Light non-aqueous phase liquids distribution and weathering in former railyard; SE Danube Basin, Slovakia

Juraj Macek[1,2] & Ján Milička[2]

[1] Centrum environmentálnych služieb, s. r. o., Kutlíkova 17, 852 50 Bratislava, e-mail: macek@cenvis.sk
[2] Univerzita Komenského v Bratislave, Prírodovedecká fakulta, Katedra geochémie, Ilkovičova 6, 842 15 Bratislava

AGEOS

Abstract: Petroleum hydrocarbons are one of the most common contaminants. Paper presents current theoretical approaches in identification and evaluation of sites with LNAPL (Light Non-Aquaeous Phase Liquids). To compare them with field results outputs from the ongoing remediation in a former railyard are utilized. New information from drilling and sampling is evaluated, with focus on the spatial distribution and migration of total petroleum hydrocarbons in soil and groundwater. Samples of LNAPL (diesel) were collected and analyzed by gas chromatography - mass spectrometry, to obtain more information about the quality, degree of weathering and the approximate age of the spill. It's a common problem to distinguish between old and new contamination, and the observation of weathering rate can help to evaluate all possible contamination sources. Weathering degree of analyzed diesel samples ranged from almost none (even light n-alkanes abundant) to complete removal of all n-alkanes, though the railyard is more than 10 years out of operation. Based on the results, new LNAPL sources were identified, possible migration pathways were discussed and the age of LNAPL in different parts if the railyard was estimated.

Key words: SE Danube Basin, Quaternary, LNAPL, Diesel fuel, Contamination, Weathering, Distribution

1. INTRODUCTION

Petroleum hydrocarbons are one of the most common environmental pollutants. They can be released to the subsurface (vadose and saturated zone) through spills, leaking pipelines and storage tanks. Light non-aqueous phase liquids (LNAPLs) are hydrophobic liquid organic chemicals that are immiscible with water and are less dense than water. They co-exist with water in the pore spaces in the aquifer. Most common LNAPLs are gasoline, diesel, heating and motor oils. Petroleum fuels are complex mixtures and in the subsurface environment undergo compositional changes over time due to volatilization, dissolution, and biodegradation (Kaplan et al. 1996; Lundegard & Johnson 2006). LNAPLs subsurface transport is complex, being a multi-phase (LNAPL-water-air) flow problem, but nevertheless is often characterized by an accumulation of buoyant hydrophobic LNAPL in the vicinity of the water table interface that is potentially able to migrate laterally or redistribute vertically due to natural or human-induced water table fluctuations (CL:AIRE, 2014). Released liquids migrate downward through vadose zone, which pore spaces are filled with air and small amounts of water. Bottom part (capillary fringe) is partially saturated with water pulled upward by capillary forces from the underlying saturated zone. Water pressure in the saturated zone is greater than atmospheric pressure, and water generally fills the pore space. By migrating downward, LNAPL displaces air in pore spaces, but generally not water. In case of release of small LNAPL volume, it can stay trapped in the vadose zone, while in case of a greater leak it may migrate to the water table.

Historically environmental geologists, dealing with old burdens, relied on a model, that assumed LNAPL is floating on the top of the water table like a pancake, and displace almost all of the water and the air in the pore space of the aquifer. The extent of contamination was assumed from the presence and thickness of free product in monitoring wells. The result was a high saturation of LNAPL on the water table, and overestimation of the overall LNAPL volume in the subsurface. Farr et al. (1990) and Lenhard & Parker (1990) provided a paradigm shift in the understanding of LNAPL distribution within the subsurface. They considered capillary pressures of various liquid phases and developed functions that related fluid contents of the porous media to capillary pressures. Extending these concepts, the LNAPL saturation profile at the water table interface of an unconfined homogeneous isotropic aquifer is predicted to assume a shark fin like shape under equilibrium conditions when capillary pressures considerations are invoked (Tomlinson et al., 2017).

2. SITE HISTORY

From the view of present research is the discovery of free phase product in well a valuable information, but the issue of identification and evaluation of LNAPL volume is more complex a one must incorporate several important factors. This paper presents current trends of evaluation of LNAPL presence in subsurface, as well as factors influencing its migration and distribution. Starting in 2018, remediation activities are running in former railyard in Štúrovo, on behalf of the Ministry of Environment of the Slovak Republic. Railyard belongs to areas, contaminated with LNAPLs, especially diesel and motor oil, and is listed in the Registry of Environmental Burdens as "NZ (029) / ŠTÚROVO – RUŠŇOVÉ DEPO, CARGO A.S. SK/EZ/NZ/601". It was operated from about 1950 until 2008, with free phase first appearing in monitoring objects in 1987 (Polák, 1987). From 1950 to 1970 the railyard consisted of a roundhouse (orange area on Figure 1), with adjacent shunting yard (purple area on Figure

Manuscript received 2020-10-19
Revised version accepted 2021-01-20

1). Around 1970 the new depot building was constructed, along with three 100 m^3 diesel underground storage tanks (UST, green area on Figure 1). Main railyard features are depicted on Figure 1. First monitoring objects were situated in the area in 1987 (5 wells), followed by 13 wells in 1988 (Solymosiová et al., 1988). Three of them contained free phase of LNAPL. In 2008 a complex geological survey in more than 40 railyards was realized by Vrana, including Štúrovo. One of the three new build wells also contained free phase of LNAPL. Heavy soil contamination was discovered, analyzed samples contained up to 51 320 mg.kg^{-1} of non-polar organic compounds (NPOC), determined by infrared spectrophotometry (NPOC-IR) or 118 400 mg.kg^{-1} determined by ultraviolet spectrophotometry (NPOC-UV). In older surveys, the extent of contamination was usually assessed by the content of non-polar organic compounds, determined by infrared or ultraviolet spectrophotometry. Due to the high contamination a remediation plan was prepared by Auxt et al., (2010). The area was monitored from 2012 to 2017, with usually 12 wells sampled twice a year; results for selected wells are in Table 1 (Kostolanský et al., 2017). Wells with LNAPL present were not sampled, values above regulatory criteria are in bold. In three wells free phase of LNAPL was observed through 2012 – 2017 (yellow marked wells on Figure 1), with thickness up to 130 cm (well StV-3). These are located around UST. It was assumed that the leaking tanks are the source of contamination. Samples of groundwater were collected from wells without free phase (red marked wells on Figure 1). Only one of those wells repeatedly showed concentrations higher than regulatory limit (1,0 mg.l^{-1} NPOC-IR or NPOC-UV according to Direction of Ministry of Environment of the Slovak Republic n. 1-2015/7).

2.1. General geological characteristic of the south-east part of Danube Basin

The fluvial gravel-sandy accumulations of the middle terraces are in some sections covered by a variable layer of loess and

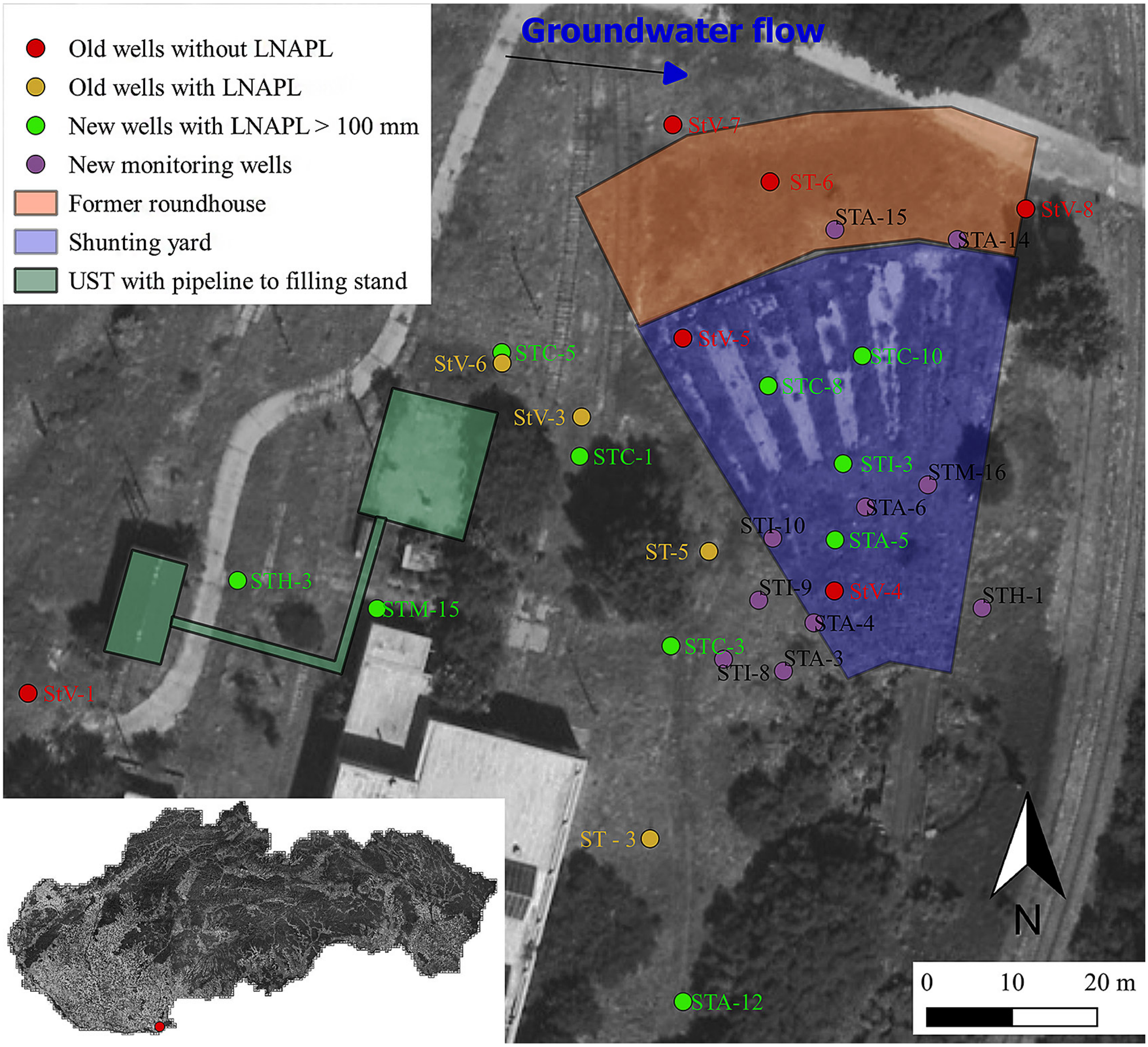

Figure 1: Sketch map of the former railyard in Štúrovo well position overview

Table 1: Results of site monitoring in 2012 – 2017 (according to Kostolanský et al., 2017)

Well	Year	Day	GWL (m)	LNAPL (mm)	NPOC-IR (mg/l)	NPOC-UV (mg/l)	Well	Year	Day	GWL (m)	LNAPL (mm)	NPOC-IR (mg/l)	NPOC-UV (mg/l)
StV-3	2012	21.3.	8.43	1300	-	-	StV-4	2012	21.3.	8.36	0	0.06	0.08
		18.9.	8.81	501	-	-			18.9.	8.73	0	0.04	0.18
	2013	26.3.	8.6	880	-	-		2013	26.3.	8.51	0	0.03	0.1
		30.9.	8.6	600	-	-			30.9.	8.73	0	0.03	0.08
	2014	11.3.	8.73	940	-	-		2014	11.3.	8.64	0	0.03	0.15
	2015	24.8.	8.78	770	-	-		2015	24.8.	8.63	0	<0.05	<0.1
	2016	15.1.	8.64	800	-	-		2016	15.1.	8.52	0	0.05	<0.1
	2017	17.4.	8.5	840	-	-		2017	17.4.	8.38	0	<0.05	0.47
StV-5	2012	21.3.	8.46	0	0.07	0.17	StV-6	2012	21.3.	9.12	10	-	-
		18.9.	8.78	0	0.05	0.22			18.9.	9.35	20	-	-
	2013	26.3.	8.56	0	0.03	0.12		2013	26.3.	9.24	10	-	-
		30.9.	8.78	0	0.06	0.23			30.9.	9.26	5	-	-
	2014	11.3.	8.7	0	0.03	0.14		2014	11.3.	9.37	5	-	-
	2015	24.8.		not sampled				2015	24.8.	9,35	1	-	-
	2016	15.1.	8.66	0	0.48	<0.1		2016	15.1.	9.24	2	-	-
	2017	17.4.	8.43	0	<0.05	0.61		2017	17.4.	9.09	10	-	-
StV-7	2012	21.3.	9.25	0	0.06	0.16	StV-8	2012	21.3.	8.44	0	0.22	**2.48**
		18.9.	9.61	0	0.04	0.19			18.9.	8.78	0	0.12	**1.28**
	2013	26.3.	9.39	0	0.04	0.12		2013	26.3.	8.55	0	0.1	0.45
		30.9.	9.61	0	0.02	0.14			30.9.	8.78	0	0.11	0.38
	2014	11.3.	9.54	0	0.04	0.14		2014	11.3.	8.7	0	0.05	0.29
	2015	24.8.	9.5	0	0.05	<0.1		2015	24.8.	8.67	0	0.43	0.38
	2016	15.1.	9.4	0	0.16	<0.1		2016	15.1.	8.58	0	0.11	<0.1
	2017	17.4.	9.26	0	<0.05	0.19		2017	17.4.	8.41	0	<0.05	**2.17**
ST-5	2012	21.3.	8.26	670	-	-	ST-6	2012	21.3.	7.92	0	0.06	0.36
		18.9.	8.58	520	-	-			18.9.	8.25	0	0.16	**1.29**
	2013	26.3.	8.35	880	-	-		2013	26.3.	8.19	0	0.06	0.51
		30.9.	8.36	600	-	-			30.9.	8.29	0	0.03	0.3
	2014	11.3.	8.48	830	-	-		2014	11.3.	8.29	0	0.04	0.19
	2015	24.8.	8.5	810	-	-		2015	24.8.	8.2	**1**	-	-
	2016	15.1.	8.38	880	-	-		2016	15.1.	8.13	0	0.07	<0.1
	2017	17.4.	8.28	560	-	-		2017	17.4.	8.9	0	<0.05	0.52

calcareous runoff from loess, loess clays, and various slope clays to loamy-sandy- and loamy-stony slope sediments and debris. Towards the surface of the fluvial sediments of the middle terraces the individual fractions are more fine-grained. Small sandy pebbles (ø 1–2 cm) and a sandy fraction are increasing and reach up to 50 % of the total mass of the middle terraces of lowland basin flows in southern Slovakia. In the hanging are usually sands covered by a thin deluvial flushes. These are undifferentiated clays or redeposited loess. In other places, the surface of the terraces is built by larger clayey sands and above them is silty- to fine grained- calcareous loam - swamp loess, loess clay and typical loess. Loess, loess clay and the slope sediments covering these gravel accumulations flatten the original forms of terraces, so in some places it is difficult to determine the exact boundary between the individual stages, or their termination up the slope. In the lowland flows, there is a variety, where in the hanging of the covered sandy-gravel fluvial sediments of the middle terraces, light yellow-, clayey-silty- to slightly sandy calcareous clays of typical loess are present. In other flows, the terraces are covered with sandy non-calcareous yellow-brown to rusty-brown loams, often with layers or lenses of sands, loess clays, or even loamy-stony slope debris (Pristaš et al., 1992).

2.2. Geological characteristic of the investigated site

The surface in the area of the rail yard is formed mainly by consolidated areas that form the accumulations under the railroad lines and access roads for motor vehicles. Directly below the thin layer of soil cover is a rough macadam directly in the railroad lines and accumulations of building waste in their vicinity.

Directly below ground level, in most areas there is a layer of anthropogenic material, up to 2.2 m thick. It consists of building rubble, macadam, gravel and loam of various mutual proportions. Below the weights are the original soils of the Quaternary fluvial and aeolian complex with exception of some wells. In these wells is a layer of light brown loess under the top soil cover. This position is present in the entire area of interest, reaching a thickness of up to 4.7 m. Below the position of the loess there is a layer of silts that reaches a thickness of up to 6.3 m. Silts are mostly light brown to brown and slightly plastic. They represent the dominant lithological type on the site.

The complex of sandy gravels occurs at the site at a depth of 8.3 – 12.2 m, while the largest layer thickness was identified as 3.8 m. In the NW part of the site, the layer of sandy gravels does not occur at all and the collector is a layer of sand. The complex is represented by well-grained gravel (up to ø 1–3 cm, occasionally up to ø 5–10 cm), mostly of brown or gray color.

Groundwater at the site of interest is bound to the location of sandy gravels of fluvial origin and is supplemented by infiltrated rainwater. The height of the water column is very variable and depends not only on the infiltrated amount of precipitation, but also on the configuration of the basement, hanging layers and the overall natural conditions at the site. In the eastern part of the terrace, the effect of precipitation is strongly dampened. This part is characterized by more permeable aquifer and less permeable loess in the top. The Danube and Hron rivers drain the area of interest.

The aquifer in the area of interest is formed by Quaternary sediments, sandy gravels and sands. This type of aquifer is characterized by intergranular permeability and free groundwater level. In Štúrovo is the aquifer confined under the layer of silts. During the realization of the geological works, the groundwater level ranged from 109.97 to 110.4 m above sea level (Urban et al., 2019). The predominant direction of groundwater flow was the W-E direction in both monitored periods.

2.3. Major features of contamination and weathering

Petroleum diesel is produced from the fractional distillation of crude oil between 160 °C and 350 °C at atmospheric pressure, resulting in a mixture of carbon chains from C_9 to C_{22} (depending on the origin of oil). It contains aromatics (benzene, toluene, o,m,p-xylenes, naphthalenes, phenanthrenes), n-alkanes, iso-alkanes (such pristane, phytane or norpristane), cyclo-alkanes and poly-aromatics plus sulfur containing compounds such as dibenzothiophenes (Kramer & Hayes, 1987). The usual aliphatic/aromatic fraction ratio is 75 % to 25 %. According to Lang et al. (2009), weathered diesel can also contain polar (nitrogen, sulfur, oxygen - NSO) fraction up to 4 %. Polar compounds are not hydrocarbons due to the incorporation of nitrogen, sulfur, and oxygen atoms in the structure of the organic molecules (e.g. Tissot & Welte, 1984), but can be extracted from samples while analyzing total petroleum hydrocarbon (TPH) concentrations and influence the results.

Once released to the environment, diesel fuel is subject to physical, chemical, and biological processes that further change their composition, toxicity, availability, and distribution. Petroleum degradation (or weathering) is a process of (Stout et al., 2002):

- evaporation, occurring when petroleum is in contact with air, causing constituents to volatilize,
- dissolution, occurring when petroleum is in contact with water, causing constituents to dissolve (water washing),
- biodegradation, the digestion of petroleum constituents by microbes.

Usually the predominant weathering process in the subsurface is biodegradation (Kaplan, 2003). With a subsurface leak (from UST and pipelines in Štúrovo), evaporation is not a significant factor. Hydrocarbons of middle distillates (diesel) are relatively insoluble in water (especially the heavier ones), so biodegradation often predominates over dissolution (Christensen & Larsen, 1993). Aromatics are more soluble than aliphatics of the same carbon number, whereas cyclo-alkanes tend to be slightly more soluble than n-alkanes (Bobra, 1992). The n-alkanes and aromatics (benzene, toluene, ethylbenzene, xylenes - BTEX) are commonly the first compounds to be removed through biological processes (Chapelle, 2001). Kaplan et al. (1997) divided the weathering process into seven stages, Oudijk (2012) proposed a weathering matrix, combining the Kaplan stages with the influence of geological environment. Weathering is affected by various factors, like soil environment, volume of contaminant released, time of the release, depth of the spill and subsurface conditions (oxygen content, microbiological populations), that cannot be omitted.

Biomarkers are often utilized for age dating of petroleum products, because of their resistance to degradation. They are organic compounds, that can be structurally related to its precursor molecule, which occurs as a natural product in a plant, animal, bacteria, spore, fungi or petroleum (Philp & Lewis, 1987). Isoprenoids pristane and phytane, contained in diesel, are biomarkers resistant to microbial alteration. Their relative concentrations compared to n-alkanes, can be used as a proxy for weathering (Schaeffer et al., 1979). The ratios n-C_{17}/pristane and n-C_{18}/phytane are indicative of weathering of petroleum products because n-alkanes degrade faster than branched alkanes such as pristane and phytane. These n-alkanes and isoprenoids have similar solubilities and partitioning coefficients and the absence of n-alkanes is a result of biological activity and not transport or sorption (Bregnard et al., 1996). Evaluation of biomarkers can also help with differentiation of petrogenic and biogenic impacts and identifying crude oil sources.

3. MATERIAL AND METHODS

3.1. Soil, groundwater and LNAPL Sampling

More than 40 new wells were built on the site during the remediation works in 2018–2020. Their depth (8.0–15.0 m below land surface, bls) and diameter (50–200 mm) depends on the method of use in the remediation - pumping, infiltration, venting, biomass application and airsparging wells. Wells with a diameter of 200 mm are the most used for LNAPL extraction. The wells were drilled with a UGB-50 (auger drilling) and HVS-497 (core drilling) mobile drilling rig. The drilling cores were lithologically evaluated and photographically documented.

Soil samples were collected immediately after drilling, according to STN EN 14899, TNI CEN / TR15310-1 to 5 and STN 01 5111). The method of sampling corresponds to the properties of the monitored contaminants.

Groundwater samples were collected using dynamic sampling according to the Slovak standard STN 5667-11 and 5667-14. Sampling was performed from existing and newly built hydrogeological wells after water level measurement and short-term pumping. During pumping, the basic parameters of water were monitored (temperature, pH, Eh, O_2, conductivity). Samples were taken after stabilization of the parameters in sample boxes supplied by the laboratory for specific types of analyzes. After collection, the samples were cooled and transported to the laboratory.

LNAPL samples were collected dynamically with using Belumi pump with a flow rate of 15 l/min. After pumping in the LNAPL column, the samples were collected and stored in glass sample boxes.

3.2. Laboratory analyses – NPOC and TPH

Non-polar extractable substances can be defined as a sum of concentrations of compounds extractable with a non-polar solvent boiling in the range of 36 °C to 69 °C. The co-extracted polar organic compounds are removed by adsorption on polar sorbents (e.g. Silica gel or Florisil). For summary determinations mainly UV and IR Spectroscopy are used.

The advantage of this method is the lower instrumental and financial requirements especially of routine evaluation of larger series of samples, regarding for example, if the limit for drinking water has been exceeded. On the other hand, this method has only a quantitative informative value and does not allow a closer identification of specific hydrocarbon components.

The method of gas chromatography (GC-FID) and/or gas chromatography- mass spectrometry (GC-MS), provides a detailed qualitative identification and also a relative amount of individual hydrocarbon components.

The NPOC method has been widely used mainly in the past, present days the GC-FID analysis in the range C_{10} to C_{40} hydrocarbons and the GC-MS analysis are preferred. The C_{10}-C_{40} analysis will be referred to as TPH content.

There are hundreds of NPOC results from the studied area, selection of them is in Table 1. Currently are the analyses of NPOC and TPH carried out in ALS Laboratories in Prague, Czech Republic according to their standard methods.

3.3. Analysis of diesel fuel

Diesel fuel and it´s residues but also the admixtures with lubricating oils are the main contaminants on the investigated site. For the detailed determination of hydrocarbon composition and biodegradation stage we use the methods of GC-FID whole oil analysis and GC-MS analysis. In both cases a free phase of diesel oil floating on groundwater table is directly analyzed without any treatment.

3.4. Gas Chromatography-Mass Spectrometry (GC-MS)

Hydrocarbons of studied diesel contamination ranging mostly from C_9 to C_{22} were analyzed in modes of TIC (total ion chromatogram) and selected ion monitoring (SIM; m/z 57). The obtained spectra offer mainly the information of the overall hydrocarbon distribution (TIC) and especially of n-alkane and isoprenoids distribution. Analyzes were carried out at the Dept. of Analytical Chemistry (Faculty of Natural Sciences, Comenius University in Bratislava) under following conditions: GC-quadrupole MS analyses were conducted on a 6890 GC and a 5973 MS system from Agilent Technologies (PaloAlto, CA, USA). A DB-5MS column (5 % Phenyl 95 % dimethylarylene siloxane; Agilent Technologies) of dimensions 30 m × 0.25 mm ID × 0.25 μm film thickness was used. The temperature program was 50°C held 2 min, heated at 3 °C/min to 300 °C. Temperature of injector was set at 280 °C and 0.2 μL of the sample without any modification was injected in split mode (split ratio 50:1) with carrier gas (He) flow rate of 1.3 $\mathrm{mL.min^{-1}}$. The transfer line was set at 300 °C and ion source at 230 °C, with electron ionisation (EI) mode set at 70 eV, and mass range 33–450 amu in scan mode. Data acquisition and processing were performed using Agilent MSD ChemStation software.

4. RESULTS AND DISCUSSION

New wells, constructed within remediation activities, provided more detailed information about the spatial distribution of different lithological layers. Evaluated aquifer is composed of sandy and sandy gravel layers. In the whole area, above all, the 0,5 m thick upper part of sandy gravel layer (8.5 – 9.0 m bls) is most contaminated. During past surveys and also in recent time several hydrodynamic tests were realized. Determined values of coefficient of hydraulic conductivity were in range from 10^{-4} to 10^{-3} $\mathrm{m.s^{-1}}$. The water – saturated bed in the area is spatially distributed into area of sandy gravels of good permeability, sandy graves of low permeability and sands without gravels of poor permeability. Water – saturated bed in Zone 1 (Figure 2) contains only sand layer. Zone 2 consists of sands with gravels, Zone 3 of gravel with sand and Zone 4 of only gravels (Kovács, 2020). Grain size determines the LNAPL saturation distribution. In fine-grained media are saturations lower than in coarse-grained media. Thus in Zone 4 higher accumulations of LNAPL could be expected, but all four zones have high potential for LNAPL recovery.

The remediation, running from 2018, is based on the pump and treat system, with dual phase extraction. Groundwater is pumped to create a hydraulic depression, from which the accumulated LNAPL is subsequently extracted. As of October

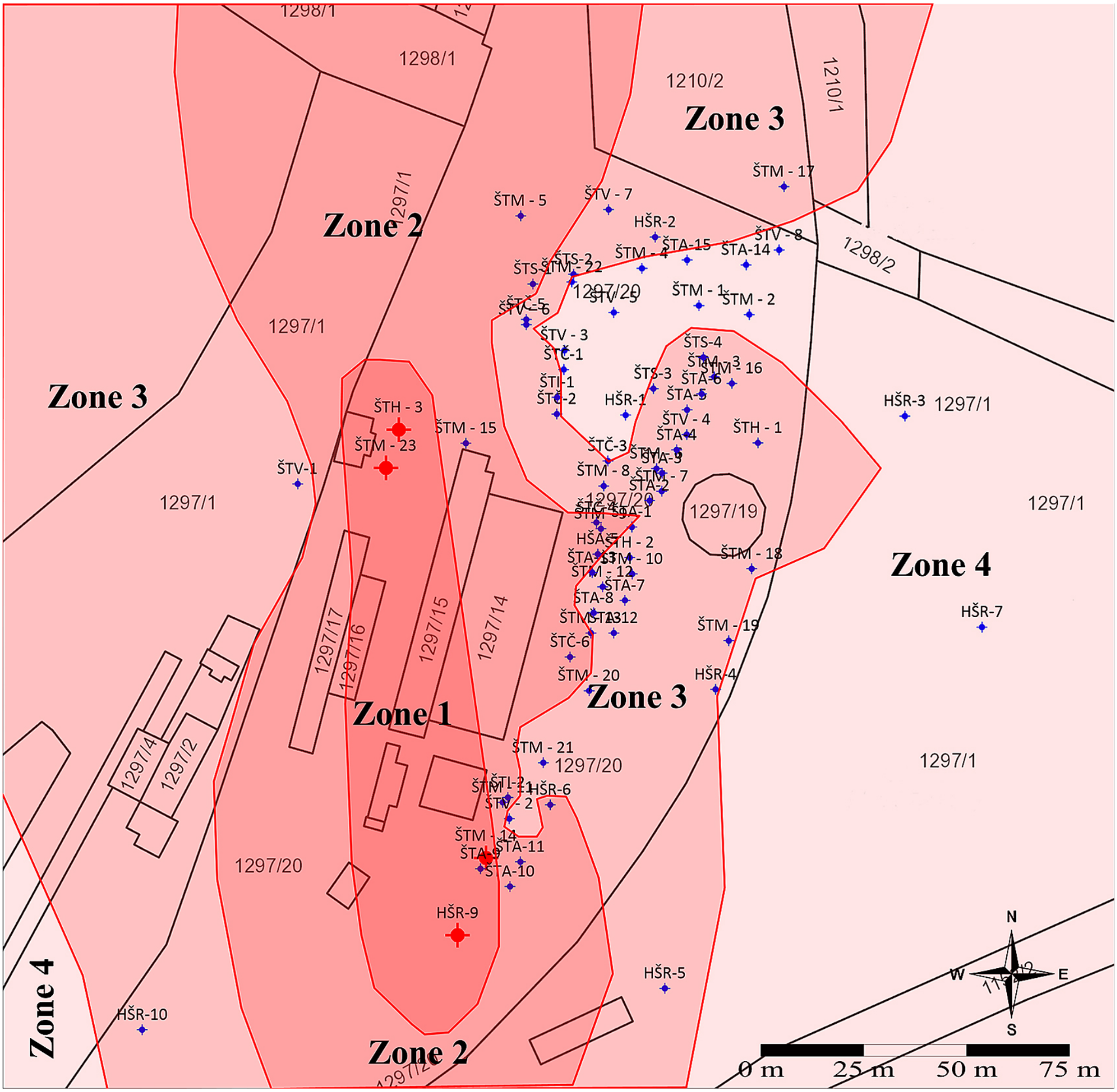

Figure 2: Spatial distribution of layers of different permeability (according to Kovács, 2020)

2020, around 3 m^3 of diesel was collected. In the long term (from 6 to 12 months), the most abundant were the STC-1 and ST-5 wells regarding the LNAPL recovery. These wells are located near underground fuel tanks. At the beginning of the LNAPL recovery (06/2019), up to 200 l of diesel was recovered from the ST-5 well during one day. This volume significantly exceeded the amount present in the well column. This indicates the immediate recharge of LNAPL into the well and a high degree of LNAPL saturation in the subsurface pore environment. This fact corresponds to the assumptions in terms of the proximity to the pollution source. On the other hand, however, water samples taken from wells in close proximity to wells with LNAPL or downgradient, do not show signs of pollution (purple marked wells on Figure 1, results in Table 2). The spreading of the LNAPL plume is probably mainly due to the volume of substances at the time of leakage and the viscosity. LNAPL appearance was observed in the subsurface for decades. Nevertheless, the LNAPL plume is relatively stable. As reported by Rice et al. (1995), the plume stabilization and its decreasing over time is the most common scenario. The study evaluated the spread of LNAPL in 271 localities with underground fuel tanks. Only in 8% was manifested the spreading of the cloud, in 59% of the cases the clouds were stable and in 33% of the cases they extent decreased. The spread of pollution in the form of petroleum substances dissolved in water has also not been documented. The above presented results of site monitoring work did not show increased concentrations of petroleum substances, determined as NPOC-IR and NPOC-UV (Table 1). The only well in which the regulatory criteria have been repeatedly exceeded is the StV-8 well. The water samples from StV-8 differ significantly from the other samples, as the water smelled of rot and had a black haze at each sampling. Control samples of groundwater were- and are also collected as part of remediation work, usually once every 2 months. Sampling points represent a "ring" of downgradient situated wells**.** The concentrations of C_{10}-C_{40}, NPOC-IR and NPOC-UV are determined in the samples. In most samples, TPH concentrations are determined below the detection limit or they are very low (Table 2). Concentrations above regulatory criteria are in bold. Therefore, we do not assume that oil substances are dissolving into groundwater. As this is an old pollution (at least 15 years old), the part of the best in water soluble hydrocarbons (low molecular weight HC) has been evaporated or degraded. Substances from the BTEX group, which are followed by n-alkanes, undergo the fastest degradation. In 2018, twenty groundwater samples were analyzed for the presence of BTEX, all of which were below the detection limit. The absence of these diesel components confirms the high age of pollution and high degradation level.

Table 2: Laboratory analyses of groundwater, concentrations of C_{10}–C_{40} in μg.l^{-1}

Well	Sampling date					
	October 2019	January 2020	March 2020	May 2020	July 2020	September 2020
STA-14	-	760	821	135	<50.0	<50.0
STA-15	<50.0	278	<50.0	<50.0	81.6	309
STA-3	<50.0	<50.0	<50.0	<50.0	<50.0	-
STA-4	176	<50.0	63.6	<50.0	<50.0	-
STA-6	-	-	-	-	<50.0	<50.0
STH-1	<50.0	<50.0	-	-	<50.0	57.7
STI-10	-	-	-	-	<50.0	<50.0
STI-8	-	-	-	-	<50.0	<50.0
STI-9	-	-	-	-	<50.0	72.3
STM-16	-	4020	226	<50.0	405	
STV-4	<50.0	-	<50.0	<50.0	-	-
STV-7	<50.0	<50.0	<50.0	<50.0	<50.0	-
STV-8	473	516	362	177	431	1030

In the shunting yard area several new extraction wells were realized (light green marked wells in purple area on Figure 1). In four of them, LNAPL accumulations were observed within a few days (up to 80 cm in well STC-8). As LNAPL is confined under layer of silts, the measured thickness is exaggerated. Currently (September / October 2020) LNAPL is recovered usually once a week, with well STC-8 the most productive. During 3 months around 200 l of diesel was recovered, without supporting water recovery. Between the shunting yard and the UST is an area, where no mobile LNPL was detected. This indicates that a new source of contamination was discovered. During remediation, 13 samples of LNAPL were collected and analyzed according to the abovementioned methodology. Samples were collected from wells with LNAPL thickness at least 10 cm (ST-3, ST-5, STA-5, STA-12, STC-1, STC-3, STC-5, STC-8, STC-10, STH-3, STI-3, STM-15, STV-4). Results of the analyzed degraded diesel samples together with two samples of fresh diesel - with and without fatty acid methyl ester (FAME), are in Table 3.

Table 3: Results of GC-MS analyses of LNAPL samples, volume in %. FAME - fatty acid methyl ester.

Well	n-C17	pristane	n-C17/ pristane	n-C18	phytane	n-C18/ phytane
Slovnaft diesel (–FAME)	1.097	0.589	1.862	0.985	0.712	1.383
Slovnaft diesel (+FAME)	0.767	0.438	1.751	0.677	0.483	1.381
STA-5	0.004	0.669	0.006	0.005	0.778	0.006
STA-12	0.007	0.672	0.01	0.003	0.847	0.004
STC-1	0.021	0.634	0.033	0.018	0.738	0.024
STC-3	0.009	0.732	0.012	0.013	0.822	0.016
STC-5	0.656	0.601	1.092	0.52	0.72	0.722
STC-8	0.534	0.608	0.878	0.434	0.702	0.618
STC-10	0.756	0.587	1.288	0.609	0.684	0.89
STH-3	1.062	0.711	1.494	0.88	0.762	1.155
STI-3	0.312	0.628	0.497	0.232	0.726	0.32
STM-15	0.008	0.707	0.011	0.003	0.796	0.004
STV-4	0.008	0.302	0.026	0.053	0.837	0.063
ST-3	0.171	0.678	0.252	0.138	0.859	0.161
ST-5	0.088	0.741	0.119	0.117	0.872	0.134

Almost a half of the samples is weathered to a high degree. The n-alkane abundance, compared to fresh diesel (without FAME), is different in terms of order. Samples STA-5, STA-12, STM-15, STV-4 are on the level of thousandths, samples STC-1, STC-3 on the level of hundredths. On the other hand, the abundance of isoprenoids, that are more resistant to degradation, is in all samples almost equal. Focusing on degradation, it's possible to separate samples into three groups. First are samples with n-alkanes almost absent, and very low n-alkane to isoprenoid ratios (STA-5, STA-12, STC-1, STC-3, STM-15, STV-4). Second are samples with very low n-alkane abundance and the n-alkane to isoprenoid ratios in values of tenths. Last group has high abundance of n-alkanes, and the n-alkane to isoprenoid ratios are close to or above one (STC-5, STC-8, STC-10, STH-3). Distribution of n-alkanes and isoprenoids of selected samples is presented on Figure 3.

The results of LNAPL analyses show a relative spatial stability. Contamination sources are the areas around UST (well STC-5), between the UST and the filling stand (well STH-3), shunting yard before the former roundhouse (wells STC-8, STC-10) and near the service pit (well STA-12). Samples from the abovementioned wells (excluding STA-12) show a low degree of degradation (Figure 4). Sample STH-3 shows minimal signs of degradation (ratio n-C_{17}/pr 1,494; n-C_{18}/ph 1,155), even though the railyard ceased operation in 2008. Subsurface environment characteristics are one of the most dominant factors, controlling

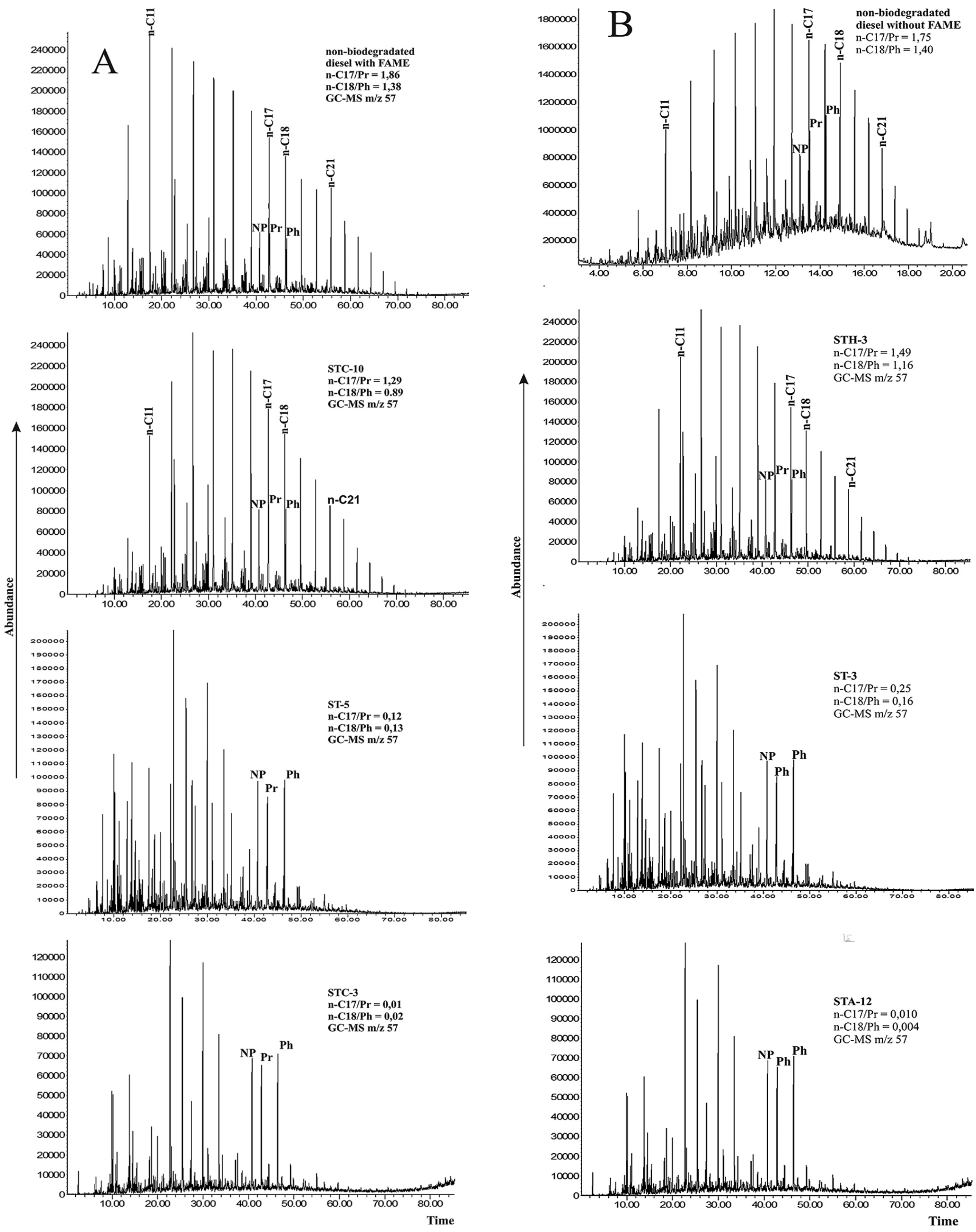

Figure 3: Distribution of n-alkanes and isoprenoids in selected LNAPL samples. Pr-pristane, Ph-phytane, NP-norpristane, n-C_x n-alkane with corresponding C atoms number; FAME-fatty acids Methyl-Ester (bio additive to diesel fuel).

the speed of degradation processes. The extent of degradation, undergone in at least 12 years, is very small. Possible explanation of the slow progress can be the LNAPL presence in waterlogged soil, without a sufficient supply of oxygen. By utilizing the Kaplan et al. (1997) progressive stages for weathering of petroleum products together with impact of environmental conditions

(Oudijk, 2012), it's possible to approximately estimate the spill age. From the five site-specific weathering-potential regimes, Štúrovo shows the attributes of a "weak" one. With the regime selected, the degree of degradation for each sample is evaluated, and the correct combination in the matrix is selected. LNAPL samples in purple area are from 40 to 48 years old, in green area from 24 to 32 years, in yellow area from 16 to 24 years and in red area from 8 to 16 years old.

Heavily degraded samples come from wells, that are from 20 to 30 m away from the contamination sources (n-C_{17}/pr and n-C_{18}/ph ratios in values of thousandths). Distance shows the maximum extent of LNAPL migration. In case of old railyards we have also to take into account the possibility, that there was not a large single leak, but numerous smaller ones in the whole shunting yard area. This could be another reason for the presence and spatial distribution of LNAPL. Choosing this scenario the migration of LNAPL was even in smaller extent. Second large source of LNAPL were the UST. As they were placed on a concrete plate, the leaking LNAPL was migrating downgradient to the east. If we assume samples STC-1 and ST-5 are from UST, then the date of the spill is around 1980. Finally, the remediation activities discovered also two minor contamination sources. First is the former service pit near well STA-12. It's the only well to contain a mixture of diesel and motor oil. All other investigated samples are pure diesel. Second is the area between the UST and the filling station, connected by a pipeline. Here the well STH-3 is located, which exposed very low degradation. Compared to samples of fresh diesel, almost all n-alkanes were still abundant (Figure 3).

In terms of source longevity, it's possible to distinct between long lasting and short lasting. Long lasting (UST, shunting yard) include wells with both high and low degree of degradation. Short lasting sources were the service pit (only high degraded sample) and the UST pipeline area (only low degraded sample). In terms of spilled volume the largest sources are the UST and shunting yard, and the small ones the service pit and the UST pipeline area. Volume of LNAPL extracted from the large sources represents almost 99 %, as the volumes from small sources are just in order of first liters.

All soil samples were collected during several stages of drilling in 2018–2020. Highest TPH contamination (rated as C_{10}-C_{40}) was found in the upper part of sandy gravel layer (8.5–9.0 m bls). Concentrations were in the range from below limit of detection (20 mg.kg^{-1}) to 23 500 mg.kg^{-1}. Contamination in the aforementioned layer is above the regulatory limit (500 mg.kg^{-1}) widespread around all four identified sources. The highest concentrations were usually detected in areas, where LNAPL was least weathered (Figure 5). A remarkable fact is, that no area with a massive contaminaion in the vadose zone was detected. However, areas with highest TPH concentrations are not the same as areas with wells of highest LNAPL yeild, or even areas with occurrence of exctractable LNAPL. From the view of extracted LNAPL volume is the most contaminated area amidst wells STC-1, STC-10, ST-5 and STA-5. Hawthorne & Kirkman (2012) published a table for quick estimation of pore saturation by LNAPL. Based on TPH concentrations in soil and porosity of the selected lithologic layer, the pore spaces of areas with high concentrations (from 10 000 mg.kg^{-1}) should contain from 7 to 17 % diesel. With layer thickness around 0,5 m, an square meter should hold approximately from 10 to 25 l of diesel. Quite important is to distinct between residual and mobile part. According to theory and praxis (Kirkman, 2014), it's almost impossible to completely remove LNAPLs solely by hydraulic means (groundwater and LNPL pumping). Presented results, based on theoretical approaches, were validated by field works. Highest contaminated soil samples from well STC-8 contained 2 830 mg.kg^{-1} TPH, which according to LSPA (2008) is too low to expect a mobile LNAPL. But just a few days after drilling the well contained 80 cm of diesel. Moreover, while extracting the LNAPL, twice the expected volume was collected, according to well diameter (200 mm), 50 l instead of 25 l. This immediate LNAPL recharge indicated very high pore space saturation.

In 2019 the anticipated source of contamination, three underground storage tanks for diesel, were removed. Soil samples from

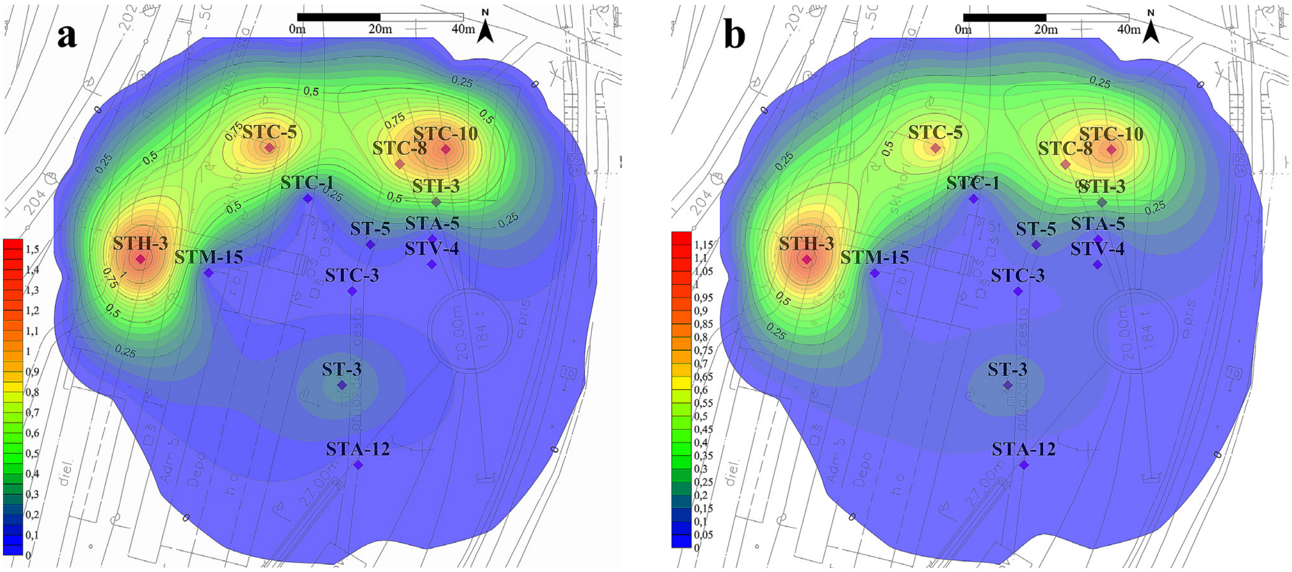

Figure 4: Degree of LNAPL degradation based on n-C_{17}/pristane (a) and n-C_{18}/phytane (b) ratios. (see also Fig. 3)

under the UST were collected (4.0 – 4.5 m bls). Determined TPH concentrations were from 4 370 to 17 000 mg.kg^{-1}. The whole area below UST was armed by a 18 x 13 m concrete plate. On the east end the plate was redrilled and the well STI-7 was constructed. Six soil samples were collected from different levels. Highest contamination concentration was identified 3.7 m below the concrete plate (TPH 9 460 mg.kg^{-1}). This could, according to LSPA (2008), indicate the presence of mobile LNAPL. Also results of past surveys and the proximity od contamination source supported the expectation of mobile LNAPL. Anyway, not even 2 months of groundwater pumping at various rates of discharge, yielded significant amounts of LNAPL. The maximum thickness in well was 2 cm. Area directly under the UST was apparently not massively affected by leaks.

6. CONCLUSIONS

Set of activities, realised during the remediation, revealed several new facts about the volume, spatial distribution and degree of degradation of the released LNAPL. The area with contaminated soil encompasses about 3 500 m^2, area with detected mobile (hydraulically extractable) LNAPL about 1 100 m^2. The upper part of the 2.0–3.0 m thick layer of sandy gravels (8.5–9.0 m bls) shows the highest degree of contamination. The volume of soil with TPH concentrations abouve regulatory criteria is approximately 1 750 m^3. Highest TPH concentrations in soil samples were detected in the shunting yard area in front of the former roundhouse (up to 23 500 mg.kg^{-1}). This area is a newly identified source of contamination, with some wells showing immediate LNAPL recharge and high yield volumes. On the other haned, the contamination plume is realtively stable. Laboratory analyses of groundwater samples, collected in close vicinty of wells containing LNAPL, usually showed small or not detectable concentrations of dissolved TPHs. Besides the volume and distribution od LNAPL, also the degradation degree was examined. Areas with different degrees were identified, based on the diesel analyses. This provided more information about the age and longevity of contamination sources. LNAPL samples were separated into four groups, depending on the estimated age, which is in rage from 8 to 48 years.

From the view of ongoing remediation are the results valuable particularly for the asessment of the weathering rate. The STH-3 sample showed almost no difference from fresh diesel, although the railyard ceased operation more than 10 years ago. The identified high degree of weathering can be connected with very low level of dissolved TPHs in groundwater. Results of several researchs from the last ten years indicate, that the dissolved degradation products are of different nature that the original hydrocarbons. During remediation a lot of uncertainities were observed, that once again confirmed the need to validate theoretical approaches in the field.

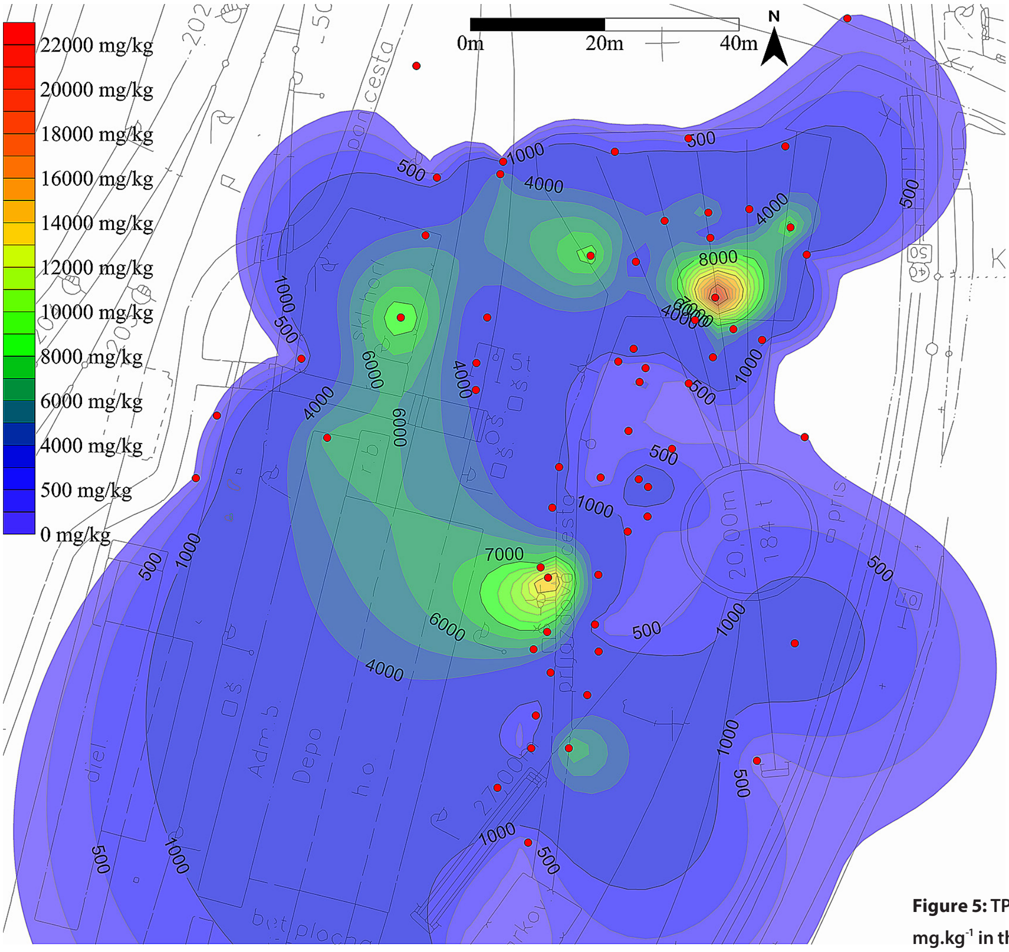

Figure 5: TPH (C_{10}-C_{40}) concentrations in mg.kg^{-1} in the most contaminated soil layer

Acknowledgements: Data presented in this paper were collected during the remediation of the old envrionmental burden **NZ (029) / Štúrovo - Rušňové depo, Cargo a.s. (SK/EZ/NZ/601)** as a part of the project Remediation of selected environmental burdens in Slovak republic (1) – Part 1: Remediation of environmental burdens in Nové Zámky, Komárno a Štúrovo (realised with financial support of the European Union from Cohesion Fund in frame of Operational Programme Environmental quality. We are also grateful to the Centre of Environmental Services, Ltd. (Bratislava) for taking part in financing this research.

Literature

Auxt A., Kovács T. & Ingár K., 2010: Vypracovanie programov opatrení v rámci prípravy plánov manažmentu oblastí povodí v súlade s požiadavkami vodného zákona a Rámcovej smernice o vode pre prevádzky ZSSK CARGO a.s. - III. etapa prác - Štúrovo – rušňové depo. [Action programme conduction in framework of developing riverside areas management plans, according to Water Law requirements and Framework Directive for water for the ZSSK CARGO a. s. operations – III. stage of works - Štúrovo – railyard]. Remediation project, archive of Cenvis, Ltd., Bratislava, 29 p. [in Slovak]

Bobra M., 1992: Solubility Behaviour of Petroleum Oils in Water. Environment Canada, Ottawa, 42 p.

Bregnard T. P-A., Hohener P., Haner A. & Zeyer J., 1996: Degradation of weathered diesel fuel by microorganisms from a contaminated aquifer in aerobic and anaerobic microcosms. *Environ. Toxicol. Chem.*, 15, 3, 299–307.

Chapelle F. H., 2001: Ground-water microbiology and geochemistry. Second Edition, John Wiley & Sons, New York, 496 p.

Christensen L. B. & Larsen T. H., 1993: Method for determining the age of diesel spills in the soil. *Groundwater Monitoring & Remediation*, 13, 4, 142–149.

CL:AIRE, 2014: An illustrated handbook of LNAPL transport and fate in the subsurface. CL:AIRE, London, 105 p.

Farr A.M., Houghtalen R.J. & McWhorter D.B., 1990: Volume estimation of light nonaqueous phase liquids in porous media. *Ground Water*, 28, 1, 48–56.

Hawthorne J.M. & Kirkman A., 2012: LCSM Tools: Conversion of TPH in Soil to NAPL Saturation. *Applied NAPL Science Review*, 2, 1.

Kaplan I. R., Galperin Y., Alimi H., Lee R-P. & Lu S-T., 1996: Patterns of chemical changes during environmental alteration of hydrocarbon fuels. *Ground Water Monitoring*, 16, 4, 113–124.

Kaplan I. R., Galperin Y., Lu S-H. & Lee R. P., 1997: Forensic environmental Geochemistry: Differentiation of fuel-types, their sources and release time. *Org. Geochem.*, 27, 5, 289–317.

Kaplan I. R., 2003: Age dating of environmental organic residues. *Environ. Forensics*, 4, 2, 95–141.

Kirkman A.J., 2014: Transmissivity – the Emerging Metric for LNAPL Recoverability – Part 1. *L.U.S.T.Line Bulletin*, 75, 6–9.

Kostolanský M., Auxt A., Urgela P., Benko J., Drábik A., Macek J. & Šuchová M., 2017: Monitoring geologických faktorov životného prostredia a udržiavanie geologických diel – rušňové depo Štúrovo. [Monitoring of geological factors of environment and preservation of geological works – railyard Štúrovo]. Final report, Cenvis Ltd., Bratislava, 17 p. [in Slovak]

Kovács T., 2020: Model prúdenia podzemnej vody v oblasti RD Štúrovo. [Model of groundwater flow in the *Štúrovo railyard area*]. Unpublished report, archive of Cenvis Ltd., Bratislava, 19 p. [in Slovak]

Kramer W. H. & Hayes T. J., 1987: Water soluble phase of number 2 fuel oil: Results of a laboratory mixing experiment. New Jersey Geological Survey Technical Memorandum 87:4, 13 p.

Lang D.A., Bastow T.P., Van Aarssen B.G.K., Warton B., Davis G.B. & Johnson C.D., 2009: Polar compounds from the dissolution of weathered diesel. *Ground Water Monitoring & Remediation*, 29, 4, 85–93.

Lenhard R.J. & Parker J.C., 1990: Estimation of free hydrocarbon volume form fluid levels in monitoring wells. *Groundwater*, 28, 1, 57–67.

LSPA (Licensed Site Professionals Association) 2008: LNAPL and The Massachusetts Contingency Plan, Part II. LSPA Technical Practices Committee, 47 p.

Lundegard P.D. & Johnson P.C., 2006: Source zone natural attenuation at petroleum hydrocarbon spill sites - II: Application to a former oil field. *Ground Water Monitoring & Remediation*, 26, 4, 93–106.

Oudijk G., 2012: Age Dating of Middle-Distillate Fuels Released to the Subsurface Environment. In Dar I.A. (Ed.), 2012: Earth Sciences. IntechOpen, Rijeka, 659 p.

Philp R. P. & Lewis C. A., 1987: Organic geochemistry of biomarkers. *Ann. Rev. Earth Plan. Sci.*, 15, 363–395.

Polák R., Bukvová J., Varga F. & Šupolíková M., 1987: Štúrovo anilín. Havária podzemných vôd. [Štúrovo aniline. Groundwater accident]. Vodné zdroje n.p., Bratislava, 35 p. [in Slovak]

Pristaš J., Horniš J., Halouzka R., Maglay J., Konečný V., Lexa J., Nagy A., Vass D. & Vozár J., 1992: Povrchová geologická mapa podunajska, 1:50 000. [Surface geological map of Podunajsko region, 1:50 000]. Unpublished Report, State Geological Institute of Dionýz Štúr in Bratislava [in Slovak]

Rice D.W., Grose R.D., Michaelsen J.C., Dooher B., MacQueen D.H., Cullen S.J., Kastenberg W.E., Everett L.G. & Marino M.A., 1995: California leaking underground fuel tank (LUFT) historical case analyses. Report UCRL-AR-122207, Environmental Protection Department, Sacramento, 65 p.

Schaeffer T., Cantwell S. G., Brown J. L., Watt D. S. & Fall R. R., 1979: Microbial growth on hydrocarbons: Terminal branching inhibits biodegradation. *Appl. Environ. Microbiol.*, 38, 4, 742–746.

Solymosiová E., Kosťov K., Bukvová J. & Sitár J., 1988: Štúrovo – znečistenie podzemných vôd ropnými látkami. [*Štúrovo* – groundwater contamination by petroleum substances]. Final report, Vodné zdroje n.p., Bratislava, 21 p. [in Slovak]

Stout S.A., Uhler A.D., McCarthy K.J. & Emsbo-Mattingly S., 2002: Chapter 6: Chemical Fingerprinting of Hydrocarbons. In: Morrison R. D. & Murphy B. M. (Eds.), 2002: Introduction to Environmental Forensics. Academic Press, San Diego, 560 p.

Tissot B.P. & Welte D.H., 1984: Petroleum Formation and Occurrence. Springer-Verlag Berlin, 702 p.

Tomlinson D.W., Rivett M.O., Wealthall G.P. & Sweeney R.E.H., 2017: Understanding Complex LNAPL Sites: Illustrated Handbook of LNAPL Transport and Fate in the Subsurface. *Journal of Environmental Management*, 204, 2, 748–756.

Urban O., Chovanec J., Keklák V., Machlica A., Šmidovičová S., Seres Z., Štefánek J., Demko M., Bednárik M., Gregor T., Kolářová J., Polák M., Zavadiak R., Fajčíková H., Borošová M., Kolesár M., Horváthová M., Vybíral V., Čopan J., Drábik A., Macek J., Bágelová A., Jurkovič Ľ., Kostolanský M., Benko J. & Urgela P., 2019. Sanácia environmentálnej záťaže NZ (029) / Štúrovo - Rušňové depo, Cargo a.s. (SK/EZ/NZ/601). [Remediation of environmental burden NZ (029) / Štúrovo - Rušňové depo, Cargo a. s.

(SK/EZ/NZ/601)]. Partial report with risk assessment. DEKONTA Slovensko Ltd., Bratislava, 89 p. [in Slovak]

Vrana K., 2008. Vypracovanie programov opatrení v rámci prípravy plánov manažmentu oblastí povodí v súlade s požiadavkami vodného zákona a Rámcovej smernice o vode pre prevádzky ZSSK CARGO a. s. – I. etapa prác a lokalitu Čierna nad Tisou – prekladisko. [Action programme conduction in framework of developing riverside areas management plans, according to Water Law requirements and Framework Directive for water for the ZSSK CARGO a. s. operations – I. stage of works and *Čierna nad Tisou* – transfer area]. Final report. HYDEKO – KV, Bratislava, 135 p. [in Slovak]