# Monitoring the impact of environmental burdens from the former Apollo Refinery, the Chemika and Gumon plants in Bratislava

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# **AGEOS**

**Abstract:** In the former industrial part of Bratislava, on the left bank of the Danube River, the Apollo Refinery was located, as well as chemical plants Chemika and Gumon. In 1944, the US Army bombed the Refinery, and it was this area from which the oil-based pollution has spread and prevailed there to-date. Complex chemical pollution was also caused by leakage from Gumon and Chemika plants, which is mainly represented by polycyclic and volatile aromatic hydrocarbons. Today, these sites are labelled in the Register of Contaminated Sites as the contaminated site of the "B" category. The register of Contaminated Sites defines Category A (potentially contaminated site), Category B (contaminated site) and Category C (remediated site). Since 2015, monitoring works have been carried out in the premises of both plants. In the scope of the monitoring the free phase of oil substances has been measured, along with the pollution and odour of groundwater, and organic contamination has been confirmed. Measurements have highlighted the intense impact of groundwater oscillation on the free phase of oil substances thickness – with the increase in groundwater table levels, the thickness of the free phase of oil substances drops, and vice versa. The work focuses on interpreting the data obtained from monitoring measurements and subsequent assessment of the impact of groundwater pollution from the environmental load of the Apollo Refinery and the chemical plants Chemika and Gumon.

Key words: Bratislava, groundwater, monitoring, environmental burdens, Apollo Refinery, Chemika and Gumon plants

### 1. INTRODUCTION

The issue of environmental burdens is currently very topical. In Slovakia, the State Programme of Environmental Burdens Remediation (SPEBR) has been implemented since 2010, when the first stage was commenced until 2015 with a continuous transition to the second stage (2016 – 2021). In addressing the SPEBR goals, the State Geological Institute of Dionýz Štúr solved the geological task of "Monitoring of Environmental Burdens on Selected Locations of the Slovak Republic" (Kordík et al., 2015), in which monitoring network was built in the area concerned; the selected burdens have been monitored, since then. Grounds of the former Chemika and Gumon companies are located in the former industrial part of Bratislava, where the Apollo Refinery in the past also stood, which in 1944 underwent bombardment by the US Army. From the Apollo Refinery a large volume of oil has leaked to the rock environment, which spreads in the environment due to the flow of groundwater. The Chemika Factory had focused mainly on the production of paints, lacquers and the distribution of various chemicals. The main activity of the Gumon Plant was the production of electro-insulating materials, bakelite, gumoid (glass textile) and asphalt. For the diversity of industrial production, pollution in soil and groundwater is varied, represented mainly by oil substances, polycyclic and volatile aromatic hydrocarbons. The article focuses on evaluating the results of monitoring measurements in the years 2015 and 2016.

# 2. THE TERRITORY OF INTEREST CHARACTERISTICS

The territory in question is located in the capital of the Slovak Republic, in Bratislava (Fig. 1). It is situated on the left bank of the river Danube, in the eastern part of the town, in the city part Ružinov, in the local part of Nivy. At present, a temporary bus station is located on the territory of the former Chemika Factory. The territory of the former Gumon Factory is abandoned.

The territory of interest belongs to the Danube catchment. Maximum flows in the summer months are caused by snow melting in the Alps (Hanzel et al., 2012). According to the Statistical Yearbook of the Capital City of Bratislava in 2016, between 2010 and 2015, the average flow rate was measured at Bratislava-Devín station  $2.031 \, \mathrm{m}^{-3} \cdot \mathrm{s}^{-1}$ .

The Podunajská nížina Lowland is composed of two basic complexes, namely Neogene and Quaternary sediments (Mazúr & Lukniš, 1986; Polák et al., 2012). In the area studied, the Neogene sediments were found in the wells at a depth of 13.5 m – 18.5 m, represented by sandy, calcareous plastic clays. The boundary between the Neogene and Quaternary complexes is formed by Neogene gravel from the period of the Pannonian and the granitoid boulders (Auxt et al., 2002). The Quaternary sediments facies were deposited by the flow of the Danube. The most extensive sediments of the Danube River are made of gravels of 8.7 m – 12.5 m thickness to a depth of up to 15 m. These

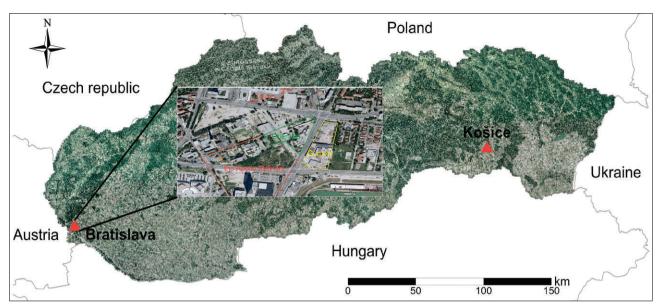


Fig. 1. Location of the surveyed area (source: Google Earth)

layers are covered by loamy, muddy clayey, sandy deposits in the investigated area. In the subject area, sand positions with a maximum thickness of 4.5 m were captured in the form of a lenses (Auxt et al., 2002). The topmost part is covered by anthropogenic fills reaching 4 to 5 m in thickness. Atop the gravel and sand sediments there can be observed remnants of bricks, cinder, reinforced-concrete fragments and others (Auxt, 2002). Closer characterization of the geological composition of the environment is given in Tab. 1, which describes the lithological composition in selected wells HG-2, HG-3, HG4 and HG-5 drilled within the geological survey in 2001 (Fig. 2; Janták & Polák, 2001).

The Neogene fine-grained sands to sandstones are poorly permeable. They create horizons characterized by a confined groundwater table level. The Quaternary sediments, represented by gravels and sandy gravel deposits, form a significant aquifer of groundwater. Together with the Neogene clastic sediments, in

which they pass smoothly at places, they form a significant water-bearing hydrogeological complex. On the basis of hydrodynamic tests, the coefficient of hydraulic conductivity in the area under investigation was set at  $4.31\cdot10^{-4}-7.6\cdot10^{-3}$  m<sup>-3</sup>.s<sup>-1</sup> (Kordík et al., 2015). The groundwater table level is affected by precipitation and the Danube River. Based on the groundwater table level measurements in 2002, it was found that the Danube level fluctuations affect the groundwater table level in the site under investigation within 72 hours (Auxt, 2002). Total dissolved solids (TDS) in groundwater in this area ranges from approximately 740 to 940 mg·l<sup>-1</sup> and is of Ca-Mg-HCO<sub>3</sub> chemical type (Hanzel et al., 2012).

# ${\bf 2.1. \, Sources \, of \, the \, pollution \, in \, the \, territory \, of \, interest}$

The area of interest is located in the former industrial complex, where the Apollo Refinery was operating until June 16, 1944.

	Gui	mon			Che	emika	
	HG-2		HG-4		HG-3		HG-5
Depth	Lithological composition	Depth	Lithological composition	Depth	Lithological composition	Depth	Lithological composition
0.0-3.1	fill	0.0-3.5	fill	0.0-2.7	fill	0.0-2.0	fill
3.1-5.9	gravel with fine soil admixture (admixture up to 10 %)	3.5-4.5	clayey sand	2.7-3.3	clayey sand	2.0-3.2	clayey sand
5.9-7.0	gravel with fine soil admixture (admixture up to 5-10 %)	4.5-4.8	sandy clay	3.3-5.5	fine-grained sand	3.2-4.2	fine-grained sand
7.0-10.6	sandy gravel 60:40	4.8-5.2	sandy gravel 60:40	5.5-7.0	sandy gravel	4.2-9.5	sandy gravel
10.6-11.0	sandy gravel 70:30	5.2-9.0	sandy gravel with sand admixture	7.0-9.2	gravel with sand admixture (5-8 %)	>9.50	gravel with sand admixture
		9.0-10.0	sandy gravel 60:40	9.2-11.5	sandy gravel 60:40		
		10.0-11.0	gravel with sand admixture (up to 10%)				

Tab. 1. Characteristic of lithological composition of hydrogeological wells a superior of the composition of the compositi

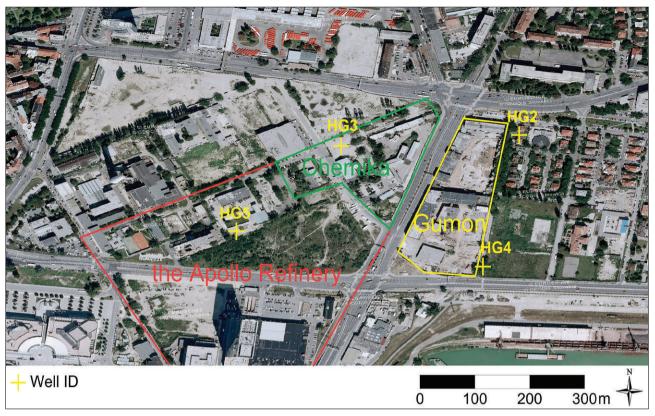


Fig. 2. Boreholes HG-2, HG-3, HG-4, HG-5 arrangement (modified according to Janták & Polák, 2001)

It was bombed by the US Army that day, causing the pollution from the Refinery to get into a relatively wide area. In addition to the Refinery in the industrial area, the factories Kablo, Gumon, Chemika, MG Tatragas, Západoslovenská energetika and Tepláreň also operated in the recent past. Each of the factories concentrated on a different type of production and industry. For this reason, groundwater and soil pollution is very diverse. From the site of the former Apollo Refinery, pollutants, especially oil substances, but also benzene, toluene, ethylbenzene, xylene (BTEX) and polycyclic aromatic hydrocarbons (PAHs), have extended.

In the register of environmental burdens, the load of Gumon is registered as B2 (006) / Bratislava-Ružinov-Gumon-plant site-SK/EZ/B2/122 and Chemika as B1 (003 / Bratislava-Staré Mesto-Chalupkova-Bottova ulica Street-plant grounds-SK/EZ/B1/116 (Kordík et al., 2015). Since 2015 under the auspices of the Ministry of the Environment of the Slovak Republic, the State Geological Institute of Dionýz Štúr (SGIDŠ) is responsible for the monitoring of both environmental burdens within the framework of the State Programme of the Environmental Burdens Remediation for the years 2010–2015 with continuation in the period 2016–2021.

The Gumon Chemical Plant was put into operation in 1911 with the original intention of supporting the production of the Subsidiary Cable Factory, Stock Company – KABLO. However, the plant gradually focused mainly on the production of electroinsulating materials, asbestos cement boards, counter plates, materials made of bakelite, asphalt, natural resin, artificial resin, stamping, gumoid, hardened paper and canvas, as well as on

bakelite production (Sabol, 2013). From Gumon, mainly polluting substances such as methanol, ethanol, epoxies, acetone, degreasers or cresols have spread to the rock environment. In the context of contaminants, these are non-polar extractable substances NES, BTEX and aliphatic chlorinated hydrocarbons (CAHs) (Auxt et al., 2002 & Kordík et al., 2015). At present, the plant site is abandoned, but in the future, there is planned investment in the area.

The Chemika Plant was a chemical factory that concentrated on paints and varnish production, and on the tapping of chemicals from railway tanks. Within the complex of the factory there was a warehouse with epoxy, polyester, glycerine and asphalt in the western part. All kinds of mineral acids, chlorinated hydrocarbons, as well as sodium hydroxide and water glass were also pumped in the Plant. In 1990, Chemika Bratislava teamed up with Messer Tatragas. The company focused on the production of various industrial gases (Kordík et al., 2015). Chlorinated aliphatic hydrocarbons (CAHs) were released from the factory. High oil substances content, such as gasoline, oil, diesel or kerosene, have also been observed within the site. However, this type of pollution originated from the Apollo Refinery (Auxt, 2002).

### 2.2. Level of survey

Several engineering geological and hydrogeological surveys have been carried out at this site since 1954 (Tab. 2). Indeed, in 1963, pollution was confirmed in 15 of the 26 wells (Otepka, 1963 in Auxt et al., 2002).

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Year	Implemented by	Site	Pollution
1971	IGHP	Presscentrum grounds	Oil substances presence at a depth of 3.5–10 m b.s.
1973	Vodné zdroje, Bratislava	Presscentrum grounds	Oil substances presence at a depth of 0.5–6.5 m b.s.
1974	IGHP	Presscentrum grounds	In 10 wells pollution of soils confirmed
1982	IGHP	Košická ulica Street	Groundwater pollution by OS in 4 wells
1995	Geotest, s r.o. Bratislava	Chemika grounds	Groundwater pollution confirmed: TTC, TTCE
1995	Hydropol, Bratislava	Kablo grounds	Confirmed pollution – soils: NES, PAHs – groundwater: NES, CAHs
1996	Hydropol, Bratislava	Chemika grounds	Groundwater pollution confirmed: CAHs, OSFP in the range of 0.3–12 cm, OS presence at a depth of 2.9–10 m b.s.
2000	Vlasko, Bratislava	Gumon grounds	Oil substances presence at a depth of 0.7–3.1 and 4.5–5.1 m b.s.

Tab. 2. Significant surveys at the study site

Note: IGHP – Inžinierskogeologický a hydrogeologický prieskum Žilina; used documents: Rajec, 1971; Drevenák, 1973; Sladký, 1974 in Auxt et al., 2002; Dolhá, 1982; Vizár, 1982; Dénesová, 1995; Polák, 1995 in Auxt et al., 2002; Polák, 1996; Vlasko, 2000 in Auxt et al., 2002

In 1997, GEOtest Bratislava, Ltd. carried out a survey; the purpose was to verify the contamination of the rock environment and groundwater in the area of Chemika. Pollution was found in these samples only in category B (500 mg·l<sup>-1</sup>) and in the case of non-polar extractable substances (688 mg·l<sup>-1</sup>) in category B-C in terms of the Guideline No. 1617/97 – min. Today, the categorization given by the above-mentioned Guideline is no longer in force. The Guideline No. 1617/97 - min defined indicators and norms for soil, groundwater and soil air contamination in category A, B, C according to the environmental impact risk. Category A defined the values of indicators close to natural content. When reaching Category B values, it was necessary to determine the source of the contamination. The exceedance of Category C demonstrated the risk of pollution migration and the resulting threat of environmental damage with the need of remediation of the contaminated environment.

In the framework of this survey, Company Geohyco, Inc. implemented 5 probes drillings which it took samples of groundwater. In one of the probes, high CAHs values exceeding category C were confirmed (50 mg·l<sup>-1</sup>) according to the Guideline No. 1617/97 – min. and the presence of oil substances (OS) at the surface. Elevated values were the result of leakage from a former warehouse of chlorinated hydrocarbons near which one of the wells was located. At the end of the survey, one hydrogeological borehole was designed to remove the pollution of CAHs and OS from groundwater (Brutenič, 1997). The Company Geohyco, Inc. Bratislava in the years 2000-2001, carried out surveys in connection with the construction of the Apollo Bridge. The purpose of the surveys was to find out the presence of the ecological load within the aquifer, the pollution of the soils with oil substances and to carry out the monitoring of the current state of the environmental burden. Over the course of two years, 33 wells were built, from which samples of soil and water were taken. The presence of oil substances in the depth range of 4 m - 9 m or 6 m - 11 m below the terrain was determined and confirmed at the same time. Increased values of aromatic and chlorinated hydrocarbons were not confirmed – they did not exceed category B (0.02 mg·l<sup>-1</sup>) given according to the then applicable the Guideline No. 1617/97 - min. The oil substances free phase (OSFP) with a thickness of 0.3 cm - 15 cm was confirmed

in five boreholes (Janták& Polák, 2001). In 2002 Company Envigeo Ltd. carried out a survey of the old environmental burden in the vicinity and the route of the Apollo Bridge. The sampling work was designed in eight profiles and the monitoring system consisted of fifteen monitoring objects. Surveys of soil, groundwater and ground air in the aeration zone and the saturation range were collected. All-in-all, 334 samples of groundwater and 528 soil samples were collected. The survey confirmed elevated values of NESs, PAHs, BTEXs, CAHs, boron and mercury in both soil and groundwater. The OSFP content was measured, too (Maloveský, 2002). Between 2004 and 2006, the remediation works were carried out in the vicinity of the former Apollo Refinery, which were implemented in connection with the construction of the Apollo Bridge. The remediation contractor was DETOX, Ltd., Banská Bystrica (Kordík et al., 2015). The main remediation process was the drainage of the oil phase from the groundwater table level. The works were planned in two stages; however only the first one was realized. It took place in an environment where the construction of the Apollo Bridge was interfered. In the first stage of the remediation works, 76 boreholes were drilled, of which 60 were pumping and 16 were infiltration objects. The thickness of the OSFPs was reduced from 46 cm to 0 cm – 14 cm. In some places (Chemika area) the OSFPs fell from 83 cm to 0 cm - 2 cm and in area of Gumon from 26 cm to 2 cm – 6 cm (Maloveský et al., 2006). At the site of Gumon, a geological survey was carried out in 2007 by Drill, Ltd., in which six boreholes were drilled to a depth of 19.1 m - 20 m. The contamination of the environment with oil substances was confirmed at a depth of 3 m - 13m (Holzer, 2007).

## 2.3. Inorganic and organic contaminants

In the area concerned, organic and inorganic substances, which have a negative impact on the environment, are still present in groundwater and in soils. They are accumulated in soils, but they can also be observed as substances dissolved in water or floating on the groundwater table due to less density than water. In Tab. 3 we briefly describe the properties of the observed inorganic and organic substances together with their impact on human health.

Tab. 3. Significant properties of monitored inorganic and organic substances

Se	Substance	Chemical formula	Occurrence	Properties	Impact
bstance	Chlorides	Cl <sup>-</sup>	Chemika	widely distributed as sodium, potassium and calcium salts	an increased dose in the human body causes an increase in blood pressure
Inorganic substances	Ammoniacal nitrogen	N-NH <sub>4</sub>	Chemika, Gumon	colourless gas, highly soluble in water; with increasing pH and temperature, toxicity increases	toxic to fish; causes methemoglobinemia
<u> </u>	Boron	В	Chemika	elemental B is not found in nature; adsorption depends on pH	toxicity low
	Benzene	C <sub>6</sub> H <sub>6</sub>	Gumon	well soluble in water; has no sorption properties; is subject to biodegradation only in an oxic environment	carcinogen, toxic; causes damage to the kidney, liver, central nervous system and bone marrow
	Naphthalene	C <sub>10</sub> H <sub>8</sub>	Chemika	subject to adsorption, biodegradation or evaporation	carcinogen; kidney damage, red blood cells - haemolytic anaemia
	Anthracene	C <sub>14</sub> H <sub>10</sub>	Chemika, Gumon	water insoluble; dissolves in some organic solvents, benzene, toluene or chloroform; strong sorption properties	damages the airways, skin
	Phenanthrene	C <sub>14</sub> H <sub>10</sub>	Chemika, Gumon	released in water first sorbs in the surrounding sediment, later on the process of biodegradation occurs	causes haemolysis, irritation of eye, nose, throat, and skin
	Chrysene	C <sub>18</sub> H <sub>12</sub>	Chemika	intensively adsorbs; subject to biodegradation	probable human carcinogen; irritates the skin and eyes
nces	Pyrene	C <sub>16</sub> H <sub>10</sub>	Chemika	not subject to biodegradation; persistent	toxic; damages the liver and kidneys
Organic substances	Benzo(a)pyrene	C <sub>20</sub> H <sub>12</sub>	Chemika, Gumon	insoluble in water, soluble in organic solvents; strong sorption properties	Carcinogen, respiratory tract disorder, digestive tract, red blood cell damage and immune system
Org	Benzo(b)fluoranthene	C <sub>20</sub> H <sub>12</sub>	Chemika	Sorption ability, biodegradability	probable human carcinogen; skin and eye irritation
	Benzo(g, h, i)perylene	C <sub>22</sub> H <sub>12</sub>	Chemika, Gumon	water insoluble, soluble in organic solutions; biodegradable, persistent	damages the lungs, irritates eyes and skin
	Indeno(1,2,3-c,d)pyrene	C <sub>22</sub> H <sub>12</sub>	Chemika, Gumon	water insoluble, soluble in organic solutions; sorption properties	probable human carcinogen
	Tetrachloroethene	C <sub>2</sub> Cl <sub>4</sub>	Chemika	well soluble in water; biodegrades in the anaerobic environment	carcinogenic; causes cirrhosis and necrosis of the liver, nephritis, eye damage but also abortion
	Cis-1,2- dichloroethene	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	Chemika	insoluble in water	toxic; attacks the central nervous system, endangers the liver and kidneys
	Vinyl chloride	C <sub>2</sub> H <sub>3</sub> CI	Gumon	not subject to hydrolysis, bioaccumulation in aquatic organisms, sediment adsorption; well soluble	carcinogenic; causes liver, lung, brain, leukaemia and lymphoma

Note: modified after: Fľaková et al., 2010; Howard, 1991 a,b; Irwin, 1997 a,b,c,d; Pitter, 1999; Sameľová et al., 2006; SEPA, 2018; Sigman et al., 1998; Sun et al., 2010; US EPA, 2018; Vengosh et al., 1998; WHO, 1996 a,b,c; WHO, 1998

# 3. METHODOLOGY

Within the framework of the geological task "Monitoring of Environmental Burdens on Selected Locations of the Slovak Republic" solved by SGIDŠ, monitoring of groundwater is carried out in the areas of former Chemika and Gumon plants. On average, twice a year measurements of general indicators are carried out at the sites (8/2015, 10/2015, 8/2015, 9–10/2016, 3/2017, 9/2017), of which samples of water are taken once a year for analytical processing in the Geoanalytical Laboratories of SGIDŠ. In the wider area of the former Apollo Refinery the SGIDŠ has carried out measurements on 32 wells, of which 17 were located in the area of Chemika and Gumon (Fig. 3).

As part of the fieldwork, the basic in-situ parameters of ground-water were measured at 11 wells. In the area of Chemika there were boreholes VN4-2, VN4-4, VN4-5, VN4-7, VR4-1 and in the territory of Gumon VN5-1, VN5-2, VN5-5, VN5-6, VN5-7, VR5-1. In the context of monitoring work, groundwater table level is being measured standardly along with electrolytic conductivity, pH, dissolved oxygen and oxygen saturation, water and air temperature, oil substances free phase (OSFP) and water sensory properties – odour, colour, turbidity. The groundwater table level was measured by Solinst TLC piezometer. Apparent electrolytic conductivity (EC), water temperature, dissolved oxygen, oxygen saturation and pH were measured by a WTW Company multimeter. In the OSFP specimens, the thickness

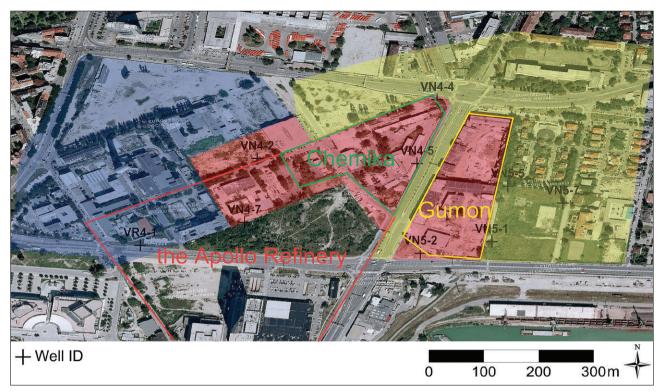


Fig. 3. Conceptual model for environmental burden (EB) Chemika, EB Gumon. Blue colour – reference area, red colour – source area, yellow colour – indication area (modified by Kordík et al., 2015)

of this phase was measured by a special device from Solinst (interfacemeter). Normally, groundwater is pumped dynamically – using the Gigant submersible pump, in justified cases (e.g. strong contamination) samples were taken by bailer.

Field measurements and sampling were carried out by SGIDŠ workers (2015 and 2017), and by staff of companies Aquifer, Ltd. and ENVIGEO, Inc. (2016). Laboratory work was carried out in Geoanalytical Laboratories (GAL) of the SGIDŠ in Spišská Nová Ves (2015 and 2017), INGEO-ENVILAB, Ltd. and ALS Czech Republic, Ltd. (2016).

For graphical data processing, the Surfer software of the Company Golden Software was used to create contour maps. A kriging method was applied. Via this software the spatial distribution of selected indicators in 2015 and 2016 is displayed. The same programme was also used in the creation of maps of hydro-isohypses. On-line Ortofotomap (2010) was used as the underlying map. The "contour map" module was used to create hydro-isohypses and distribution maps, in which a grid with specific data for individual maps (e.g. latitude and length of individual boreholes, concentration of substances in individual boreholes,...) was selected.

The results of the in-situ measurements and laboratory analyses were compared with the Directive of the Ministry of the Environment of the Slovak Republic of 28 January 2015 No. 1/2015-7 to develop a risk analysis of the contaminated area. The Directive of the Ministry of Environment of the Slovak Republic No. 1/2015-7 sets indication and intervention criteria for individual indicators. The Directive defines the Indication Criterion (ID) as the threshold value of the concentration of the pollutant determined for the soil, the rock environment and the groundwater, the exceeding

of which may endanger human health and the environment; this situation requires the monitoring of the contaminated area. The Directive the Intervention Criterion (IT) defines as the critical value of the concentration of the pollutant determined for the soil, the rock and the groundwater, the exceeding of which for the given use of the territory assumes a high probability of endangering human health and the environment; it is necessary to conduct a detailed geological survey of the environment with analysis of the risk of pollution.

### 4. RESULTS

# 4.1. Changes in groundwater table level and flow direction

Fig. 4 shows the direction of groundwater flow from the data obtained in August 2016. It is clear from the map that the water flows in the WSW-ENE direction. Based on the information from the previous works, it can be stated that the general direction of the groundwater flow does not change significantly in the area.

# 4.2. Inorganic pollution

Selected organic and inorganic substances are determined annually in the groundwater by laboratory testing. In 2015, chemical analyses were carried out in samples taken from wells VO4-1, VO4-2, VO4-3, VO4-4, VO5-1 and VO5-2 (June 11 and 12), wells VN4-2, VN4-4, VN4-5, VN4-7, VR4-1, VN5-1, VN5-2, VN5-5, VN5-6, VN5-7, VO4-5, and VR5-1 (August 13) and

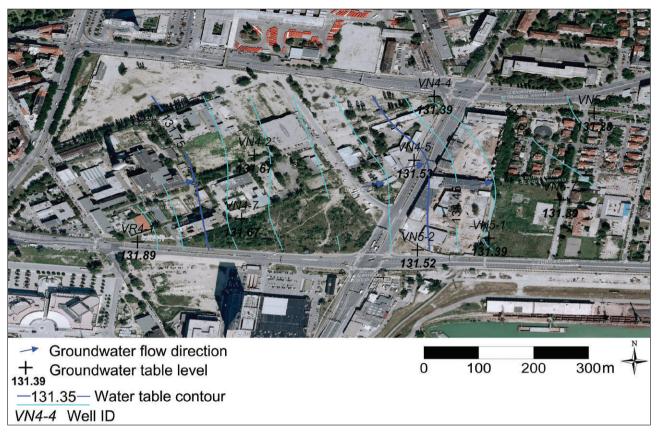


Fig. 4. Map of groundwater table levels in Gumon and Chemika grounds (measured on August 4, 2016)

well VO5-4 (September 8). In 2016, chemical analyses were carried out on samples of water taken from the boreholes VN4-2, VN4-4, VN4-5, VN4-7, VN5-1, VN5-2, VN5-5, VN5-6, VN5-7 and VR5-1 in the period of September 27 till October 1. In 2017, chemical analyses were carried out in March and October, in samples from wells VN4-2, VN4-4, VN4-7, VO4-1, VO4-2, VN5-1, VN5-6, VN5-7, VO4-6, VO5-2 and VO5-4. In addition to basic physico-chemical indicators and trace elements, organic substances – volatile aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and volatile aromatic hydrocarbons have also been set up in groundwater.

The most important indicators were selected to show the distributions of inorganic indicators in maps, charts and tables.

The basic inorganic physicochemical indicators significantly exceed the indication and intervention criteria set out in the Directive of the Ministry of Environment of the Slovak Republic No. 1/2015-7 of 28 January 2015 for ammonium ions and chlorides. In samples from the VN4-5 well, the ammonium ion intervention criterion was exceeded for both measurements – NH<sub>4</sub> $^+$ (2.4 mg·l $^-$ 1). It should be noted that some of the measured values are closer to the indication criterion (1.2 mg·l $^-$ 1) from the results of the October 2015 measurements. These are samples from the VN4-4 borehole with 0.98 mg·l $^-$ 1, from the VN5-6 borehole with 0.98 mg·l $^-$ 1 and from the VN5-7 borehole of 1.07 mg·l $^-$ 1. In 2017, the indication criterion was not exceeded in any sample of groundwater. Fig. 5 shows the NH<sub>4</sub> $^+$  values from the

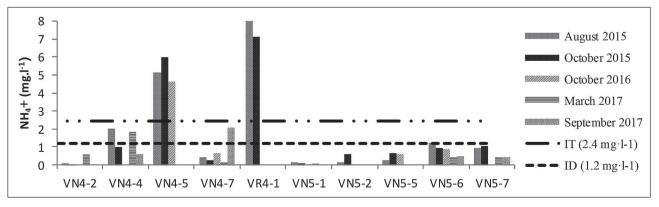


Fig. 5. Concentration of  $NH_4^+$  in groundwater in August and October 2015, October 2016 and March and September 2017. According to the Directive of the MoE SR no. 1/2015-7 of 28 January 2015 there are set for  $NH_4^+$  the indication criterion  $ID = 1.2 \text{ mg} \cdot I^{-1}$  and the intervention criterion  $IT = 2.4 \text{ mg} \cdot I^{-1}$ 

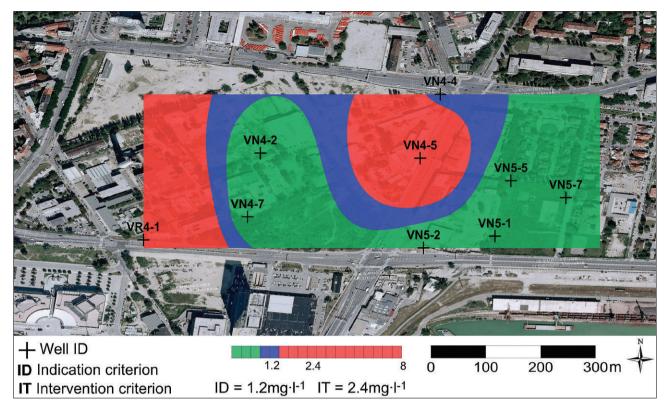


Fig. 6. Ammonium ion distribution in August 2015

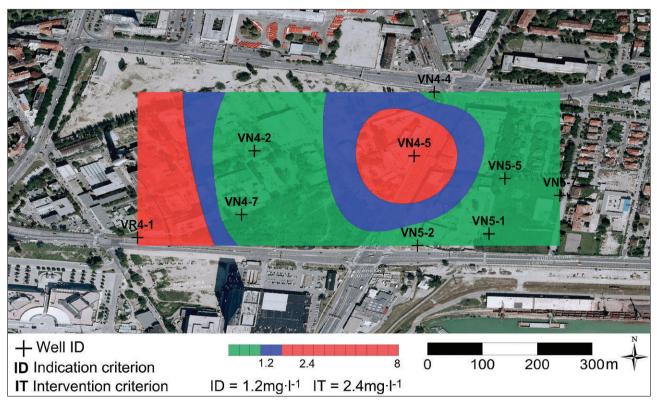


Fig. 7. Ammonium ion distribution in October 2015

August and October 2015, October 2016 and March and September 2017 measurements. The distribution maps are shown in Fig. 6 to 8.

In the case of **chloride**, the intervention criterion  $(250\,\mathrm{mg}\,\mathrm{l}^{-1})$  was exceeded three times. The indication criterion  $(150\,\mathrm{mg}\,\mathrm{l}^{-1})$  was exceeded five times. In the VN4-2 well  $(126\,\mathrm{mg}\,\mathrm{l}^{-1})$  October

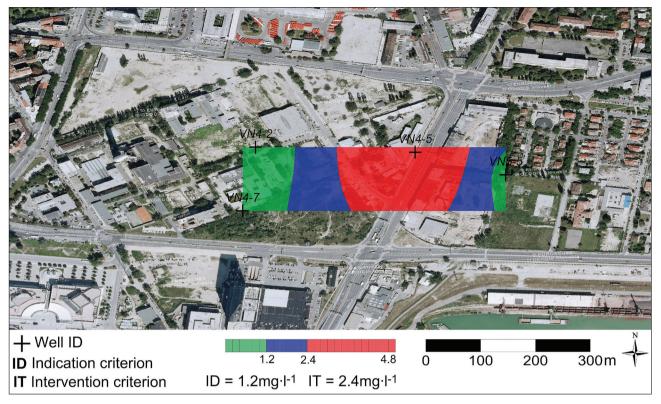


Fig. 8. Ammonium ion distribution in October 2016

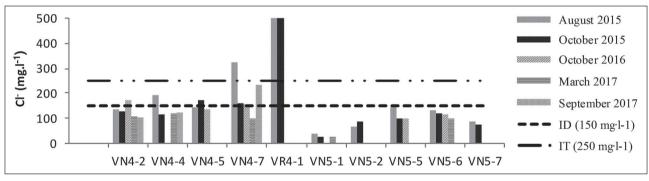


Fig. 9. Chloride concentration in groundwater in August and October 2015, in October 2016 and in March and September 2017. According to the Directive of the Ministry of Environment of the Slovak Republic no. 1/2015-7 of 28 January 2015 there are set for Cl<sup>-</sup> indication criterion ID = 150 mg·l<sup>-1</sup> and intervention criterion IT = 250 mg·l<sup>-1</sup>

2015), the measured reading approaches the indication criterion (150 mg·l $^{-1}$ ). In the wells in which the concentrations of chlorides in both years have been laboratory determined, the chloride contents are almost the same (Fig. 9). A larger decrease can be observed in VN4-7 borehole. In Figure 9, the graph shows the values of the measurements from August and October 2015, October 2016 and March and September 2017. According to the graphs interpretations of Cl $^{-1}$  and NH $_4^{+1}$  it is obvious, that elevated values Cl $^{-1}$  and NH $_4^{+1}$  are concentrated in wells VN4-4, VN4-5, VN4-7 and VR4-1, that means on the grounds of Chemika.

### 4.3. Organic Pollution

An important indicator of pollution in the area under investigation is the presence of oil substances free phase (OSFP). In Fig. 10

there are 10 marked boreholes where a film of oil substances (OS) was observed or OSFP was measured in August 2016. In Tab. 4, the levels of groundwater (GWTL) measured in summer and autumn in 2015 and 2016, and the OSFP thickness or the presence of OS in the boreholes, are shown.

The OSFP thickness depends on the groundwater table level. From the observations in 2015, 2016 and 2017, it can be perceived that the thickness of the OSFP will increase with the decrease of the groundwater table level and vice versa. This rule was violated in VN5-2, where a groundwater table level of 131.03 m asl was measured in August 2015 with a thickness of the OSFP of 13 cm and in October 2015 at 130.98 m asl with the OSFP thickness of 11 cm. This means that when the groundwater table level drops, the thickness of the OSFP also drops. In fact, the thickness of mobile free phase decreases because a part of free

**Tab. 4.** Groundwater levels and free phase of oil substances thickness measured during the measurements in 2015, 2016 and 2017

1100		5	2M IL	OSFP	GWTL	OSFP	GWTL	OSFP	GWTL	OSFP	GWTL	OSFP	GWTL	OSFP
Neil 1	<b>August 2015</b> (m asl)	<b>August 2015</b> (cm)	October 2015 (m asl)	October 2015 (cm)	<b>August 2016</b> (m asl)	August 2016 (cm)	<b>October 2016</b> (m asl)	<b>October 2016</b> (cm)	<b>March 2017</b> (m asl)	<b>March 2017</b> (cm)	<b>June 2017</b> (m asl)	<b>June 2017</b> (cm)	September 2017 (m asl)	September 2017 (cm)
VN4-2	131.11	Film OS	131.17	Film OS	131.67		131.20	Spills OS	130.41		130.2	,	130.2	,
VN4-4	130.94	Film OS	130.88	Turbidity	131.39	Film OS	130.98	Film OS	130.83		131.04		130.7	
VN4-5	131.03	6	130.99	11	131.53	6.28	131.07	6	131.69	6.51	131.47	6.71	131.43	6.76
VN4-7	130.65	Turbidity	130.75	Film OS	131.67	Film OS	131.19	Film OS	131.21	Film OS	130.99	Film OS	130.95	Film OS
VR4-1	131.25		131.30	Film OS	131.89	Film OS	,		,		131.18	,	131.15	,
VN5-1	130.90		130.88	Film OS	131.39		130.92		131		130.78	Odour	130.7	
VN5-2	131.03	13	130.98	11	131.52	7.9	132.05	2	131.16	8.2	130.86	8.42	131.06	
VN5-5	130.99	,	131.00	Film OS	131.48	,	131.01	1	131.05	6.13	130.84	6.31	130.8	8.3
VN5-6	130.85	,	130.81	Film OS	131.28	Film OS	130.86	0.1	130.8	Film OS	130.66	Film OS	130.69	6:39
VN5-7	130.90	,	130.90	Film OS	131.39	Weak film OS	130.94	0.1	130.99	Film OS	129.79	Film OS	130.86	Film OS
VR5-1	130.96			,	131.46	ı	129.75		131.05		129.86		130.77	Film OS

phase remains as residual disconnected blobs in porous media. In August 2016, the groundwater table level at 131.52 m asl was measured in the VN5-2 borehole and the OSFP thickness was 7.9 cm. The groundwater table level was measured at 132.05 m asl in October 2016 with the OSFP thickness of 2 cm. The validity of the rule was subsequently confirmed in VN5-2 drilling in measurements of 2016. In other specimens, a film of oil was observed on GWTL.

The most significant indicators of  $COD_{Mn}$ , anthracene and phenanthrene, chrysene, and BTEX concentrations in two depth levels in a selected well in 2015, 2016 and 2017 were chosen to show the distribution of organic indicators in maps, charts and tables. The limit value of the intervention criterion IT  $COD_{Mn}$  (10 mg·l<sup>-1</sup>) was exceeded in samples from six wells. In one case, the ID (5 mg·l<sup>-1</sup>) was exceeded. It is clear from the graph (Fig. 11) that the concentrations do not change rapidly in the wells.

The concentrations of anthracene and phenanthrene in August and October 2015 and October 2016 are shown in Fig. 12. The anthracene values exceeding the IT (10 μg·l<sup>-1</sup>) were recorded only in August 2015 in two wells. The marked drop in anthracene concentration in VN4-5 and VN5-2 in October 2015 is attributed to a different groundwater sampling method. Exceeded IT (10 μg·l<sup>-1</sup>) of the phenanthrene could be observed in VN5-1 and VN4-5 in August 2015 and in VR4-1 in October 2015. In VN4-5 borehole in the other two measurements the ID was exceeded (5  $\mu$ g·l<sup>-1</sup>). The cause of a significant decrease in phenanthrene concentration in the borehole is attributed to a different method of sampling and determination of phenanthrene in groundwater samples. The exceeded values of the IT and ID of the mentioned indicators within the meaning of the MoE Directive no. 2015/7-1 are concentrated in VN4-5 and VN5-2, in which the OSFP thickness was measured, too. In 2017, the anthracene and phenanthrene values did not exceed the indication criterion  $(5 \,\mu\text{g} \cdot \text{l}^{-1})$  and most of the values were below the detection limit.

The chrysene concentrations in the selected wells in August and October 2015 and October 2016 are shown in the graph in Fig. 13. Significantly exceeded IT (0.2  $\mu g \cdot l^{-1}$ ) was measured in August 2015 in six wells and ID in one well. IT was exceeded in October 2015 only in three wells. In 2016 IT was exceeded in one hole. In March and September 2017, the ID was not exceeded in any of the measurements. Most of the values were below the detection limit.

In VN4-5 well, samples of water from two depth levels (VN4-4a below GTWL and at the bottom of the drilling VN4-4b) were taken on September 27, 2016, and BTEX concentrations were determined for the aforementioned depth levels. The depth of the borehole was 19.44 m (originally 20.0 m). In Fig. 14 is a graph showing the concentrations of individual BTEX markers (benzene, toluene, ethylbenzene, meta-& para xylene, ortho-xylene and BTEX sum). Due to the lower density of BTEX, the substances are concentrated at the GWTL, respectively, just below the GWTL and, moreover, they have volatile properties, causing higher concentrations of substances below the GWTL than at the well's bottom. Based on the chart, it can be stated that with drops in depth the concentrations of

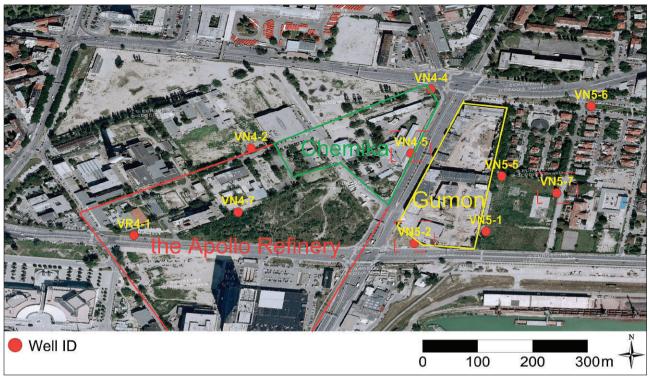


Fig. 10. Situation of boreholes on which measurements were carried out on August 4, 2016

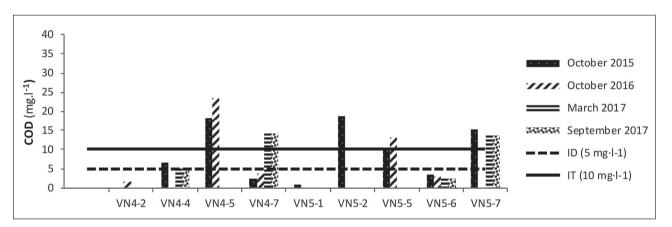


Fig. 11. Values of COD<sub>Mn</sub> in groundwater in October 2015, October 2016 and March and September 2017. According to the Directive of the Ministry of Environment of the Slovak Republic no. 1/2015–7 of 28 January 2015 there are set for COD<sub>Mn</sub> ID = 5 mg·l<sup>-1</sup> and IT = 10 mg·l<sup>-1</sup>

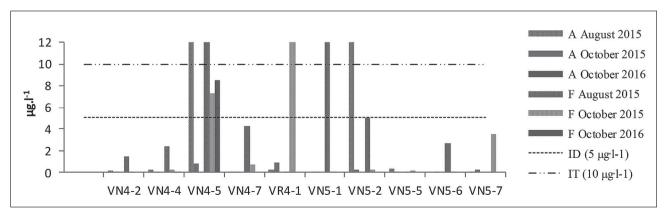


Fig. 12. Concentration of anthracene (A) and phenanthrene (F) in groundwater in August and October 2015 and October 2016. According to the Directive of the MoE SR no. 1/2015–7 of 28 January 2015 there are set for anthracene and phenanthrene ID = 5 µg·l¹ and IT = 10 µg·l¹

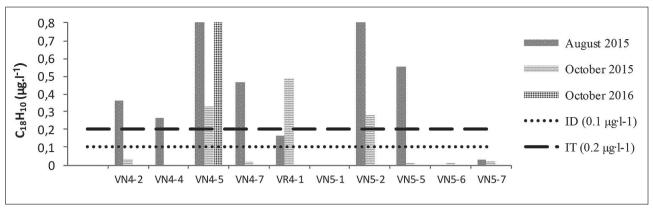


Fig. 13. Chrysene Concentration in Groundwater in August and October 2015 and October 2016. According to the Directive of the Ministry of Environment of the Slovak Republic No. 1/2015-7 of 28 January 2015 there are set for chrysene ID =  $0.1 \, \mu g \cdot l^{-1}$  and IT =  $0.2 \, \mu g \cdot l^{-1}$ 

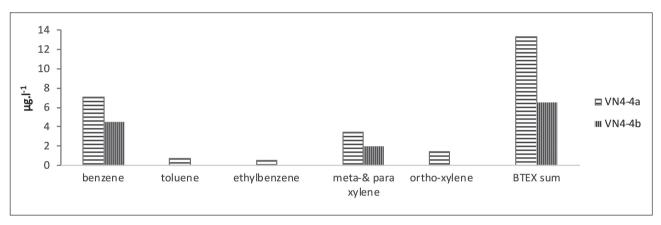


Fig. 14. BTEX concentration in VN4-4 borehole at two depth levels (VN4-4a – below groundwater table level, VN4-4b – at the toe of the well)

individual indicators decrease. In neither of the indicators the ID is exceeded (benzene –  $15 \, \mu g \cdot l^{-1}$ , toluene –  $350 \, \mu g \cdot l^{-1}$ , ethylbenzene –  $150 \, \mu g \cdot l^{-1}$ , xylene –  $250 \, \mu g \cdot l^{-1}$ ).

### 5. DISCUSSION

The territory of interest served in the past as an industrial area of Bratislava, where a number of chemical plants, including the Apollo Refinery, Chemika and Gumon, were concentrated. Due to the large anthropogenic burden within the area, the pollution found in the soils and groundwater in this area is varied and represented mainly by the OSFP, NES and PAH. In 1944, the Apollo Refinery was bombed by the US Army. Oil pollution originating from the Refinery has the largest share in the pollution of the area, mainly represented by the OSFP. The first data from geological and hydrogeological surveys date back to 1954, when pollution at Čulenova Street was not confirmed yet (Energoprojekt, Praha 1954; Auxt et al., 2002). In 1963 the survey in the Tepláreň territory confirmed the pollution (Otepka, 1963; Auxt et al., 2002). In terms of pollution, at the end of the 20th century the attention has begun to focus more with the onset of massive investment construction in the wider area of the territory of interest, and especially in connection with the construction of the Apollo Bridge. A number of surveys have been carried out

to identify contaminants and monitor ecological burdens. On the basis of the surveys, the pollution of OS was concentrated in the depth of 4 m – 11 m in 2001 (Janták & Polák, 2001). In 2002, a survey was conducted to map the groundwater, soil and ground air pollution, where samples of soil from 112 wells and groundwater from 116 wells were taken (Maloveský, 2002). The maximum NES and BTEX concentrations set in these surveys were in the groundwater at a depth of  $5.0 \,\mathrm{m} - 9.0 \,\mathrm{m}$ . The highest observed NES concentrations (> 1000 mg·l<sup>-1</sup>) were measured in the Chemika area and in the southern part of the Gumon area. The NES plume with lower concentrations ( $10 \text{ mg} \cdot l^{-1} - 1{,}000$ mg·l<sup>-1</sup>) ranged from the west side of Čulenova Street, from the south to the harbour, from the east till the Votrubova Street and from the north to Mlynské nivy, which continuously passes along the crossroads to the Prievozská Street. Spatial pollution by the BTEX was smaller than by the NES. The highest concentrations of the BTEX were concentrated in the southern part of the Chemika area (20,705 mg·l<sup>-1</sup>) and in the central part of the Gumon grounds (7,415 mg·l<sup>-1</sup>). The plume extended from the west side to the Chalupkova Street, from the south to the Landererova Street, from the eastern part to the Plátenická Street, and from the northern side it did not cross the borders of the Chemika and Gumon grounds (Maloveský, 2002). In the period 2004 - 2006 a two-stage remediation was designed in the territory. However, only one of the stages was performed. Nevertheless,

the remediation work has significantly reduced the contaminants presence in soil and groundwater.

Since 2015, the SGIDŠ staff has carried out monitoring work in the area concerned. The results of the monitoring of 2015, 2016 and 2017 show the presence of oil pollution in soil and groundwater. This fact is reflected in the laboratory results, which show that ID and IT have been exceeded for inorganic indicators of NH<sub>4</sub><sup>+</sup>, Cl and EC and organic indicators for TOC and NES in 2015 (for 2016 no data are available),  $COD_{Mp}$ , surfactants, PAH, TTCE, chlorethene and benzene. The highest concentrations of inorganic and organic indicators are concentrated in VN4-5, VN5-2 and VN5-7 wells, where the OSFP was measured in 2015, 2016, and 2017. The OSFP does appear in VN5-7 drilling in October 2016. This phenomenon may be a sign that oil pollution is still spreading in the direction of groundwater flow. At the same time, it can be a warning signal of the spread of environmental pollution. In the vicinity of the monitored area the Danube River flows, which significantly affects the GWTL elevation at the site. On the basis of the map of hydro-isohypses it can be stated that the general direction of the flow is WSW-ENE. The survey has confirmed the rule that the thickness of the OSFP decreases when the GWTL increases, and vice versa. The exception was observed in drill VN5-2 in 2015, when with the drop in the GWTL also the thickness of the OSFP decreased. The GWTL is an important factor in the spread of pollution, in this case the OSFP, both in the soil horizon and groundwater. Inorganic and, above all, organic pollution is present at the site in question. The inorganic indicators within the monitoring period implemented by the SGIDS staff in 2015, 2016 and 2017 significantly exceed IT of NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup> and EC. In the well VR4-1 high concentrations of Cl dominate, which affect the elevated EC value (460 mS·m<sup>-1</sup> and 520 mS·m<sup>-1</sup>). In terms of the organic indicators, the ID and IT are exceeded mainly in the TOC and NES contents in 2015 (no data available for 2016),  $COD_{Mn}$ , surfactants, PAHs, TTCE, chlorethene and benzene. From the detailed description of the individual indicators selected on the basis of the ID or IT exceedance (Directive No. 1/2015-7 of the Ministry of the Environment of the Slovak Republic), it can be seen that most of the substances are carcinogenic and dangerous for living organisms. Water in the area of interest does not meet the drinking water standards. On the basis of a thorough analysis of the data from laboratory measurements, it is clear that the highest concentrations of inorganic and organic indicators are concentrated in VN4-5 and VN5-2 wells, where the OSFP was found in 2015 and 2016. The presence of the OSFP in the above mentioned wells is conditioned by the geological setting in the area of the wells, or by presence of lenses. In VN5-7, the OSFP was observed in 2016 and was again measured in 2017. Overdriven IDs and ITs of several indicators were also registered in the VR4-1 borehole in 2015. The borehole is currently no longer functioning.

### 6. CONCLUSIONS

After the bombing of the Apollo Refinery in 1944, oil pollution began to spread through the environment, which was

intensified by the leakage of chemicals from nearby Chemika and Gumon factories. Nowadays, the premises of these factories are environmental burdens. Since 2015, the burdens have been monitored twice a year by the SGIDŠ staff. The paper is dedicated to evaluating the results of monitoring measurements. The monitoring work confirmed the presence of the OSFP in three boreholes. In other wells, the water was coloured or had a specific odour. Laboratory analyses show the presence of organic pollutants, in particular.

The failing in realization of the second stage of remediation works in 2004 - 2006 is the reason for the ongoing presence of contaminants in soil and groundwater. The predicted way of pollution spreading is through two transport media - the rock environment and groundwater. The spread of the pollutants in the rock environment is also induced by precipitation, which penetrate the soil and the pollution kept on the soil migrates through the soil cover or directly into the groundwater. In the groundwater, the pollution is concentrated within the aquifer, that is, in the Quaternary fluvial sediments of the Danube River, in which it migrates in the direction of the groundwater flow, depending on the Danube River. Based on the results, it can be argued that the pollution has spread to areas previously remediated due to precipitation and groundwater flow. At present, the construction of polyfunctional buildings is being realized on the territory. From the moral point of view, it can be assumed that the pollution poses a certain risk to the inhabitants living in this zone, and from the construction point of view it is a risk for the foundation construction of individual buildings. Directive of the Ministry of the Environment No. 1/2015-7, which replaces the Guideline No. 1/2012-7, obliges the builder to carry out an Environmental Health Risk Assessment on a site considered a environmental burden and subsequently to take corrective measures to eliminate pollution, its risks and adverse effects. The fact that the builder fulfils his obligation to remediate the area in question affects the environment positively. Although contamination in the construction site is remediated, the pollution in the immediate vicinity of the site remains unaffected. Due to groundwater flow and groundwater oscillation, residual pollution continues to concentrate and spread in the environment, thereby reducing the resulting cleaning effect of the building site. This fact requires a complex solution for similar situations.

Concrete resistance against aggressiveness and choice of individual types of foundation structures must be selected in accordance with the presence of contamination, which could have an adverse effect on these structures. This construction could in the future complicate or make completely impossible any remediation. In the future, it would be advisable to continue to monitor the area and remediate the area, consequently.

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