodies (Lake Gorzelec – 250 m from the base, a clay-pit – 600 m from the base, Karpik – 300 m from the base). The results of the analysis are presented in Table 8.

In July 2011, near the selected observation holes, the measurements of pH, insolation, and soil moisture were taken. The results are presented in Table 9.

Numerous physical and chemical factors influence the decomposition of hydrocarbons by microorganisms in the natural environment. The factors include temperature and pH of soil, its moisture, and the concentration and chemical structure of contamination, physicochemical properties of soil, and content of biogene salts, oxygen availability, content of organic compounds. The optimal temperature for the biodegradation of petroleum-derived hydrocarbons is 25-30ºC. The temperature affects the physical and chemical properties of oil components, the speed at which the microorganisms will be able to metabolize them, and the content of their population [11].

The pH reaction of the environment, which affects the speed and direction of biological processes in soil, should amount to 6.0-9.9, with the optimal range of 6.5-7.5. This reaction is favorable for the growth of bacteria, which play crucial roles in the process of biodegradation. It is also the reaction that limits the growth of fungi [11].

The petroleum-derived products that contaminate the studied area proved to be susceptible to decomposition by the bacteria straits of *Pseudomonas* sp. and *Bacillus* sp. The petroleum-derived compounds are the only source of carbon and energy in the processes of metabolism and biodegradation. The enzymes produced and excreted by microorganisms increase the solubility of petroleum-derived components and their penetration inside the cell. The growth of microorganisms on the surface of petroleum-derived components and forming agglomerates make it easier for the substratum to penetrate through the cell membrane [5].

Implementing the method of biological treatment of soil in the area of the base (71) was the reason necessary for activating the process of remediation. Due to the fact that the process of natural biodegradation is limited by the degree of natural diffusion of oxygen and the amount and growth of bacteria that decompose petroleum-derived hydrocarbons, it was intensified by: airing the contaminated zones, adding nutritious substances (fertilizing the soil), watering the contaminated areas, and enriching the existing microflora by introducing selected, indigenous microorganisms grown in the field bioreactor or by adding ready-made bacteria prepared for the environment [13].

Conclusions

The surface water and soil in the studied area indicated high contamination with petroleum-derived substances, mainly the fractions of fuel characteristic for petrol and diesel oil (the predominance of contamination related to petrol). The following criteria were considered in the contamination assessment: for underground water – allowable concentrations for zone C, according to the Methodological Guidelines of the Polish Institute of Environmental Protection – petrol 0.15 mg/dm^3, oil 0.6 mg/dm^3, for soil – the Resolution of the Minister of the Environment of 09.09.2002 on the standards for the quality of soil and ground (Polish Journal of Laws No. 165(1359)) – group C, depth 2-15 m, water permeability $> 1 \times 10^{-7}$ m/s – petrol – 50 mg/kg, oil – 1000 mg/kg [9].

The migration of contamination beyond the base area (71) resulted from complicated hydrogeological conditions [16]. The area of the base (71) is located within the zone of glaciotectonic disturbances, which is suggested by the shallow deposition of tertiary forms (silts, dusts, brown coal) in the form of isolated patches. Additionally, the complicated situation is affected by unevenly formed clay substratum, which occurs at different depths, causing the separation of water-bearing layers. Moreover, within the pipe-like structure, the water at the first water-bearing level is characterized by high (up to 1.5 m) variations of the table level and changing directions of flow. High water levels cause migration of petroleum product beyond the area of the influence of the gas bailing system. The disturbances in the natural flow of groundwater may be caused by the underground infrastructure (tanks, transmission pipelines) in the area of the base.

This also causes the inflow of product into the exploitation holes and the secondary contamination of the soil-water environment (possible gradual "emission" of petroleum-derived product from the inactive underground installations).

The multiple analyses of soil revealed significant exceedances of the allowable standard values. In 2007 the norms (NDS) were exceeded 12.5 times for oil (September 2007 – the sum of oil amounted to 12534.6 mg/kg at point OP3). Petroleum-derived substances in groundwater also occur in amounts significantly exceeding allowable concentrations.

The main components of petroleum and its products are aliphatic and aromatic hydrocarbons. Aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes), defined by the common name of BTEX, are regarded by the US Environment Protection Agency (USEPA) as primary contaminants due to the threat they pose to human health [11]. Considering the fact that even minimal concentrations of aliphatic and aromatic hydrocarbons are easily detectable in water, making it unsuitable for drinking, the studied area poses a serious threat to the health of the local inhabitants and it requires further monitoring.

References

1. Report No. 4 of the remediation works in the period from April 2009 to September 2009 in the area of storage base of PKN ORLEN No. 71 in Międzychód [In Polish].

2. Report No. 5 of the remediation works in the area of storage base of PKN ORLEN No. 71 in Międzychód [In Polish].

3. Report No. 1 of the remediation works in the area of storage base of PKN ORLEN No. 71 in Międzychód [In Polish].

4. Final report of the remediation works in the period from April 2007 to January 2010 in the area of storage base of PKN ORLEN No. 71 in Międzychód Bielsko, Przemysłowa Street

5. MALINA G. Eliminating the threat to the soil-water environment in contaminated areas, Polish Association of Sanitation Engineers and Technicians, Wielkopolska Branch, Poznań, **2011**.

6. SIBILSKA I., SIDEŁKO R. Migration of aromatic hydrocarbons in the area of the municipal waste disposal site, Ecology and Technology, **5**, (65), 19, **2003**.

7. ZIEŃKO J. Technologies of reducing the negative effect of terminals, bases and petroleum-derived fuel stations on the environment, Ecology and Technology, **4**, 107, **1999**.

8. KLUSKA M. Assessment of the content of polycyclic aromatic hydrocarbons in soil along the Siedlce – Ostrołęka route", Ecology and Technology, **3**, (63), 11, **2003**.

9. Polish Institute of Environmental Protection. Methodological guidelines concerning the degree of contamination of soil and groundwater with petroleum products and other chemical substances in remediation processes, Warszawa, **1995**.

10. KOŁWZAN B., GRABAS K., NOWAKOWSKA M., PAWEŁCZYK A., KADAROWSKA B., STEININGER M. Bioremediation of soil contaminated with petroleum products using the compost heap method on the example of the disposal site in Łężyca, Chemical waste and hazardous petroleum waste, Poznań, March, pp. 37/I-43/I, **2001** [In Polish with English abstract].

11. HAWROT-PAW M. Biodegradation of selected petroleum products in variable temperature conditions and pH of the environment, Acta Sci. Pol., Formatio Circumiectus **9**, (4), 17, **2010**.

12. STELIGA T., KLUK D., ŻAK H. Use of indigenous bacterial flora in the treatment of soils contaminated with petroleum-derived products, Contamination of the environment with petroleum products, their monitoring and removal in the aspect of the EU integration process, Poznań, pp. 87-95, **2003**.

13. KOŁWZAN B., TARCZEWSKA T., PIEKARSKA K., JUCHNIEWICZ M. Microbiological assessment of biodegradation properties of soil contaminated with petroleum products" Materials from the V Polish Symposium of Science and Technology. Environmental Biotechnology. Ustroń Jaszowiec, pp. 11-16, 10-12 December **1997**.

14. MALISZEWSKA-KORDYBACH B. Microbiological transformations of polycyclic aromatic hydrocarbons in soil environment, Post. Mikrobiol. **26**, (3), 233, **1987**.

15. NERYNG A. Metabolizing hydrocarbons by microorganisms, Post. Mikrobiol. **15**, (1), 57, **1976**.

16. SZYCZEWSKI P., SIEPAK J., NIEDZIELSKI P., SOBCZYŃSKI T. Research on Heavy Metals in Poland, Pol. J. Environ. Stud., **18**, (5), 755, **2009**.