

UDC 550.837

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DETERMINATION OF THE PETROLEUM POLLUTION SOURCES FOR GROUNDWATER (ON THE EXAMPLE OF SOLOTVIN TERRITORY IN THE PRECARPATHIANS)

(Рекомендовано членом редакційної колегії д-ром геол. наук, проф. О.Є. Кошляковим)

The article is dedicated to solution of groundwater oil products pollution problem within area of Solotvin village, which is located in Precarpathians, Ivano-Frankivsk region of Ukraine. Contamination was found in the wells of drinking water supply with specific taste and smell. The alternative sources of pollution are considered: conserved oil well, oil pipeline and gas station (GS).

All owners of these facilities submitted survey or test documents confirming tightness (well and gas station tanks) or lack of hydrocarbons (inactive pipeline). A paradoxical situation arose: there is pollution, but there are no sources of pollution. To solve the problem, the complex of geochemical and geophysical methods was applied.

Geochemical studies were conducted for water samples taken from wells in the contaminated area and adjacent areas. In addition, samples of near-surface air in the soil were collected on the condensed network. The level of heavy and light hydrocarbons in polluted water samples exceeded the background values by tens of times and exceeded the permissible concentrations. Laboratory tests of air samples clarified and detailed the contaminated area.

According to the results of geochemical surveys it was found that the source of pollution can be located on the GS territory.

Geophysical studies have allowed finding out the lithological structure of the upper part of the section and establishing the depth of the roof and the bottom of the groundwater collector and, accordingly, the underlying aquifer roof. At the same time, the filtration direction in aquifer and a location of old river channel that are in correlation with spreading of groundwater from GS to polluted wells.

The report on the causes of groundwater pollution with oil products and on the established source of pollution was submitted to the relevant authorities of the State Service of Ukraine for Emergency Situations.

Keywords: oil products, pollution, chink, geophysics, geochemistry, underground gas.

The relevance of issue. Analysis of literary data.
Pollution of groundwater, as discussed in the article, is related to the area of Solotvin village, which is located in Precarpathians in Ivano-Frankivsk region of Ukraine in the Bystrytsia Solotvynska river basin, which is a tributary of the Dniester River.

Pollution was first found in 2007 in several wells that are the sources of household water supply. Pollution was found according to chemical and bacteriological indicators but overtime it decreased. But in 2013 next "flash" of pollution was marked. The results of laboratory studies showed evidence of oil products in water with major excess of maximum allowed concentration. The square of polluted area was 900 m².

Objects, which could be potentially sources of pollution, were considered to be decommissioned in 1986 oil pipeline "Kosmach – GU Starunia", conserved chink (for gas) "15 – Babche", gas station within the urban-type village of Solotvin.

As water quality starting from 2013 didn't improve over time, in 2016 at the request of village council all the companies-owners of mentioned objects gave conclusions about their ecological state. The results of examinations, according to introduced official conclusions, point on absence of pollution possibility of groundwater as a result of activity of companies on these objects. So, a paradoxical situation has arisen: pollution exists, but its' sources – don't.

Analysis of groundwater pollution on the territory of Ukraine is a topic of survey of many scientists. In particular, in oil products pollution professor M.S. Ohnianyk was engaged. Works (Ohnianyk et al., 2013; Ohnianyk et al., 2017) suggested the principle of evaluation of oil products pollution danger of natural and household objects and creation of warning zone around potential pollution objects – sources of geological environment and location of observation points in it.

Determination of pollution via complex of methods on objects of oil and gas, mining and chemical industry is represented in works (Osadchy et al., 2004; Hrytsyk et al., 2004; Dryhulych et al., 2003; Levashov et al., 2004), where it is suggested use of geoelectrical and geochemical methods of research for detection and outline of oil pollution zones.

Works (Onyshchuk et al., 2010; Onyshchuk et al., 2006; Onyshchuk et al., 2006; Bahrii and Kuzmenko, 2010) are dedicated to determination of pollution within industrial objects (tailings dams, salt dumps, tailings ponds, objects with mineral fertilizers etc.).

Geophysical and geochemical methods of research are successfully used also abroad. Works (Abdullahi et al., 2016; Burazer and Burazer, 2017; Dahlin et al., 2010; Guerin et al., 2004; Koo and Yoon, 1994; Lohva et al., 2007; Papyrin and Pustozerov, 1998) presented their efficiency for detection and outline of polluted territories. After analysing mentioned and other works, we could conclude, that complex of geophysical and geochemical methods will allow to find source of pollution for indicated territory.

Goal and tasks of research. Conducted geochemical and geophysical surveys set the goal for finding the source of pollution of groundwater and routes of pollution spreading.

For accomplishing of the set goal the following actions were done:

Sampling from wells and analysis for oxidation-reducing indicator (pH) and content of hydrocarbons for determination of level and area of pollution;

Sampling of free underground gas from depth of 0,5 m and analysis for hydrocarbons content for determination of area of pollution by light fractions;

Geophysical research by natural electric field method for mapping of filtration flows;

Geophysical research by vertical electric sounding method for mapping the roof of indigenous rocks and the determination of the capacity of the aquifer.

General characteristics of research area. Geological structure of the research territory was carefully studied in previous years due to oil and gas capacity of the region and is described in numerous reports of different organizations. In terms of location of oil and gas deposits, territory of research is located within mining drainage Bytkiv-Babche oil and gas condensate field. The closest to pollution area is oil well – Rakovets-1. It is located 225 meters from pollution zone down to underground water flow – in northeast direction and currently is liquidated. Well No. 15 – Babche is situated 830 meters from pollution zone. Well was drilled in 2013 and conserved in the same year, like one that didn't give industrial oil products rush.

In geostructural relation territory of research is included into zone of connection of Sambir zone with the Bilche-Volyn zone of the Carpathian precipice. Geological structure of region is represented by sedimentary rocks belonging to the Paleozoic, Mesozoic and Cenozoic ages, and mainly by sandy-clay, argillite and siltstone fractions.

It is clear that we are interested in the upper part of the section, within which there is an aquifer, whose water was contaminated. In fig. 1 is a section, built by us on basis of the description of rocks extracted during the tunnel in the beginning of July 2017 within the area of a farmland in the territory of research.

Closer to the edge of the valley of the river, argillites in the wells are set at a depth of 4,5 meters, that is, the capacity of alluvial river deposits decreases. It should be noted that the direction of movement of groundwater within the contaminated area is approximately parallel to the direction of the Bystrytsia Solotvynska, as evidenced by the location of the water outlets in the wells. This groundwater is formed on the territory of the floodplain of the river due to infiltration of atmospheric precipitation. The aquifer, which is used by the inhabitants of the village, is a pebble alluvial horizon, formed in ancient times by the Bystrytsia Solotvynska River.

Period	Horizon	AGE	Lithology	Depth	Thickness
Q	Quaternary deposits		Black-brown clay (Polyanytska suite)	0,8	
Q _{al}	Upper quaternary alluvial deposits of the floodplain terraces of Bystrytsia Solotvynska		Small pebble with a sandy-clay filler of gray color, from large to fine-grained	4,2	
Pz _{ml-bst}	Paleozoic, minilite horizon		Shallow argillite	0,8	

Note: groundwater level at a depth of 4,5 meters

Fig. 1. Lithostratigraphic section of the research site

The results of gas geochemical research. Water gas capture. Water gas capture was conducted to identify a potential source of groundwater contamination of wells by hydrocarbons. For this purpose, 15 samples of water from the wells were selected on contaminated and adjoining territory. It is clear that such analyses, together with an evaluation of the potential route of groundwater from potential pollution objects, can provide an answer to the location of a specific source of pollution. Fig. 2 shows a scheme for sampling water from wells. The selected samples of water are degreased by the method of thermo-vacuum degassing, which resulted in the release of water-soluble gases in them and appropriate chromatographic analyses. The results are shown in table 1. In the waters, the oxidation-reducing parameter (pH) of the medium was also determined. In all waters, the reaction of the medium is slightly acid to neutral (pH = 5,9–6,8), indicating the presence of oxidants in water, which are hydrocarbons dissolved in water.



Fig. 2. Places of sampling water from wells

Table 1

Results of chromatographic analysis of water-soluble gases

Sample number	Unit	Gas mixture composition									Total CH ₄ -C ₆ H ₁₄ mg/m ³	
		CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-C ₅ H ₁₂	n-C ₅ H ₁₂		
No. 1 SI.	% , x10 ⁻⁴	12,12	0,88	0,08	1,06	—	0,37	1,33	1,19	1,19	0,52	18,76
	mg/m ³	8,68	1,18	0,10	2,08	—	0,96	3,46	3,85	3,84	2,01	26,18
No. 2 SI.	% , x10 ⁻⁴	4,49	0,20	0,07	0,30	—	0,09	0,22	0,16	0,20	0,19	5,96
	mg/m ³	3,21	0,27	0,09	0,60	—	0,25	0,57	0,52	0,66	0,73	6,94
No. 3 SI.	% , x10 ⁻⁴	74,72	7,15	0,80	1,33	—	2,58	19,99	67,88	26,05	0,11	200,64
	mg/m ³	53,49	9,59	1,00	2,62	—	6,69	51,85	218,5	83,86	0,45	428,08
No. 4 SI.	% , x10 ⁻⁴	10,84	0,63	0,12	0,30	—	0,25	1,56	3,87	1,94	0,14	19,69
	mg/m ³	7,76	0,85	0,15	0,59	—	0,65	4,06	12,48	6,24	0,56	33,39
No. 5 SI.	% , x10 ⁻⁴	16,09	0,40	0,05	0,31	—	0,09	0,52	0,58	0,41	0,08	18,55
	mg/m ³	11,59	0,53	0,06	0,61	—	0,23	1,35	1,87	1,34	0,32	17,86
No. 6 SI.	% , x10 ⁻⁴	6,65	0,34	0,06	0,54	—	0,20	0,76	0,53	0,43	0,27	9,82
	mg/m ³	4,77	0,46	0,07	1,06	—	0,53	1,98	1,72	1,39	1,06	13,08
No. 7 SI.	% , x10 ⁻⁴	7,31	0,15	0,06	0,20	—	0,07	0,76	0,79	0,64	0,14	10,16
	mg/m ³	5,24	0,20	0,08	0,40	—	0,20	1,98	2,54	2,06	0,53	13,26
No. 8 SI.	% , x10 ⁻⁴	6,73	0,14	0,05	0,17	—	0,05	0,44	0,39	0,35	0,02	8,39
	mg/m ³	4,82	0,19	0,06	0,35	—	0,15	1,16	1,27	1,14	0,08	9,25
No. 9 SI.	% , x10 ⁻⁴	3,21	0,06	0,02	0,04	—	0,01	0,07	0,03	0,07	0,08	3,61
	mg/m ³	2,29	0,08	0,03	0,07	—	0,04	0,18	0,11	0,22	0,32	3,38
No. 10 SI.	% , x10 ⁻⁴	4,21	0,02	—	0,04	—	0,04	0,08	0,24	0,02	0,12	4,80
	mg/m ³	3,01	0,03	—	0,09	—	0,11	0,23	0,77	0,07	0,48	4,08
No. 11 SI.	% , x10 ⁻⁴	3,77	0,03	—	0,03	—	0,01	0,04	0,04	0,06	0,09	4,10
	mg/m ³	2,70	0,04	—	0,06	—	0,03	0,11	0,12	0,20	0,38	3,67
No. 12 SI.	% , x10 ⁻⁴	4,21	0,04	0,20	0,04	—	0,02	0,02	0,01	0,05	0,07	4,69
	mg/m ³	3,01	0,06	0,25	0,08	—	0,06	0,06	0,04	0,16	0,28	4,04
No. 13 SI.	% , x10 ⁻⁴	3,91	0,04	0,04	0,04	—	0,01	0,04	0,02	0,09	0,10	4,32
	mg/m ³	2,80	0,05	0,05	0,08	—	0,04	0,11	0,07	0,28	0,38	3,91
No. 14 SI.	% , x10 ⁻⁴	3,86	0,06	0,11	0,05	—	0,01	0,08	0,03	0,08	0,15	4,47
	mg/m ³	2,76	0,08	0,14	0,11	—	0,02	0,21	0,11	0,28	0,59	4,34
No. 15 SI.	% , x10 ⁻⁴	3,89	0,04	0,08	0,02	—	0,03	0,07	0,02	0,07	0,07	4,33
	mg/m ³	2,78	0,06	0,10	0,05	—	0,08	0,19	0,08	0,22	0,29	3,89

According to the results, in all samples, methane and its homologues to C₆ + were detected inclusively. Also, in almost all samples (except for 10-SI. and 11-SI.) unsaturated ethylene homologue (C₂H₄) was found.

The content of methane in water is in the range of 2,7 ÷ 53,49 mg/m³. Moreover, for wells from No.1 to No. 8, the content of dissolved methane is more differentiated and is within the range of 3,21 ÷ 53,49 mg/m³ at the maximum value in the well No. 3-53,49 mg/m³, and for the wells from No. 9 to number 15 it is slightly smaller, more stable and varies from 2,29÷3,01 mg/m³ and only in the sample from well No. 3 the maximum value is 53,49 mg/m³.

The content of butane in water for wells 9÷15 varies mainly from 0,124 mg/m³ at to 0,347 mg/m³, and for wells 1÷8 is slightly larger – 0,57÷51,85 mg/m³ with a maximum value of 51,85 mg/m³ in the well No. 3.

Capture of underground gas of free state. In the process of the implementation of near-surface gas geochemical survey, 28 samples of free groundwater from a depth of 0,5 m were selected. Fig. 2 depicts gas sampling points.

The capture was conducted in order to find the possible source of groundwater contamination by oil products. In total, four main objects were surveyed: a gas station, a liquidated well, a non-operating oil pipeline link and eight wells (No. 1÷8), in which relatively high levels of hydrocarbon dissolved in water were detected.

Analyses of gas-air mixtures, as compared with the analysis of water samples in wells, have the advantage that they are not limited in area by the presence of wells, but can be selected anywhere. The results of chromatographic analyses of selected near-surface gas mixtures are shown in table 2.

On fig. 3 the graphical distribution of background and abnormal gas geochemical zones is depicted.

Gas station. A total of 10 underground gas samples were selected around the gas station, six of which revealed homologues of methane up to C₆ (hexane) inclusive. In two

samples No. 18 and No. 19, unsaturated ethylene was detected.

The content of methane in the subterranean atmosphere varies within 1,880 ÷ 6,516 x 10⁻⁴ % vol. and an average of 3,098 x 10⁻⁴ % vol., which according to STK 320,2007720.0162000 refers to the 1st degree of gas content of near-surface sediments and under the conditions of gas safety, refers to safe backgrounds.

Liquidated well 15-Babcie. It is located at the distance of nearly 900 m southwest from the epicentre of groundwater contamination. 4 samples of subsoil gas were selected around the well. The content of methane in the subsoil deposits varies from 6,075 to 13,849 x 10⁻⁴ % vol. and an average of 9,97 x 10⁻⁴ % vol. This indicates the presence of dead passes in this well. In all samples homologues of methane to C₆ were found. Unsaturated hydrocarbons are absent.

Links of inactive oil pipeline. Six samples of subsoil atmosphere have been selected. Methane and its homologues, to C₆, are defined in all trials. Hexan plus higher was found in samples No. 13 and No. 14. Also, unsaturated ethylene – Ordinary alcohol in samples No. 13, No. 14, No. 12 and No. 11 was detected.

The content of methane in samples above the oil pipeline varies in the range of 2,900 ÷ 5,673 x 10⁻⁴ % vol. and an average of 4–00 x 10⁻⁴ % vol.

Wells. Methane and all of its homologues to C₆ were detected in underground gas samples taken near 8 wells (No. 1÷8). The content of methane in the underground atmosphere has low values, varying within the range of 2,571÷3,728 x 10⁻⁴ % vol. and an average of 3,170 x 10⁻⁴ % vol. Unsaturated ethylene is detected only in sample No. 8.

Based on the received data of subterranean gas surveying, gas pollution maps and analysis of their results, it can be noted that two zones of relatively high gas content under the surface sediments are allocated on the surveyed

area – a zone of gas stations where the high gas content of near-surface sediments is allocated by light, heavy and total carbohydrates , and somewhat displaced zone with respect

to the well number 3 in the direction of the movement of groundwater, which is also allocated for light, heavy and aggregate values.

Table 2

Results of chromatographic analyses of gas-air mixtures

Sample number	Unit	Gas mixture composition									Total CH ₄ -C ₆ H ₁₄ mg/m ³
		CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-C ₅ H ₁₂	n-C ₅ H ₁₂	
No. 1-Ch	% [,] x10 ⁻⁴	3,564	0,052	–	0,071	–	0,011	0,048	0,041	0,043	0,071
	mg/m ³	2,551	0,070	–	0,140	–	0,029	0,124	0,132	0,138	0,273
No. 2-Ch	% [,] x10 ⁻⁴	2,606	0,066	–	0,039	–	0,034	0,082	0,043	0,024	0,019
	mg/m ³	1,865	0,089	–	0,077	–	0,088	0,213	0,138	0,077	0,073
No. 3-Ch	% [,] x10 ⁻⁴	2,571	0,062	–	0,034	–	0,013	0,047	0,041	0,046	0,018
	mg/m ³	1,840	0,083	–	0,067	–	0,034	0,122	0,132	0,148	0,069
No. 4-Ch	% [,] x10 ⁻⁴	2,709	0,053	–	0,03	–	0,013	0,03	0,013	0,018	0,019
	mg/m ³	1,939	0,071	–	0,059	–	0,034	0,078	0,042	0,058	0,073
No. 5-Ch	% [,] x10 ⁻⁴	3,492	0,054	–	0,021	–	0,020	0,048	0,030	0,035	0,173
	mg/m ³	2,500	0,072	–	0,041	–	0,053	0,125	0,096	0,111	0,667
No. 6-Ch	% [,] x10 ⁻⁴	3,728	0,045	–	0,085	–	0,029	0,074	0,061	0,04	0,053
	mg/m ³	2,668	0,060	–	0,167	–	0,075	0,192	0,196	0,129	0,204
No. 7-Ch	% [,] x10 ⁻⁴	3,516	0,048	–	0,028	–	0,033	0,065	0,054	0,051	–
	mg/m ³	2,517	0,064	–	0,055	–	0,086	0,169	0,174	0,164	–
No. 8-Ch	% [,] x10 ⁻⁴	3,113	0,06	0,019	0,052	–	0,025	0,05	0,043	0,035	0,08
	mg/m ³	2,228	0,080	0,024	0,102	–	0,065	0,130	0,138	0,113	0,308
No. H9-Ch	% [,] x10 ⁻⁴	4,099	0,078	–	0,074	–	0,047	0,065	0,045	0,034	–
	mg/m ³	2,934	0,105	–	0,146	–	0,122	0,169	0,145	0,109	–
No. H10-Ch	% [,] x10 ⁻⁴	5,123	0,093	–	0,057	–	0,029	0,062	0,057	0,056	–
	mg/m ³	3,667	0,125	–	0,112	–	0,075	0,161	0,183	0,180	–
No. H11-Ch	% [,] x10 ⁻⁴	2,900	0,044	0,013	0,039	–	0,047	0,051	0,018	0,024	–
	mg/m ³	2,76	0,059	0,016	0,077	–	0,122	0,132	0,058	0,077	–
No. H12-Cr	% [,] x10 ⁻⁴	2,314	0,053	0,02	0,028	–	0,027	0,097	0,01	0,011	–
	mg/m ³	1,657	0,071	0,025	0,055	–	0,070	0,252	0,032	0,035	–
No. H13-Ch	% [,] x10 ⁻⁴	3,841	0,089	0,024	0,046	–	0,057	0,07	0,067	0,049	0,104
	mg/m ³	2,749	0,119	0,030	0,091	–	0,148	0,018	0,216	0,158	0,400
No. H14-Ch	% [,] x10 ⁻⁴	5,673	0,107	0,059	0,082	–	0,035	0,069	0,051	0,055	0,15
	mg/m ³	4,061	0,144	0,074	0,161	–	0,091	0,179	0,164	0,177	0,577
No. GS15Ch	% [,] x10 ⁻⁴	3,099	0,077	–	0,047	–	0,022	0,038	0,032	0,043	–
	mg/m ³	2,218	0,103	–	0,092	–	0,057	0,098	0,102	0,139	–
No. GS16Ch	% [,] x10 ⁻⁴	1,880	0,062	–	0,035	–	0,033	0,037	–	–	–
	mg/m ³	1,346	0,083	–	0,069	–	0,086	0,097	–	–	1,681
No. GS17Ch	% [,] x10 ⁻⁴	3,295	0,043	–	0,022	–	0,024	0,032	0,034	0,015	–
	mg/m ³	2,358	0,058	–	0,043	–	0,062	0,083	0,111	0,048	–
No. GS18Ch	% [,] x10 ⁻⁴	3,463	0,074	0,092	0,061	–	0,023	0,031	0,01	0,02	0,015
	mg/m ³	2,479	0,099	0,115	0,120	–	0,060	0,080	0,032	0,064	0,058
No. GS19Ch	% [,] x10 ⁻⁴	4,135	0,162	0,062	0,08	–	0,048	0,075	0,033	0,045	0
	mg/m ³	2,960	0,217	0,078	0,157	–	0,124	0,194	0,106	0,145	0,000
No. GS20Ch	% [,] x10 ⁻⁴	2,369	0,035	0	0,028	–	0,016	0,081	0	0	0
	mg/m ³	1,696	0,047	0,000	0,055	–	0,041	0,210	0,000	0,000	2,049
No. GS21Ch	% [,] x10 ⁻⁴	3,476	0,132	–	0,064	–	0,025	0,040	0,021	0,041	–
	mg/m ³	2,488	0,177	–	0,126	–	0,064	0,104	0,066	0,133	–
No. GS22Ch	% [,] x10 ⁻⁴	4,723	0,134	–	0,108	–	0,028	0,080	0,027	0,048	–
	mg/m ³	3,380	0,180	–	0,212	–	0,074	0,207	0,088	0,154	–
No. GS23Ch	% [,] x10 ⁻⁴	4,545	0,113	–	0,091	–	0,031	0,066	0,036	0,058	0,108
	mg/m ³	3,253	0,152	–	0,179	–	0,080	0,171	0,116	0,187	0,415
No. GS24Ch	% [,] x10 ⁻⁴	6,516	0,272	–	0,215	–	0,014	0,067	0,065	0,064	0,12
	mg/m ³	4,664	0,365	–	0,423	–	0,036	0,174	0,209	0,206	0,461
No. GS25Ch	% [,] x10 ⁻⁴	7,981	0,315	–	0,259	–	0,014	0,167	0,061	0,093	0,154
	mg/m ³	5,713	0,423	–	0,510	–	0,036	0,432	0,196	0,299	0,593
No. GS26Ch	% [,] x10 ⁻⁴	11,94	0,459	–	0,325	–	0,103	0,207	0,101	0,148	0,057
	mg/m ³	8,548	0,616	–	0,638	–	0,267	0,536	0,324	0,476	0,220
No. GS27Ch	% [,] x10 ⁻⁴	13,84	0,589	–	0,475	–	1,452	0,322	0,160	0,192	0,193
	mg/m ³	9,913	0,790	–	0,934	–	3,765	0,834	0,515	0,619	0,741
No. GS28Ch	% [,] x10 ⁻⁴	6,075	0,477	–	0,526	–	0,051	0,310	0,128	0,139	0,017
	mg/m ³	4,348	0,640	–	1,035	–	0,132	0,803	0,412	0,447	0,065

These data and the presence at two points of the inspection in the area of the gas station (GS18Ch and GS19Ch), as well as over the oil pipeline (sample H11-Ch and H12-Ch), unsaturated hydrocarbon gas (ethylene) speaks of its technogenic origin (the process of distillation of oil), which allows to call the gas station a source of pollution. Visually, the site of increased gas content is one abnormal zone to which the gas station is adjoined.

Results of geophysical research. Geophysical investigations are performed by two methods: vertical electrical sounding (VES) and natural electric field (NEF), and the location of the points of the VES and NEF is presented on fig. 2.

The method of VES is executed for the purpose of mapping the covering of the rocks on the profile, passing through the contamination area across the groundwater movement. After all, it is known from geological reports that

on the right bank of the Bystrytsia Solotvynska River, where research was conducted, pebble-sand forms of the first, second and third floodplain terraces are developed, and on the left bank there is the formation of the fourth floodplain terrace. That is, the river changed its position, forming a wide valley, where river alluvial deposits are developed.

It can be assumed that during its movement it formed the deep channels that exist under the surface of the earth and are the dominant element of groundwater filtration. Consequently, the specific purpose of the work by the VES method is to find such a channel for specifying the location of the groundwater flow.

Physical substantiation of the VES method is the differentiation of rocks in depth by electrical resistance. The presence of a reliable geological section, along with analysis of the curves of the VES allowed making the following table 3 correspondence of lithology, that is, the composition of rocks of the cut, and electric resistance.

All curves of VES are of the same type and correspond according to the table 3 to correlation of resistance $\rho_1 < \rho_2 > \rho_3 > \rho_4$. As an example in fig. 4 is shown one of the curves of the VES with the designation of the correspondence of the branches of the curve selected by four geoelectric layers, as indicated in table 3.



Fig. 3. Total hydrocarbon content in subsoil gas

Table 3

Characteristics of the section of rocks and their electric resistance

No. of the layer	Characteristics of the rock	Electric resistance, Om
I	Surface clay-sand formation	40–1000
II	Sand and pebbles dry rocks of river deposits	300–900
III	Sand and pebble water bodies of river deposits	35–70
IV	Root watered argillite rocks	3–7

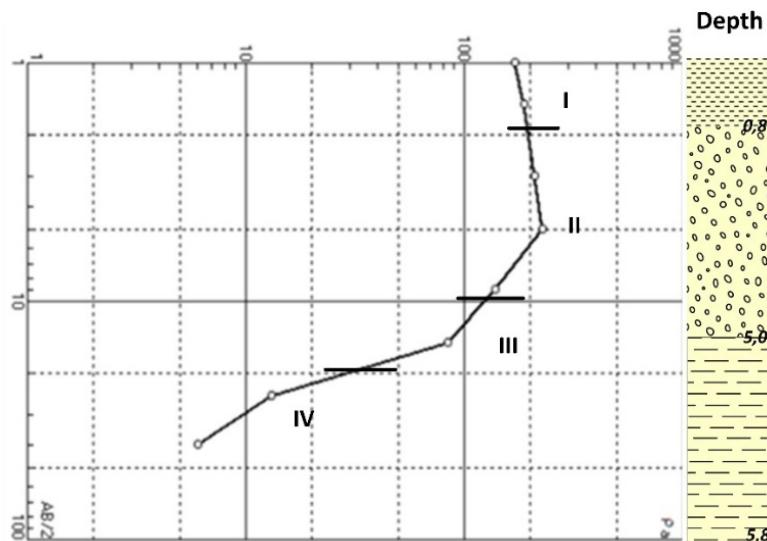


Fig. 4. Typical VES curve

In the section of imaginary resistance on a qualitative level, the tendency to increase the depth of occurrence of indigenous rocks and the presence of the ancient channel within the zone of pollution is reflected, which is the main way of filtration of groundwater in the eastern direction. The places of the largest depths in general coincide with the line of pollution. Consequently, contamination clearly lies from west to east in the sub-latitudinal direction.

In the geoelectric section, the result is reproduced in quantitative units. In fig. 5 arrows indicate the areas of the largest depths of the alluvial formations, that is, contours of the ancient channel. As can be seen, the pollution in general coincides with the data of electrical probing, because the

flow of groundwater has a local direction, from west to east. This is the direction of movement of groundwater from the gas station. Thus, the findings regarding the pollution of groundwater in the gas station territory received an indirect confirmation by the data of geoelectric studies.

The NEF method was conducted to trace the paths of active groundwater filtration. The method is based on this variant on the ability of ions of different signs in underground waters to move at different speeds, resulting in anomalies of the potential of the electric field.

The resulting map of the NEF method is a map of distribution of potentials by profiles (fig. 6).

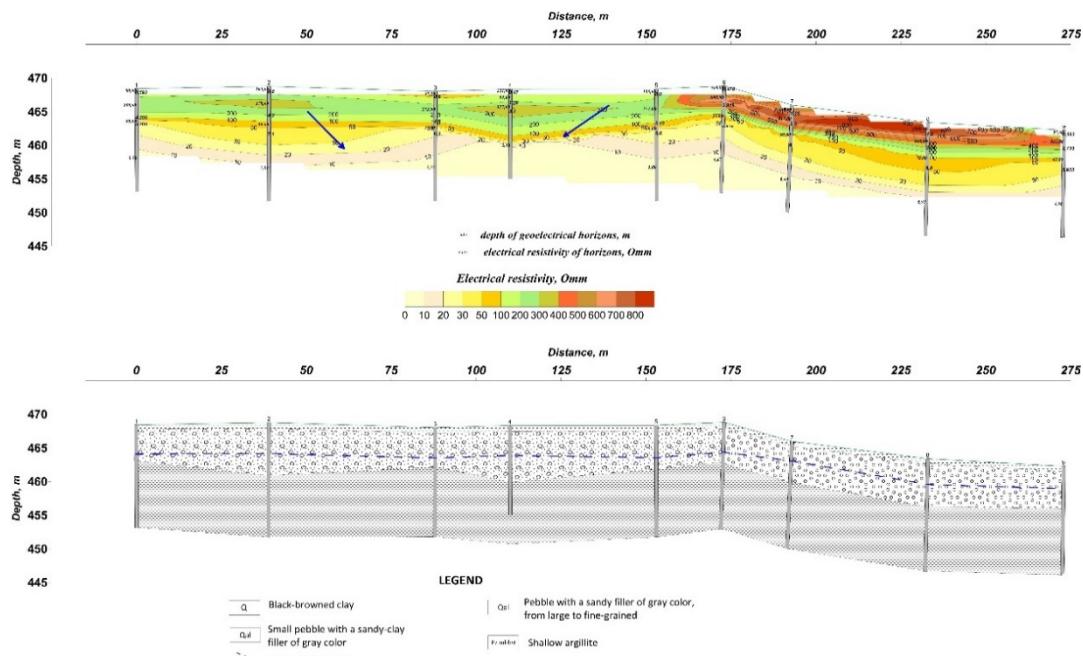


Fig. 5. Geoelectric section (according to VES)

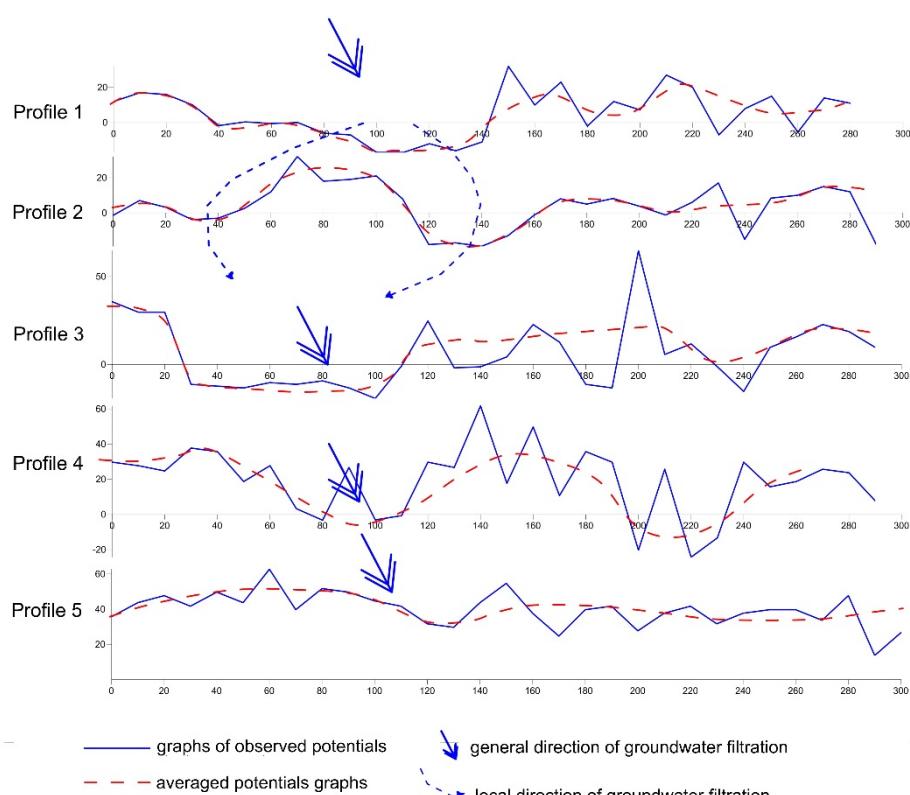


Fig. 6. Graphs of natural electrical potentials

In fig. 6, in addition to the output graphs of potentials, the averaging lines are depicted, and the arrows indicate the direction of filtration of groundwater. Negative anomalies corresponding to filtration flows correlate, that is, they are coordinated according to different profiles. The direction of movement of groundwater corresponds to the direction from the gas station to the pollution areas.

Planned distribution of potentials confirms the tendency for anomalies of lower potential in territories adjacent to the territory of the gas station.

Conclusion. According to the results of geochemical research in the territory of Solotvyn (August–September 2017) contaminated water was defined in eight wells on an area of 900 m² (the total content of light and heavy hydrocarbons from 9,258 to 428,087 mg/m³, with their contents in "clean" wells from 3,387 to 4,826 mg/m³).

The analysis of the presented cartographic materials, primarily the distribution of the content of light and heavy hydrocarbons in water and near-surface gas, suggests that the source of pollution is in the gas station, where in previous years it was likely that the oil products release in the ground occurred (possibly even in different years). At present, the pollution of the filling station territory by hydrocarbons after analyses of near-surface gas with a tendency of displacement of this pollution towards the wells is noted.

The distribution of electric resistance and natural filtration potentials obtained from geophysical studies has established the direction of filtration in the aquifer, which is consistent with the location of the ancient river bed or its sleeve, and corresponds to the distribution of groundwater from the gas station to contaminated wells.

The experience of self-cleaning groundwater due to their natural filtration shows that this process will take decades, depending on the velocity of groundwater. In order to accelerate the full water purification of hydrocarbons, it is necessary to conduct intensive pumping out of water from the wells, accompanied by periodic analyses on the content of hydrocarbons.

Prospects for the further development of research in this area are connected, firstly, with further regime observations for the purpose of monitoring and implementation of measures to eliminate sources of groundwater pollution in the object specified in the article, and secondly, using the above scientific developments and experience gained on other territories.

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ВИЗНАЧЕННЯ ДЖЕРЕЛ ЗАБРУДНЕННЯ ПІДЗЕМНИХ ВОД НАФТОПРОДУКТАМИ (НА ПРИКЛАДІ ТЕРІТОРІЇ СОЛОТВИНО В ПРИКАРПАТІ)

Присвячено розв'язанню проблеми забруднення підземних вод нафтопродуктами на території селища Солотвино, розташованого в Прикарпатті в Івано-Франківській області України. Забруднення виявлено в колодязях питного водопостачання за смаковими якостями і специфічним запахом. Як альтернативні розглядалися такі можливі джерела забруднення: законсервована нафтова сурволовина, нафтопровід, автозаправна станція (АЗС).

Усі власники зазначених об'єктів представили документи обстежень або випробувань із підтвердженням герметичності (сурволовина і резервуари АЗС) або відсутності углеводнів (недіючий нафтопровід). Виникла парадоксальна ситуація: забруднення є, а джерел забруднення немає. Для вирішення питання застосовано комплекс геохімічних і геофізичних методів.

Геохімічні дослідження проведено для проб води, відібраних з колодязів по території забруднення та прилеглих ділянок. Крім того, погущені мережі відібрали проби приповерхневого ґрунтового повітря в ґрунті. Вміст важких і легких углеводнів у забруднених пробах води перевищує фонові значення в десятки разів і перевищує гранично допустимі концентрації. Лабораторні дослідження проб повітря дозволили уточнити і деталізувати територію забруднення. За результатами геохімічних досліджень установлено, що джерело імовірного забруднення є на території АЗС.

Геофізичні дослідження дозволили з'ясувати літологічну будову верхньої частини розрізу і встановити глибини залягання покрівлі підошви колектора підземних вод і відповідно покрівлі підстилаючого водоупору. При цьому однозначно визначено напрямок фільтрації у водоносному горизонті й розташування давнього русла річки, яке відповідає шляху поширення підземних вод від АЗС до забруднених колодязів.

Мотивований висновок про причини забруднення підземних вод нафтопродуктами та про встановлене джерело забруднення передано до відповідних органів Державної служби України з надзвичайних ситуацій.

Ключові слова: нафтопродукти, забруднення, сурволовина, геофізика, геохімія, підґрунтовий газ.

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ОПРЕДЕЛЕНИЕ ИСТОЧНИКОВ ЗАГРЯЗНЕНИЯ ПОДЗЕМНЫХ ВОД НЕФТЕПРОДУКТАМИ (НА ПРИМЕРЕ ТЕРРИТОРИИ СОЛОТВИНО В ПРИКАРПАТЬЕ)

Посвящено решению проблемы загрязнения подземных вод нефтепродуктами на территории поселка Солотвин, находящегося в Прикарпатье в Ивано-Франковской области Украины. Загрязнение выявлено в колодцах питьевого водоснабжения по вкусовым качествам и специальному запаху. В качестве альтернативных рассматривались следующие возможные источники загрязнения: законсервированная нефтяная скважина, нефтепровод, автозаправочная станция (АЗС).

Все владельцы указанных объектов представили документы обследований или испытаний с подтверждением герметичности (скважина и резервуары АЗС) или отсутствия углеводородов (недействующий нефтепровод). Возникла парадоксальная ситуация: загрязнение есть, а источников загрязнения нет. Для решения вопроса применен комплекс геохимических и геофизических методов.

Геохимические исследования проведены для проб воды, отобранных из колодцев по территории загрязнения и прилегающих участков. Кроме того, по сгущенной сети отобраны пробы приповерхностного почвенного воздуха в грунте. Содержание тяжелых и легких углеводородов в загрязненных пробах воды превышало фоновые значения в десятки раз и превышало гранично допустимые концентрации. Лабораторные исследования проб воздуха позволили уточнить и детализировать территорию загрязнения.

По результатам геохимических исследований установлено, что источник вероятного загрязнения находится на территории АЗС.

Геофизические исследования позволили выяснить литологическое строение верхней части разреза и установить глубины залегания кровли и подошвы коллектора подземных вод и соответственно кровли подстилающего водоупора. При этом однозначно определено направление фильтрации в водонесущем горизонте и расположение древнего русла реки, которое соответствует пути распространению подземных вод от АЗС до загрязненных колодцев.

Мотивированное заключение о причинах загрязнения подземных вод нефтепродуктами и об установленном источнике загрязнения передано в соответствующие органы Государственной службы Украины по чрезвычайным ситуациям.

Ключевые слова: нефтепродукты, загрязнение, скважина, геофизика, геохимия, подпочвенный газ.