

Evolution of Groundwater Quality in the Area of Chemical Platform

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The purpose of this study was to determine the physico-chemical characteristics of groundwater in the area of an industrial platform for a period of three years, by examining the 18 drillings in the vicinity of polluting installations from platform. These groundwater samples were compared with water from four fountains located upstream and downstream of the industrial platform. Water samples were collected quarterly from each sampling point in the study. We followed the evolution of the main physico-chemical contaminants to highlight qualitative change while of groundwater studied in relation to standards for groundwater.

Keywords: groundwater, monitoring, drilling, fountains

Water is an important element for life and development of human communities. The fact that the first life forms arose in the aquatic environment, the first human settlements were established near rivers and streams, to have the water necessary for drinking and household needs, that water is the environment in which it carries out all metabolic processes the tissues and organs of all living things contain water in a large proportion of paramount importance to prove the role of water in the emergence and maintenance of life, as in the development of human societies over [1 – 3].

Nowadays, the drinking water source is surface water and groundwater. Surface waters have very different compositions and variable over time. Parameters that influence their composition are: the nature of the rocks that make up the bed, tributaries and rainfall, current or accidental discharges of wastewater, physical phenomena, chemical and biological processes that occur. In contrast, groundwater (groundwater) show relatively constant parameters. They are characterized by high mineralization, rich in carbon dioxide and low oxygen concentration. In terms of quality, groundwater is considered clean and fall in standards for drinking water or industrial uses less demanding.

Water pollution is, as a general definition, directly or indirectly modifying the composition of its normal as a result of human activity, in such an extent that affects all other uses to which water could be used in its natural state. Water pollution involves pollution biological, physical and chemical and determines, ultimately, change the ecological balance.

Activities that generate pollution of groundwater permit identification of four main forms of pollution: pollution of domestic, industrial, agricultural and transport. World Health Organization, health and medical research councils and environmental agencies promotes a precautionary approach to protect groundwater used by consumers [4 – 14]. The quality of water intended for human consumption

is an important goal included in EC Directives, aimed at protecting public health objective.

Given the importance of the quality of groundwater, studies presented in this paper were aimed at monitoring the quality parameters of groundwater in the area of industrial sites.

Experimental part

Materials and methods

Areas studied

This paper aims at monitoring groundwater in the area of industrial sites. Groundwater samples were taken from drillings located within control inside and in the vicinity chemical platform.

Groundwater samples studied were taken from drillings located in the industrial platform (zone I) and from drillings upstream and downstream industrial platform (zone II). The groundwater samples were collected from each sampling point. Content of these samples was analyzed in general contaminants: chlorides, sulfates, carbonates, ammonium, calcium, sodium, mercury, filterable residue, using standardized techniques for each indicator. Specific organic pollutants were analyzed by Gas - Chromatography.

Reagents

Reagents used were of recognized analytical quality (Merck, Fluka, etc.) which were used as such. Distilled water was used for quality 2 according to ISO 3696. Determination of quality indicators was done according to standards water in force specific to each indicator analyzed.

Apparatus

Spectral measurements were carried out with a UV-Vis spectrophotometer PERKIN ELMER LAMBDA 25 in quartz cuve of one cm. Gravimetric determinations for filterable residue were performed in a water bath GFL 1041, using an oven 50. Measurement was performed on a precision

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Table 1
INFORMATION ABOUT THE ANALYZED SAMPLES (ARRANGEMENT OF DRILLING, DRILLING WATER LEVEL)

Place of the sampling	Name of the sample	Water level in drilling from the surface soil [m]											
		2008				2009				2010			
		I	II	III	IV	I	II	III	IV	I	II	III	IV
Near	H ₅₂	4.75	4.92	6.01	6.37	6.16	6.2	6.16	6.2	5.31	5.45	5.31	5.45
	H ₅₄	4.85	4.94	6.48	6.55	5.5	5.6	5.5	5.6	5.15	5.24	5.15	5.24
	H ₅₅	6.15	6.25	8.57	7.6	7.68	7.7	7.68	7.7	7.22	7.25	7.22	7.25
	H ₆₀	5.29	5.39	5.5	5.8	5.38	5.3	5.38	5.3	4.8	5	4.8	5
	H ₆₂	6.4	6.4	7.56	7.6	7.59	7.6	7.59	7.6	6.85	7	6.85	7
Inside	F ₁	5.2	Clogged	Clogged	Clogged	Clogged	Clogged	Clogged	Clogged	4.6	4.9	4.6	4.9
	F ₂	5.35	5.77	6	5.96	5.96	5.95	5.96	5.95	4.8	5.43	4.8	5.43
	F ₃	7.43	5.44	5.8	7.7	5.65	5.15	5.65	5.15	5	5.24	5	5.24
	F ₄	5.35	5.44	5.72	5.95	5.7	5.63	5.7	5.63	5.14	5.2	5.14	5.2
	H ₁₆	7.92	8.0	8	8.18	8	7.98	8	7.98	7.6	7.7	7.6	7.7
	H ₅₃	Clogged	Clogged	Clogged	Clogged	7.35	Clogged	7.35	Clogged	7.15	7.13	7.15	7.13
	F _{cop.}	*	*	*	*	*	*	*	*	*	*	*	*
Upstream of the industrial platform	F _{ca2.}	*	*	*	*	*	*	*	*	*	*	*	*
	H ₂₁	4.5	4.8	5.59	5.4	5.4	5.4	5.4	4.51	4.6	4.51	4.6	
	H ₂₂	4.1	4.4	5.75	5.82	5.65	5.65	5.65	5.65	4.75	4.9	4.75	4.9
Downstream of the industrial platform	F _{stop}	*	*	*	*	*	*	*	*	*	*	*	*
	F _{stol}	*	*	*	*	*	*	*	*	*	*	*	*

* Constant level

balance XB 220 A. Organic substances were determined with a Gas chromatograph GC AGILENT TECHNOLOGIES NETWORK 6890 N detector FID, ECD, NPD. Measurement of pH was performed using a pH meter HI 8424.

Methods

Analyses of groundwater quality parameters were made according to international and European standardized methods of water quality adopted by national legislation [15].

These methods have been implemented in our laboratory and are certified in accordance with EN ISO 17025: 2005. For a number of laboratory chemical indicators participated in international interlaboratory tests obtaining values of z score <2 which allowed estimation laboratory performance as satisfactory.

Procedure

Groundwater samples were collected in polyethylene containers new 1L. Each container was washed with water collection site drilling to reduce the possibility of contamination of the sample with impurities resulting from the manufacturing process of the container. Water sampling location is shown in table 1, it is rendered and the depth of drilling water sampling. To avoid oxidation subsequent processes that can occur at water-air interface, the containers were completely filled with water and close the lid was done during immersion. Samples were stored at 4°C until analysis to minimize degradation.

Groundwater samples were collected from depth (drilling soles) with a harvester made for this purpose, after water has previously been emptied 3 times with a motopomp. For each water sample analyzed concentrations were determined following indicators: chlorides, sulfates, ammonium, calcium, sodium, residue filterable, COD and organic contaminants (VOCs - volatile organic compounds).

Values obtained for physic-chemical parameters investigated in momentary samples collected each quarter from the three years of the study were pooled and analyzed from the procedure of assessment of water status in accordance with the limit values specified by the norm on the benchmarks for determining quality drinking water [15, 16] and groundwater [17].

Results and Discussions

Harvested for analysis of groundwater drillings located both inside and near of the industrial platform (zone I) to evaluate the physic-chemical pollutants at different distances from polluting sources. It is assumed that test results for drillings closer (F3, H62, F2, F4, H16, H52, H54 and H55) may exhibit a higher degree of contamination.

To reflect the degree of pollution of groundwater samples were deep water drillings and boreholes in the vicinity of industrial platform (zone II), in areas upstream and downstream of the industrial platform. The pollutants specific organic (volatile organic compounds - VOCs) were determined in water from drillings. In parallel were made

Nr. crt.	Quality indicator	Limit allowed under H.G. 53/2009 and direction Olt water (groundwater body ROOT08)	Limit allowed under Law 458/2002 on drinking water quality and the Law 311/2004 amending and supplementing Law 458/2002 on drinking water quality
	U.M.	mg/L	mg/L
1	Ammonium	2,6	0,5
2	Sulfati	250	250
3	sulfates	250	250
4	mercury	-	0,001
5	CCO-Cr	-	5
6	sodium	-	200

Table 2
THE LIMIT ALLOWED UNDER CURRENT LEGISLATION

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
F ₁	0.615	-	-	-	-	-	-	-	0.74	1.15	1.92	2.15
F ₂	0.706	0.57	0.98	1.14	1.46	0.98	0.55	1.02	1.56	1.5	1.80	1.68
F ₃	0.204	0.3	0.43	0.79	0.21	1.1	0.18	0.09	0.5	0.15	0.50	0.71
F ₄	0.889	0.66	0.89	1.49	1.16	1.34	1.14	1.38	0.5	0.678	2.15	1.37
H ₁₆	2.87	2.5	1.96	3.23	5.55	3.6	2.25	4.04	4.28	4.46	2.86	3.02
H ₅₃	-	-	-	-	2.3	-	-	-	2.86	3.04	2.67	3.57

Table 3
AMMONIUM QUALITY INDICATOR (NH₄⁺) FOR DRILLINGS LOCATED NEAR OF THE INDUSTRIAL PLATFORM (mg/L)

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
F ₁	430.8	-	-	-	-	-	-	-	698.7	533.3	543.64	452.62
F ₂	32.3	24.5	38.1	49.5	29.8	41.5	9.4	10.7	14.2	33.6	14.71	39.12
F ₃	64.7	49	54.9	64.6	54	51	34.7	27.9	81.1	35.8	31.12	38.02
F ₄	25	19.9	30.8	43	48.7	32	23	21	140.9	81.4	75.91	100.52
H ₁₆	17.8	19.6	28.3	34.3	43.4	34.7	8.04	14	19.2	7.9	10.61	23.80
H ₅₃	-	-	-	-	25.6	-	-	-	9.54	11.8	61.20	13.95

Table 4
SULFATES QUALITY INDICATOR (SO₄²⁻) FOR DRILLINGS LOCATED NEAR OF THE INDUSTRIAL PLATFORM (mg/L)

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
F ₁	155.9	-	-	-	-	-	-	-	921.8	1240.8	1418.1	2410.80
F ₂	921.8	964.3	921.8	992.6	638.1	638	389.9	425.4	1099	1347	1382.6	1028.13
F ₃	567.2	297.8	382.9	425.4	226.9	212.7	283.6	2127	531.8	283.6	425.43	319.07
F ₄	779.9	992.7	510.5	978.5	623.9	709	893.4	992.7	779.7	1240.7	1701.7	1808.10
H ₁₆	255.2	326.1	510.5	595.6	1659.2	1347	1063.6	1063.6	1134.4	1489	1630.8	1134.49
H ₅₃	-	-	-	-	538.9	-	-	-	709	709	460.8	638.15

Table 5
CHLORIDES QUALITY INDICATOR ((Cl) FOR DRILLINGS LOCATED NEAR OF THE INDUSTRIAL PLATFORM (mg/L)

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
H52	0.04	0.34	0.32	0.08	0.41	0.51	0.63	1.96	0.37	0.52	0.60	0.42
H54	0.71	0.59	0.61	0.55	0.67	0.8	0.8	0.63	0.49	0.63	0.69	0.25
H55	1.19	0.29	0	0	0.087	0.21	0.6	0.15	0.43	0.1	0.39	0.07
H60	1.66	0.93	0.96	0.67	0.76	0.8	1.2	1.1	0.96	1.64	0.75	0.62
H62	1.19	0.77	0.96	1.26	1.17	0.51	0.8	0.87	0.55	0.58	0.78	0.36

Table 6
AMMONIUM QUALITY INDICATOR ((NH₄⁺) FOR DRILLINGS LOCATED INSIDE OF THE INDUSTRIAL PLATFORM (mg/L)

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
H52	49.6	45.6	38.3	37.3	45	37.4	41.5	37.4	102.4	24.9	337.77	29.27
H54	27.6	52.8	49.2	54	58.5	48.3	39.4	34	33.3	29.2	24.28	27.08
H55	34	44.4	14.8	23.8	30	49.7	34.7	17.6	106	54	51.30	59.50
H60	12	19	25	47.7	28	26.5	21	14.9	16.9	5.25	14.71	15.56
H62	13	32	5.74	22.2	28.3	24.4	24.4	21.7	33.2	11.6	17.44	11.45

Table 7
SULFATES QUALITY INDICATOR (SO₄²⁻) FOR DRILLINGS LOCATED INSIDE OF THE INDUSTRIAL PLATFORM (mg/L)

determination of mercury from drillings upstream and downstream industrial platform.

The results of physic - chemical properties are shown in tables 3 - 11 and compared with the maximum permissible values according to Law 458/2002 - on drinking water quality, the Law 311/2004 amending and supplementing Law 458/2002 on drinking water quality and HG 53/2009 and Direction Olt water (groundwater body ROOT08) (table 2) [17].

Ammonium analysis

The limit allowed under H.G. 53/2009 and direction Olt water (groundwater body ROOT08) for ammonium quality indicator is 2.6 mg/L. Thus, ammonium quality indicator:

-Drilling arranged in the vicinity of industrial platform, exceeds the limit imposed according to law for H16 and H53 boreholes. Other drillings in this graph do not exceed the allowed limit (table 3).

-Drilling arranged in the vicinity of industrial platform, does not exceed the limit imposed according to law for any of the drillings in this graph (table 6).

-Drilling and drillings located upstream and downstream of the industrial platform exceeds the limit imposed according to law for samples from drillings and drilling Stolniceni H21 in the fourth quarter of 2010. Other drillings and boreholes do not exceed the allowed limit (table 9).

Analysis of sulfates

The limit allowed under H.G. 53/2009 and direction Olt water (groundwater body ROOT08) quality indicator sulfate is 250 mg/L. The quality indicator sulfates for:

-Drilling arranged in the vicinity of industrial platform, exceeds the limit imposed according to law for drilling F1 in 2010 and first quarter of 2008. Other drillings in this graph do not exceed the allowed limit (table 4).

-Drilling arranged inside of industrial platform, exceeds the limit imposed according to law for drilling H52 in 2010, only in the third quarter. Other drillings in this graph do not exceed the allowed limit (table 7).

-Drilling and drillings located upstream and downstream of the industrial platform, exceeds the limit imposed according to law for Fountains Stuparei and Copacelu in 2009, in the IV quarter. The other drillings in this graph do not exceed the allowed limit (table 10).

Chloride analysis

The limit allowed under H.G. 53/2009 and direction Olt water (groundwater body ROOT08) quality indicator chlorides is 250 mg/L. The quality indicator for chloride:

-Drilling arranged in the vicinity of the industrial platform, exceeds the limit imposed according to law for all drilling and for the whole period analyzed, except F1 drilling in 2008, in the first quarter (table 5).

-Drilling arranged inside of the industrial platform, exceeds the limit imposed under the legislation in force for almost all drilling and about all period. The exception had drilling H52 which generally was situated in the limit imposed by law (table 8).

-Drilling and drillings located upstream and downstream of the industrial platform, exceeds the limit imposed according to law for all these years in Fountains Stuparei and Copacelu in 2010, in the third quarter. The other boreholes and drillings do not exceed the allowed limit (table 11).

Analysis of Mercury

Mercury was determined from fountains located upstream and downstream of the industrial platform and also for drilling situated near of the industrial platform (H52), was located in some installations that used mercury.

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
H52	184.3	163	283.6	127.6	248	283.6	255	255.2	212.8	319	354.53	212.71
H54	163	283.6	425.4	283.6	460	35.4	269	311.9	297.8	395	319.07	248.17
H55	212.7	376	397	425.4	354	283.6	244	183.4	255.2	411.2	354.53	389.98
H60	576.2	435	482	354.5	496.3	638	440	333.2	609.8	567.2	602.70	425.43
H62	595.6	624	709	638	709	425.4	248	269.4	254	156	336.80	354.53

Table 8
CHLORIDES QUALITY INDICATOR (Cl) FOR DRILLINGS LOCATED **INSIDE** OF THE INDUSTRIAL PLATFORM (mg/L)

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
F _{stup}	0	0	0.028	0.036	0.14	0.038	0	0	0	0.08	0	0.02
F _{stol}	0	0.051	0	0.036	0.14	0.05	0.046	0.02	0.018	0	0.01	1.842
F _{cop}	0.035	0	0.028	0.032	0.18	0.23	0	0.02	0.062	0.04	0.03	0.032
F _{caz}	0.035	0.16	0.062	0.05	0.109	0.05	0.053	0.053	0.062	0.04	0.04	0.102
H ₂₁	0.023	0.085	0.028	0.051	0.168	0.12	0.023	0.03	0.15	0.08	0.10	1.90
H ₂₂	0.023	0	0.097	0.05	0.168	0.075	0	0.053	0	0.026	0	0.02
PS	1.33	0.14	2.24	0.64	1.38	0.75	3.18	3.16	0.86	0.44	0.56	3.91

Table 9
AMMONIUM QUALITY INDICATOR (NH₄⁺) FOR DRILLINGS AND FOUNTAINS LOCATED UPSTREAM (F_{cop}, F_{caz}, H₂₁, H₂₂, PS) AND DOWNSTREAM (F_{stup}, F_{stol}) FROM INDUSTRIAL PLATFORM (mg/L)

Table 10
SULFATES QUALITY INDICATOR (SO₄²⁻) FOR DRILLINGS AND FOUNTAINS LOCATED UPSTREAM (F_{cop}, F_{caz}, H₂₁, H₂₂, PS) AND DOWNSTREAM (F_{stup}, F_{stol}) FROM INDUSTRIAL PLATFORM (mg/L)

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
F _{stup}	99.2	112.9	127.5	66	55.5	43	35.4	581.4	133.2	149.6	179.17	253.65
F _{stol}	47	72	63.4	37.3	34.3	28	79.8	85	73	48.3	82.55	10.68
F _{cop}	84	103.3	93.6	67.5	26.8	33.3	77	283.6	200.7	78.5	91.62	97.79
F _{caz}	159	181	203.9	66.8	31.3	27.8	66.1	10.6	83.2	162.7	179.17	198.96
H ₂₁	39	39	44.1	62.3	35.8	19.6	41.6	42.5	47.9	86.1	73.02	42.39
H ₂₂	45.4	45.6	61.5	73.6	60	48	89.6	42.5	70.8	56.6	108.72	55.52
PS	196	228	1018.1	240	216	193	294.6	4750.7	220.8	253.6	147.01	167.08

Table 11
CHLORIDES QUALITY INDICATOR (Cl) FOR DRILLINGS AND FOUNTAINS LOCATED UPSTREAM (F_{cop}, F_{caz}, H₂₁, H₂₂, PS) AND DOWNSTREAM (F_{stup}, F_{stol}) FROM INDUSTRIAL PLATFORM (mg/L)

Drilling name	2008				2009				2010			
	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV	Trim I	Trim II	Trim III	Trim IV
F _{stup}	794	624	886.32	815.4	695	638	602.7	107.8	588.5	624	779.96	425.43
F _{stol}	71	78	78	70.9	212.7	71	56.7	72	78	85	77.99	14.18
F _{cop}	191.4	184.3	248.15	233.9	63.8	213	319	24.4	141.8	63.8	127.63	113.44
F _{caz}	99.2	78	106.35	63.8	35.4	39	49.6	66.1	42.5	106.6	63.81	106.35
H ₂₁	35.4	35.4	70.9	56.7	53	106	113.4	39.5	21.3	42.5	56.72	63.81
H ₂₂	33.5	63.8	56.7	49.6	49.6	78	49.6	36.8	34.4	49.6	49.63	42.54
PS	3190.7	4963	44316.2	3970.7	3545	4432	10900	256.3	3722	2268.9	6381.54	2481.7

Following the results, the mercury was below the limit of 0.001 mg/L in all four subjects and for drilling H52 was observed that mercury contamination depends on the sampling period (weather) of the water in drilling and production in facilities near the borehole during sampling.

Analysis of VOCs
We determined the VOCs in fountains upstream and downstream industrial platform and find that fountain Stuparei was one that contains significant concentrations of VOCs throughout the study.

Analysis of CCO-Cr

The limit allowed under Law 458/2002 on drinking water quality and the Law 311/2004 amending and supplementing Law 458/2002 on drinking water quality - Thresholds for intervention, for quality indicator COD is 5 mgO₂ / L.

Following the results for the entire period and for all investigated areas was observed that for almost all fountains and drillings studied quality indicator COD exceeds the limit allowed by the legislation in vigor.

Filterable residue analysis

Filterable residue was determined during the investigation, for all fountains and drillings studied and found that it is higher for drillings located in zone I of investigation (drillings located inside and near of the industrial platform) from zone II investigation (upstream and downstream of the platform industries), generally depending on the inorganic loading of these drillings. For the investigation in zone II of filterable residue concentration was higher for drillings downstream to the upstream industrial platform.

Analysis sodium

The limit allowed under Law 458/2002 on drinking water quality and the Law 311/2004 amending and supplementing Law 458/2002 on drinking water quality - Thresholds for intervention, for quality indicator Na is 200 mg/L. Following the results for the entire period and for all investigated areas was seen as a quality indicator sodium concentration was found above the limit imposed under the laws in vigor in almost all studied drillings except drillings generally located upstream of the industrial platform.

Conclusions

In this paper are presented studies on groundwater quality monitoring in the area of industrial sites and from drillings upstream and downstream industrial platform. Water samples used in the study were taken from two areas: Zone I (drillings located inside and near of the industrial platform) and zone II (drillings upstream and downstream of the industrial platform). For these samples were determined a series of quality indicators: chlorides, sulfates, ammonium, calcium, sodium, residue filterable, COD and organic contaminants (VOCs - volatile organic compounds).

Based analyses indicated that, depending on the place of harvest, the quality of groundwater varies. For groundwater collected from drillings located inside and near of the industrial platform in physic-chemical analyzes it was observed that a number of physicochemical and specific contaminants were higher near pollutant sources.

In assessing groundwater pollution was observed as deep water samples from drillings in the vicinity of the platform industry contain more pollutants in areas downstream to the upstream industrial platform. Regarding the time evolution of the analyzed samples is found that it depends on:

-Sampling period (season when they were sampled), thus the weather at the time of sampling;

-Depth of water in drillings with as drilling depth was greater the more polluted it is weaker;

-The area where drillings are located (inside, near, upstream and downstream of the industrial platform);

-The activity of industrial platform (possible damage to the installations located in this area of production in that period).

In the zone I have found exceeding the maximum permitted levels for most quality indicators analyzed. Water samples taken from zone II had exceeded the maximum permitted levels higher downstream towards the upstream industrial platform, which means that pollution comes from activities that take place inside of the industrial platform. It can be considered that the waters of fountains and drillings studied are exceeded permissible values are polluted due to seepage from industrial activities taking place on the industrial platform.

Industrial pollution, as can be seen from the results of this study persist over time and is felt at depths of over 4 m and at distances over 5 km of industrial platform (platform drillings downstream industries). Considering the data obtained we can say that it is difficult for such a polluted industrial area to a decommissioned. Disposal of such areas may take decades.

We find it useful to continue investigations on changing physic-chemical characteristics of groundwater in the

industrial platform, to take measures to reduce the risk of pollution.

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