

Contamination of soils and groundwater by petroleum hydrocarbons and volatile organic compounds – Case study: ELSTAV BRNO

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Abstract. The complex system of interactions between basic environmental components is very often complicated by anthropogenic pollution. Petroleum hydrocarbons and volatile organic compounds represent the most frequent pollutants in the area of the Czech Republic. Our attention was therefore focused especially on these substances. Model reference locality of ELSTAV, Ltd. on Jílkova Street in Brno (former MEZ) was chosen for the monitoring of capture, release, degradation, persistent fixation and migration of dangerous pollutants (VOC – volatile organic compounds and TPH – total petroleum hydrocarbons) under surficial conditions of incoherent sediments. Activities performed within the scope of research works include drilling works, hydrodynamic test, soil and ground-water sample collection and laboratory analyses. A brief overview containing physical and chemical properties of chosen pollutants, their behaviour in soils and ground water and their impact on human health and the environment was also completed. The findings obtained during the research works at the chosen contamination site and from laboratory analyses are in agreement with information gained from the literature. It appears that TPH contamination of loamy sediments is relatively stable and the contaminant mobility is negligible.

Key words: TPH, VOC, contamination, NAPL, LNAPL, DNAPL, ground water and soil analysis

Introduction

The interaction between basic components of the environment – rocks and groundwater – is connected with material redistribution and interaction of both reacting units and the system as a whole. Such complex system of interacting factors is very often complicated by anthropogenic pollutions. As a consequence of various spills, extraneous organic and inorganic compounds contaminate soils and groundwater or surface water and become involved in fluid migration.

Factors determining migration rate and the subsequent fate of both organic and inorganic pollutants in natural environment are mainly interactions between the carrier medium – water (together with dissolved substances, including pollutants) – and the soil, with which they interact.

A complete understanding of the processes of interaction between water environment and sediments requires not only the combination of theoretical studies, computational modelling and laboratory experiments (conducted under conditions similar and comparable to natural conditions), but also a necessary backward comparison with pollutant behaviour in natural systems.

The environment of incoherent sediments, especially alluvial-plain sediments along surface watercourses, seems to be the most relevant, as for the possible occurrence of the interaction with pollutants.

As considerable financial resources is being annually contributed from the FNM (The National Property Fund) for the remediation of contaminated localities, our attention was focused especially on substances, which mostly represent prior pollutants at localities affected by the so-called “chronic threat”, such as VOC-Cl (volatile chlorinated hydrocarbons) and TPH (total petroleum hydrocarbons).

Model reference locality of ELSTAV, Ltd. on Jílkova Street in Brno (former MEZ) was chosen for the monitor-

ing of capture, release, degradation, persistent fixation and migration of dangerous pollutants (VOC-Cl and TPH) under surficial conditions of incoherent sediments.

Drilling works, hydrodynamic test, soil and water sample collections and laboratory analyses were carried out within the study of this site. A brief overview was completed, featuring physical and chemical properties of chosen pollutants, their behaviour in soils (both in saturated and unsaturated zones) and their impact on human health and the environment.

Distribution of contaminants in soil

Fuels (TPH) and chlorinated hydrocarbons (VOC-Cl) may occur in soils in four different forms: dissolved in water, sorbed on solid particles, comprising the soil gas and, due to their limited solubility, forming an individual liquid phase, known as NAPL (non-aqueous phase liquid). NAPLs can generally be divided into two individual groups according to their specific gravity – denser than water (dense – DNAPLs) and less dense than water (light – LNAPLs). A group of DNAPLs consists of VCH and denser oil fractions such as tar, which comprises mostly aromatic hydrocarbons. The vast majority of commonly used oil substances (e.g., fuels and light gas oils) are less dense than water.

Unsaturated zone

In the case of NAPL (TPH or VOC-Cl in non-diluted form) spill into the soil, vertical pollutant migration occurs, due to gravitational and capillary forces. Capillarity is also responsible for lateral migration of NAPL. NAPL gradually ceases to be a continuous phase and forms individual residual globules, which remain entrapped in pores by capilla-

ry forces – a residual saturation is established. As the contamination permeation proceeds, the source of contamination becomes exhausted and NAPL remains retained in the unsaturated zone in the form of residual saturation. However, larger volumes of contaminant may cause a permeation of NAPL into the saturated zone.

Consecutively, leaching (dissolution) of NAPL residual saturation by water, percolating through the unsaturated zone to the water table, takes place. The leachate reaching the saturated zone results in groundwater pollution by soluble hydrocarbons. Moreover, the residual saturation close to the water table is exposed to dissolution during seasonal water-table fluctuations.

Fuels and chlorinated hydrocarbons might occur in soils in four different forms:

- 1) Gas (air) phase – contaminants may volatilise into the soil gas.
- 2) Solid phase – contaminants may adsorb onto solid particles.
- 3) Liquid (water) phase – contaminants may dissolve in water according to their solubility.
- 4) Immiscible phase – contaminants may be present as an individual phase.

A pollutant distribution among individual phases can be represented by empirical relationships referred to as partition coefficients. Partition coefficients depend both on

the properties and composition of the soil and on the pollutant type. That is why the distribution among individual phases may change in time and location within the scope of one locality and during different stages of site remediation. The concept of phase distribution is fundamental for the evaluation of soil pollution and for the actual remediation. In the unsaturated zone, a concept of four-phase system behaviour (Huling and Weaver 1991) can be expected for DNAPL-type substances (VOC-Cl). Contaminants are re-distributed among air, water, rock and DNAPL with respect to their partial coefficients (see Fig. 1). The pollution descends from the place of input almost apeak to the water table. Direction of the drop can be locally modified by petrographic, tectonic or hydraulic parameters of saturated rocks as shown, e.g., in Fig. 2.

NAPL in the form of residual saturation is more or less immobile in the unsaturated zone and can only migrate when dissolved in water (with respect to the extent of its solubility) or when vaporized into the soil gas (volatile substances).

One or more of the following phases might fill porous space in the unsaturated zone: gaseous, liquid and immiscible phase. NAPL in the form of an immiscible phase is potentially mobile. However, the mobility of NAPL in soils has to be evaluated individually, case by case.

Saturated zone

Whenever a spill of large amount of pollutant occurs, the pollutant phase is not completely retained in the unsaturated zone and permeates to the water table. The groundwater pollution by LNAPLs and DNAPLs differs significantly and will therefore be discussed separately. LNAPL contaminants tend to accumulate at the water table while DNAPL contaminants permeate through the saturated zone and tend to cumulate on the aquifer base.

LNAPL

If sufficient LNAPL is released, it migrates through the unsaturated zone down to the water table and the zone of the so-called capillary fringe (zone with water retained by capillary forces above the water table). As NAPL reaches a zone with growing water saturation, lateral migration may also occur. Lateral migration is determined by pressure distribution in LNAPL. Generally, principal migration is supposed to be in the direction of the groundwater flow (i.e., in the direction of maximum dip of the water-table). However, some migration might occur initially in other directions, according to the hydraulic gradient arising from the NAPL accumulation. Relatively high LNAPL accumulation might cause compression or a complete collapse of capillary fringe or, potentially, even a water-table drop.

LNAPL accumulated on, or near, the water table can be washed off by the fluctuating water table. Mobile LNAPL accumulated above the water table might move up and down with the fluctuating water surface, remain in pores, thus eventually forming a residual saturation. If the water table drops, a residual saturation by LNAPL might remain

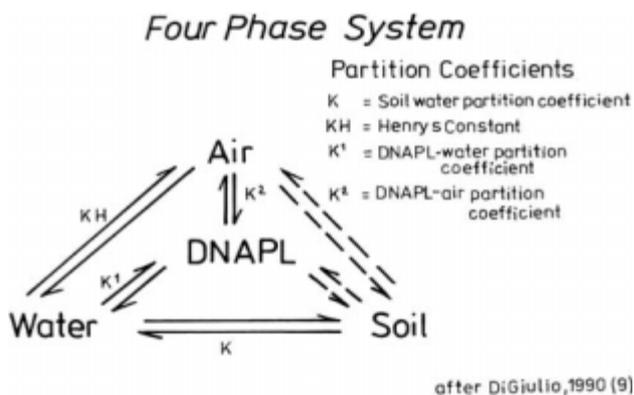


Fig.1. Distribution of DNAPL between the four phases found in the vadose zone (Huling and Weaver 1991).

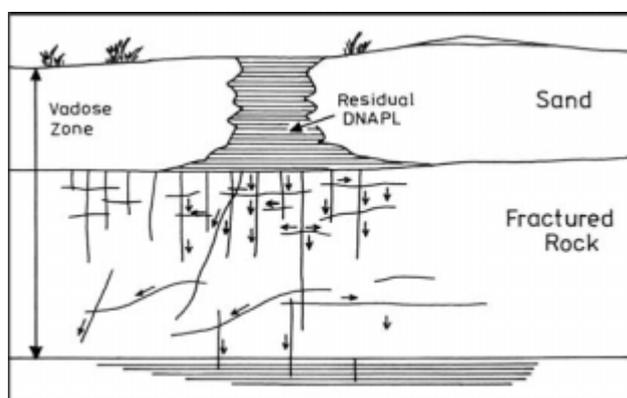


Fig. 2. DNAPL spilled into fractured rock systems may follow a complex distribution of the preferential pathways (Huling and Weaver 1991).

under the water table after its return to the initial level. A similar situation may occur as a consequence of remediation works – LNAPL accumulates in the cone of depression caused by pumping, resulting in residual saturation after the pumping is terminated.

DNAPL

Unlike LNAPL (oil substances), substances denser than water (DNAPL) such as VCH carry on descending vertically even after permeation to the saturated zone until their volume is exhausted by residual saturation formation. A vertical migration progress might be disturbed by the presence of lower permeability aquifer zones, which could lead to lateral migration.

Since the gas phase is absent in the saturated zone, a system containing DNAPL can be regarded as three-phase system: solid, liquid and immiscible liquid (see Fig. 3). Contaminant distribution in three-phase system is less complex than the one in four-phase system of the unsaturated zone. Though the saturated zone is considered to be a three-phase system, DNAPL in the gas phase may affect the groundwater quality.

In case that the whole volume of DNAPL is not exhausted for residual saturation, DNAPL carries on migrating vertically until reaching a layer possessing lower permeability. Then it starts to migrate laterally. Permeability in the vertical direction is usually smaller than in the horizontal direction and one can therefore expect the pollution to spread horizontally in particular. In the case of a “bowl-shaped boundary”, DNAPL becomes stratified, forming a sort of reservoir. The presence of various less permeable aquifer “interbeds” is relatively frequent, and the contamination may thus occur in many “hanging reservoirs” in various silt and clay interbeds, as well as in low reservoirs. Soluble fractions of DNAPL dissolve into water both from zones of residual saturation and from the reservoirs. In the saturated zone, the direction of pollution spread corresponds mostly to the direction of the groundwater flow but even in such system, slight deviations caused by different petrographic, tectonic or hydraulic parameters of saturated rocks can be observed. The direction of pollution spread may be even opposite to the groundwater flow in special cases (see Fig. 4).

The NAPL transport through rocks depends largely on the rock composition and the existence of possible preferential ways possessing higher permeability or, conversely, on the presence of interbeds of less permeable materials. Other parameters affecting the transport and fate of NAPL in rocks are to be discussed in more detail in the next chapter.

NAPL transport and dissolution in geological environment

The nature of smearing at localities with LNAPL depends on the order of dissolution of smearing zones. Zones with higher residual phase content dissolve most slowly. Water quality at localities with more significant water-table fluctuations may be remediated more rapidly than at those with

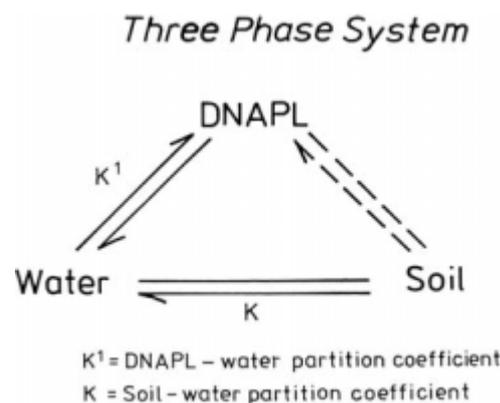


Fig. 3. Distribution of DNAPL between the three phases found in the saturated zone (Huling and Weaver 1991).

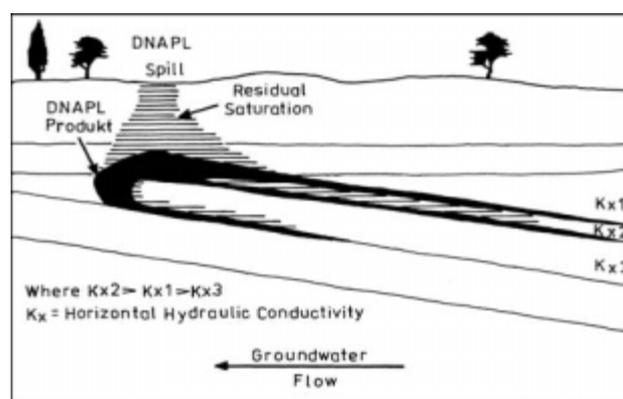


Fig. 4. Non-horizontal stratigraphic units with variable hydraulic conductivity may convey DNAPL in a different direction than the groundwater flow direction (Huling and Weaver 1991).

smaller water-table fluctuations. This is due to the fact that the pollutant phase is more spread in larger smearing zone and thus provides better contact with the air in the unsaturated zone and with the flowing groundwater in the saturated zone.

In a porous scale, the process of dissolution may have two different effects on the NAPL residual phase. In case that NAPL comprises mostly soluble substances, such as TCE, pure xylene, or a mixture of soluble substances, the droplets of NAPL become smaller and smaller and, eventually, disappear. Provided that NAPL comprises both soluble and insoluble substances, the droplets of NAPL dissolve and diminish but do not disappear completely. An example of such system is LNAPL of fresh gasoline, comprising mostly (over 80 %) insoluble organic compounds such as unbranched hydrocarbons (e.g., octane), or DNAPL of chlorinated solvents mixed with an insoluble mineral oil.

Borden and Kao (1992) proved in their model studies that the residual volume of gasoline decreased by as little as 2 % in porous environments, even though the concentration in the aqueous environment dropped to negligible values. Sometimes, the droplets of NAPL residual phase find themselves out of groundwater flow (e.g., blind pores), thus lowering the overall rate of dissolution significantly.

In these cases, diffusion is the only active transport mechanism by which the pollutant can be transported from the residual droplet to the flowing groundwater. Such a droplet remains in a blind pore even though the droplets placed in groundwater flow were dissolved long since. This diffusion process may be one of the factors determining the origin of the so-called “dissolution tail”.

The external surface of NAPL droplet exposed to the groundwater flow might be significantly limited by the structure of the porous medium.

Column experiments supported the concept of relatively small contact surface between the NAPL droplets and the flowing groundwater. For example, Powers et al. (1991) used these studies as a ground for the assumption that the effective external surface of residual NAPL droplets constitutes 1 to 50 % of the overall droplet surface. A small external surface of residual NAPL interacting with groundwater represents another reason why so many remediation works failed in achieving their objectives. Rock can be regarded as a “reactor” where no stirring occurs and where the surface free for any reaction (such as dissolution or biodegradation) is very small. In such a reactor, space for the acceleration of contaminant transport rate from NAPL to groundwater is very limited.

Residual NAPL characteristics in the saturated zone

Most of the aforementioned models describe NAPL migration within a locality and show the size of residual NAPL zones originating during the smearing of NAPL layer on the fluctuating water table and DNAPL channels formed by the permeation to the aquifer base. Such residual NAPL zones belong to significant sources of in-water-dissolved pollutants, which form the contaminant plume. Therefore, the assessment of residual phase distribution in rocks is of a rather high importance.

Wilson and Conrad (1984) discussed two possible mechanisms leading to the formation of the residual NAPL: “snap off” and “by-pass”. At the moment water enters the upper pore, the droplet of residual NAPL secedes from the receding NAPL and remains entrapped in pore by capillary forces. The snap off depends largely on pore size (body/throat ratio) and on NAPL wettability. In case of a small body/throat ratio, i.e., in case of similar throat and body sizes, the hydrocarbons can be almost completely replaced and the snap off is relatively rare. On the other hand, this case is not very common in natural porous environments and the snap off plays an important role in residual NAPL capture.

One can note that when NAPL transforms from a continuous phase into a residual phase, individual NAPL droplets are very strongly fixed in the porous environment by capillary forces. Wilson and Conrad (1984) assessed the force required for mobilisation and complete wash-away of residual droplets as a function of hydraulic gradient, with the pumping system causing:

- 1) Start of the droplet mobilisation.
- 2) Mobilisation of all droplets in porous medium.

Such a relationship, presented as a hydraulic gradient

dependence on desired hydraulic conductivity, indicates that the mobilisation of NAPL droplets by remediation pumping comes into play only in the case of very coarse-grained porous environment, possessing a high value of hydraulic gradient. The rest of droplets remain in porous medium as a long-term source of water pollution.

Residual saturation from the viewpoint of laboratory experiments

Residual saturation is a porous volume fraction filled with virtually immobile hydrocarbons (entrapped by strong capillary forces) after the snap off or by-pass disruption of continuous NAPL. Several sources present different ranges of residual saturation values. Mercer and Cohen (1990) assembled data from different sources and presented residual saturation ranges between 10 and 20 % for the unsaturated zone and between 15 and 50 % for the saturated zone. Nevertheless, it will be mentioned later that before utilisation of the residual saturation concepts, the measurement scale must be taken into consideration.

Several other aspects of residual NAPL phase behaviour were observed under laboratory conditions. For example, laboratory studies proved that residual NAPL saturation increased with decreasing porosity, increasing body/throat ratio and heterogeneity of pore-size distribution. Keuper et al. (1993) observed that residual saturation in a laboratory column depended on the initial saturation (i.e., porous volume fraction filled with continuous NAPL), however, the correlations using theoretical models did not match the measured values. The authors explained these results by an observation that a great deal of pores is filled with NAPL and therefore purveys a higher number of pores for residual NAPL saturation formation. Nonetheless, Wilson et al. (1998) emphasized that residual saturation analysis is always affected by rock properties and concluded that:

- 1) Residual saturation prognosis in a given rock is highly uncertain.
- 2) Similar rocks may possess different residual saturation.
- 3) Even small clay or silt proportions may shape significantly the observed residual saturation.
- 4) Residual saturation seems to be relatively indifferent to liquid properties but, at the same time, very sensitive to the properties and heterogeneity of the rock.

Based on the above mentioned facts, it is generally possible to state that residual saturation at field localities is very difficult to measure and can be a source of substantial mistakes (Mercer and Cohen, 1990).

According to the completed NAPL studies based on organic liquid solidification in a porous medium or on corroded glass micromodels with addition of coloured organic compounds (Wilson et al., 1998; Powers et al., 1991), the real residual NAPL distribution is rather complex. These methods helped to depict a migration of NAPL and to observe NAPL distribution after the termination of snap-off and by-pass mechanisms, with bare residual NAPL saturation remaining.

Behaviour of volatile chlorinated hydrocarbons and petroleum hydrocarbons in the environment

Chlorinated hydrocarbons

VOC-Cl appearance in the environment is solely a result of human activity. They leak from industrial production, from dumps, arise from burning of vinyl-containing compounds and appear as products of gradual decay (reductive dehalogenation) of PCE to TCE, cis-DCE and trans-DCE (2 : 1) or 1,1-DCE, vinyl chloride and finally to ethene or ethane, respectively. Natural shrinkage of VO-Cl concentrations in the environment takes place by attenuation, dehalogenation and oxidation. U.S. EPA defines the natural attenuation as a remediation course, which includes a variety of physical, chemical or biological processes that, under favourable conditions, act without human intervention to reduce the mass, toxicity mobility, volume or concentration of contaminants in soil and groundwater. These *in situ* processes include biodegradation, dispersion, dilution, sorption, volatilisation and chemical or biological stabilisation, transformation or destruction of pollutants.

Liquid fuels

Fuels undergo both aerobic and anaerobic biodegradation processes in the geological environment. Aerobic biochemical degradation of fuels is dependent mainly on the presence and species of microorganisms in water, temperature, concentration of toxic and biogenic elements, fuel contamination, content of oxygen in water and surface area of fuel droplets. The contact area between fuel and water plays an important role as well. The degradation rate can increase due to the emulsification by one or two orders of magnitude.

Anaerobic fuel degradation is about ten-times slower than the degradation in aerobic environment. The most feasible microorganism-assisted degradations are those of n-alkanes, decomposition of aliphatic hydrocarbons with branched chain and cycloalkanes is somewhat less feasible and the least feasible degradation is the one of aromatic compounds. The rate of biological degradation is not the same for all aromatic hydrocarbons. Aromatic compounds having three or four condensed rings are very stable; naphthalenes are, on the other hand, comparatively unstable.

Possible risk for human health and ecosystems

Chlorinated hydrocarbons

1,2-Dichloroethylene (1,2-DCE)

1,2-DCE may get into the organism through respiratory system, by drinking, bathing, and dishwashing in contaminated water or by direct contact with contaminated materials.

Inhalation of high doses of 1,2-DCE may cause nausea, lethargy or tiredness. Even higher doses may eventually cause death. High concentrations in the air may heavily

damage animals' liver, lungs, kidneys, and, in even higher doses, also heart. Low oral doses of cis isomer reduce the concentration of red blood cells. When ingested, concentrations of 20–50 ppm pose a comparatively low risk for human health. However, long-term exposure to doses exceeding given limits may cause damage to liver, circulatory and nervous system. Trans isomer is probably even twice as effectual as the cis derivative. DCE attacks the central nervous system, circulatory system, kidneys, liver, eyes and skin. EPA does not classify cis- and trans-1,2-DCE as potential human carcinogens.

Trichloroethylene (TCE)

Trichloroethylene may enter the organism through a respiratory system by inhalation of contaminated air or vapour of polluted water, or possibly from domestic preparations (e.g., typewriter or stain eraser). It can also get into the organism by ingestion of contaminated water, by swimming or bathing in it, by direct contact with contaminated soil or during the act of smear or paint removal from skin.

Inhalation of high TCE doses may cause heart malfunction, coma and even death. Long-term inhalation may result in damage of nervous system, lungs, kidneys or liver and also eye and larynx irritations. Respiration of small dosages within short periods of time might lead to headache, lung irritation, poor limb coordination and concentration. Long-term exposure may cause anorexia, nausea and sickness.

Ingestion of a high TCE dosage might cause nausea, liver and lung damage, cramps, heart malfunctions, coma and death. Long-term ingestion of small amounts may damage kidneys and liver, affect nervous system, cause malfunctions of the immune system and, in case of pregnancy, disorders in embryogenesis. Direct contact with skin induces rash.

Exposure to very high doses (10,000 ppm) may result in death, in the case of lower doses in drowsiness, confusion or euphoria. Absorption by skin, through inhalation and ingestion is fairly fast. In the course of TCE metabolic pathways, several toxic substances are formed: trichloroethanol, trichloroacetic and dichloroacetic acid.

People exposed to TCE within long periods of time are more likely to develop cancer than the rest of the population. Unlike NIOSH, IARC does not classify TCE as a human carcinogen. EPA classifies it as a potential human carcinogen. TCE affects the CNS, lungs, kidneys, liver, eyes and skin. In low concentrations (between 0.1 and 1 ppm for respiration and about 2 ppm in case of ingestion), however, TCE poses minimal danger to humans.

Tetrachloroethylene (PCE)

The most common exposure paths are respiration of contaminated air or ingestion of contaminated water and food. Entering of PCE through skin is limited, though it may cause its irritation. PCE may also be present in milk of mothers exposed to its sources.

If occurring in high concentrations in air, even a single exposure may affect the CNS, cause dizziness, headache,

somnolence, confusion, nausea, speech and movement difficulties, respiratory system irritation, tachyarrhythmia and sometimes fainting or even death. Experiments on animals with doses many times exceeding common concentrations in the environment induced severe damage of kidneys and liver, kidney and liver cancer and leukaemia. Short-term exposure to air with PCE concentration over 100 ppm caused health damage both to humans and animals.

Considering the results of animal experiments, it is estimated that respiration of air with 1 ppm PCE concentration for 70 years increases the liability to cancer illnesses. Ingestion or respiration of doses between 0.1 and 1 ppm poses minimal risk for human health. Nevertheless, if occurring in higher concentrations, PCE may affect the CNS, kidneys, eyes and liver.

Fuels

Exposure of skin to liquid fuels may lead to dermatosis and sometimes even to skin neoplasia (especially in case of hydrocarbons of higher molecular weights). It is worth mentioning that fuels enhance the solubility of organic compounds and thus facilitate their penetration through the skin. The danger of direct poisoning by ingestion is minimal, however, hydrocarbons of lower molecular weights, possessing significant narcotic effect, may result in acute poisoning by inhalation. Chronic exposition may cause weariness, headache, blood production malfunction and irritation to eyes and lungs. Chronic exposure of skin might lead to degenerative changes in liver, kidneys and spleen. The most dangerous fuel component is benzene, which is a proven human carcinogen.

Another significant negative effects of fuels are deterioration of organoleptic properties of water and debasement of water sources in concentrations as low as $0.002 \text{ mg} \cdot \text{l}^{-1}$. Toxic effect can be observed at higher concentrations. Fuels can generally be pronounced as less toxic to humans than to water ecosystems.

Ecotoxicity is determined by chemical composition of individual products, their solubility in water, degree of emulsification, etc. It is generally claimed that lighter oil fractions (e.g., petrol or kerosene) are remarkably more toxic than heavier fractions (oils). The most toxic is petrol, which inhibits biochemical functions already in amounts as low as $3 \text{ mg} \cdot \text{l}^{-1}$. Kerosene and motor oils are toxic for invertebrates in concentrations of $7.7 \text{ mg} \cdot \text{l}^{-1}$ and $40 \text{ mg} \cdot \text{l}^{-1}$, respectively. Sensitivities of various fish species to fuels are various. Fingerlings of ferocious fish species (silver salmon, pikeperch, trout) are the most sensitive to fuel exposure, catfish and roach are, on the other hand, considered comparatively resistant. Sturgeon-like fish perish at raw oil concentrations between 200 and $1000 \text{ mg} \cdot \text{l}^{-1}$, concentrations of about $50 \text{ mg} \cdot \text{l}^{-1}$ cause a deceleration of their growth. It can generally be stated that concentrations higher than $1 \text{ mg} \cdot \text{l}^{-1}$ may bring about an acute toxic effect.

Reference locality

The locality of interest is situated on the left bank flood plain of the Svitava River on the precinct of ELSTAV, Ltd. (former MEZ) on Jílkova Street in Brno.

From the viewpoint of geomorphological classification (Czudek et al., 1972), this locality is a part of a Bohemian Highland province, Bohemian-Moravian system and Brno Highland subsystem, which can further be divided into southern Bobrava Highlands and northwestern Boskovice Furrow. These units are separated by the Brno Basin, which narrows in the northwest direction. The Brno Basin originated at the intersection of fold systems, mostly trending E-W, NNE-SSW and especially NW-SE. The latter system possesses traits of a wide fold zone, consisting of blocks appearing on the surface as horsts. Horsts and horst ridges divide the area of the Brno Basin into several sub-basins.

From the viewpoint of climatic classification (Quitt 1971 in Myslík 1987), the locality can be ranked as a part of moderately warm locality MT-11, characterized by long and dry summers and short, mild and dry winters with short-lasting snow blanket. The temperature averages $-2.4 \text{ }^\circ\text{C}$ in January and $19.2 \text{ }^\circ\text{C}$ in July.

The locality of interest is formed by rocks of the Brno massif. The Brno massif represents a complex of rocks produced by magmatic differentiation, including the oldest hornblendites, granodiorites, quartz diorites, biotite granodiorites, and leucocratic granites. The Brno massif is predominantly tectonically limited, with the only exception of the eastern transgressive tangency of magmatites with Devonian rocks of the Moravian Karst, covered by sediments of the Carpathian Foredeep. Rocks of the Brno massif are overlain by Devonian conglomerates and mostly plastic Neogene calcareous clays, which form the pre-Quaternary subsoil of the locality of interest. Due to its hydraulic parameters (low permeability: k_f ranging from $n \cdot 10^{-7}$ to $n \cdot 10^{-9} \text{ m} \cdot \text{s}^{-1}$), the subsoil forms a basal aquitard of Quaternary groundwater. The top of Neogene subsoil lies 6.8 metres under the surface.

Quaternary sediments are represented by fluvial deposits of the Svitava River flood plain. Coarse-grained gravels, comprising of the bottom part, constitute the main aquifer. Subrounded grains of these gravels have an average diameter of 50 to 80 mm, sporadically reaching 150 mm. Boulders are formed mostly by quartz, fragments of the Brno massif rocks and, to a smaller extent, by conglomerates. The sand-sized fraction (ca. 15–20 %) is medium- or coarse-grained. The hydraulic conductivity coefficient reaches, according to the results of hydrodynamic test on HP-3 borehole, the value of $7.57 \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$, the transmissivity coefficient the value of $1.36 \times 10^{-3} \text{ m}^2 \cdot \text{s}^{-1}$. The above values characterise the groundwater layer as an environment possessing high permeability (permeability class III, Jetel, 1982) and transmissivity (transmissivity class II, Krásný, 1986). This location can be therefore used for regular groundwater extraction of sectional extent (smaller central ducts). The thickness of the Quaternary

sediments reaches about 1.3 m. The complex of strata of coarse- or medium-grained sands passes upward into sandy and clayey flood loams, which, due to their limited permeability ($n \cdot 10^{-7}$ to $n \cdot 10^{-8} \text{ m} \cdot \text{s}^{-1}$), form the hanging wall aquitard of the aquifer. The natural surface of the locality is overlain by layers of embankments and, on the very top, by a concrete floor (in the hall) and concrete panels (outside).

Applied methodology

Within the research works, a borehole (HP-3) 267 mm in diameter was drilled and cased down to the depth of 8 m (2001). Additional six boreholes with no casing (V-1 up to V-6) of a total length of 39.8 m were drilled. Thirty-seven samples of soil, 1 sample of concrete, 1 sample of oil phase from HP-1 borehole, 1 sample of liquid from waste reservoir and 8 samples of groundwater were collected. A preclusive hydrodynamic test and hydraulic calculations were carried out. A thickness of a free phase on the water table was measured. All soil and groundwater samples were analysed in a laboratory.

The second stage, pursued last year (2002), included drilling of 3 non-cased boreholes of the total length of 22.5 m, serving for soil sampling. Several groundwater samples were also collected. All the soil and groundwater samples were analysed, and contents of organic pollutants were determined.

In total, one pilot borehole cased down to the depth of 8.0 m and 9 more non-cased boreholes of the overall length of 62.3 m were drilled. Seventy soil samples, 12 groundwater samples, 1 sample of concrete, 1 sample of oil phase from HP-1 borehole, 1 sample of liquid from waste reservoir in the hall were collected.

Results of an ecological audit, accomplished by SEPARA-EKO, Ltd., were also used for the research works. The audit included drilling of two boreholes, cased down to a depth of 8 m, serving for collection of soil and groundwater samples. All research works were documented and evaluated in the final report (Müller et al. 2002).

Drilling works

One observational hydraulically complete well (HP-3) was drilled about 1.2 m deep into the relatively impermeable Neogene clay (total depth of the borehole was 8.0 m). The borehole was excavated using a drilling kit provided by a geo-exploring division of UNIGEO and cased with PVC well screen (160 mm in diameter), which was perforated at the depth interval of 2–8 m. The annulus between borehole walls and the kit was filled with sorted gravel (4 to 8 mm fraction). The upper part of the annular space was sealed by clay. The well head was plugged by TGB-1 stopper and concreted. A slightly confined water level appeared at a depth of 2.2 metres under the surface and settled on 1.99 m.

Further, 6 more boreholes were drilled for collection of soil samples (and a sample of floor concrete) in the machinery hall number 115, situated on the plot of descriptive number 1091/4. The actual drillings were preceded by pre-drilling of concrete floors, completed by workers of HYDROGEO, Ltd. Six boreholes of about 1 m depth were drilled. Consecutively, boreholes V-3 – V-6 were excavated by a drilling set of the Czech Geological Survey, down to the final depths of ca 3.5 metres. Several soil (and concrete) samples were continuously collected throughout the drilling works.

In the consecutive stage (year 2002), three non-cased boreholes (V-3a, V-4a and HP-5a) were drilled in the immediate vicinity of the original boreholes V-3, V-4 and HP-5. The depths of about 6.5 m (V-4a), and 8.0 m (V-3a, HP-5a) were reached. These boreholes were excavated by HYDROGEO, Ltd., using the LUMESA drilling kit.

Hydrodynamic test

A pumping test and a subsequent recovery test (each lasting 4 hours) were accomplished on hydrogeological borehole HP-3 on 8th November 2001. The goal of the hydrodynamic test was to determine values of hydrodynamic parameters of the groundwater body in the vicinity of the tested borehole. Pumping was initiated on a water discharge level of $0.77 \text{ l} \cdot \text{s}^{-1}$ and this value was kept constant throughout the whole pumping test time. The water column in borehole HP-3 amounted to 4.69 m – measured from the groundwater body base – before the initiation of pumping (relatively impermeable clays). When measured from the borehole bottom (depth 8.0 m), the water column reached the height of 5.99 m. The groundwater table was about 1.19 m lower at the end of pumping, which is about 25 % of the original water column (measured from the groundwater body base). A comparatively rapid rise of the water table was observed during the consequential recovery test – the water level rose by 1.15 m in an hour.

The actual hydrodynamic test was performed by Rudolf Lidařík company, in full compliance with ČSN 73 6614 norm “Testing of groundwater sources”. The pumping was accomplished using Grundfos 3A-6 pump with tube filter cast at a depth of 5.3 m under the surface. The drawn water was deviated through a 6 m long pipe into a local drain. Characteristic hydrological data, such as the water table level, the amount of pumped water, water temperature, air temperature and actual weather conditions were registered within relevant intervals. The water table level was determined by an electro-acoustic G-10 level meter; the water discharge was measured by a volumetrically calibrated 20 l vessel. All registered data were taken down into the daily report on the pumping and recovery test. Before a pumping test initiation, a thickness of the oil contamination phase (LNAPL) on the water table in borehole HP-1 (in the hall No. 115) was determined. The value of the free phase thickness came to 1.30 m.

Consecutively, water table levels and oil phase (LNAPL) thicknesses in HP-1, HP-3, HP-4 and HP-5 bore-

holes were assessed (18th July 2002). The following data were obtained:

	LNAPL level (in metres under the surface)	Water table level (in metres under the surface)	LNAPL thickness (in metres)
HP-1	2.29	3.38	1.09
HP-3	–	2.12	0
HP-4	2.525	2.52	0.05 (film)
HP-5	2.40	2.51	0.11

Hydraulic calculations

(Sub-delivery from Ing. F. Mašek, Geotest Brno, joint-stock company)

The results of drilling works and hydrodynamic test served as fundamentals for hydraulic calculations, which aimed to determine basic hydraulic parameters of the aquifer. Hydraulic parameters were calculated in accordance with the theory of steady and unsteady flux of groundwater to a hydraulically cased borehole. Hydraulic parameter values according to the theory of steady flux were calculated using HGT-1 program on TI 59 programmable calculator. Parameter values according to the unsteady flux theory were calculated using ČZ 1.5 program on Pentium PC. Input data for the calculations were compiled from data obtained during the pumping test and from drawn semi-logarithmic or logarithmic curves – dependences of water level fluctuations on a logarithm of time (durations of pumping and recovery tests). The intervals of water level measurements applied to the pumping test were applicable for evaluations according to both unsteady and steady groundwater flux theories.

More long-term groundwater fluctuations could not be observed and recorded due to limited duration of the test. No precipitation, which could potentially affect the groundwater table at the locality, was registered throughout the testing period. The water table rose by 1.15 m after the first hour of recovery, reaching a level just 0.04 m lower than was the original one (before pumping), which indicates a fairly swift filling of the depression. An almost steady state of groundwater flux was achieved during the pumping. The pumping was not interrupted and the test may be considered correct and proper from a technical point of view. The measured values could be very well applied to the further determination of hydraulic parameters.

A thickness of the confined aquifer in HP-3 equaled 1.8 m. The groundwater body thickness was determined from petrography and groundwater table measurements accomplished before the pumping. The groundwater body at the locality of interest is connected with porous environment of Quaternary clay and coarse-grained sands/gravels.

Trends in progress of the recovery test indicated faster initial rise rate in the first 40 minutes of recovery over against the rate of decrease during pumping. Nevertheless, the rates of rise and decrease were about the same in final stages of both tests. Owing to the fact that no proximal

observational objects were located in the vicinity of the pumped borehole, which could be used for the determination of time dependency of water level decrease and for the calculation of storativity coefficient value, this value was, taking account of petrographic description (coarse-grained sands/gravels), assessed by a qualified estimate to equal ca. 10 %. In a horizontal direction, a boundary condition of an “unlimited layer” was chosen for the purpose of hydrodynamic test calculations. This condition fully fits the presumptive groundwater body extent for the given test duration (4 hours). The rate at which the water level rose in the borehole during the recovery test indicates that the groundwater body is very well maintained, and that a flat and not very extensive depression will form in the case of a long-term exploration. The decrease of the water level will be, especially at further distances, rather small. In the case of the intended groundwater exploitation, a long-term pumping on the order of $1 \cdot \text{s}^{-1}$ will be possible.

Final evaluation of hydraulic parameters

The groundwater body at the locality of interest comes under a shallow groundwater circulation in the environment of coarse-grained Quaternary gravels. The achieved results affirm the homogeneity of hydraulic parameters in the groundwater body.

Results of the hydrodynamic test and consecutive hydraulic calculations indicate, that the water-bearing environment of the Quaternary coarse-grained gravels and loamy sands, with hydraulic conductivity coefficient equal to $7.57 \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$ and transmissivity coefficient equal to $1.36 \times 10^{-3} \text{ m}^2 \cdot \text{s}^{-1}$, represents a highly permeable (permeability class III, Jetel, 1982) and transmissive environment (transmissivity class II, Krásný, 1986). Such a location can be therefore used for regular groundwater extractions of sectional extent (smaller central ducts), which is very favourable from the viewpoint of water supplementation.

The tested borehole HP-3 proved safe for groundwater drawing at water discharge of $0.8 \text{ l} \cdot \text{s}^{-1}$ (at most $1.0 \text{ l} \cdot \text{s}^{-1}$). In the case of pumping, the pump will have to be embedded at a depth of 6 m under the surface. Considering the built-up surroundings and the concentration of factories and other potential contamination sources in the neighbourhood, it will not be possible to ensure a protection of the water source in a way, which would make it a source of drinking water.

Soil sampling

During the drilling works, soil samples were collected from individual horizons, so that all present rock-types were included. The samples collected during the excavation of HP-3 borehole were, due to the method of drilling, collected as unbroken.

In addition to the aforementioned samples, three drill core samples were collected from borehole HP-3 for the purpose of rock horizon characterization.

Tab. 1. Chemical analysis of groundwater

Sampling site	HP-3					HP-1
	Before PT	After PT	3 m	5 m	7 m	
Date	8. 11. 2001		21. 8. 2002			21. 8. 2002
	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
TPH	40	< 30	110	< 20	< 20	90
Trichloromethane	0.1	< 0.1	< 0.1	< 0.1	< 0.1	27.3
Tetrachloromethane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	3.6
1,1-Dichlorethane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1,2-Dichlorethane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1,1,1-Trichlorethane	< 0.1	< 0.1	1.0	5.1	8.0	12.0
1,1,2-Trichlorethane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1,1,1,2-Tetrachlorethane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1,1,2,2-Tetrachlorethane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Bromodichloromethane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Dibromochloromethane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Tribromomethane	0.4	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1,1-Dichloroethene	0.3	0.5	2.3	2.6	< 0.1	< 0.1
trans-1,2-Dichloroethene	3.5	2.2	22.3	26.1	14.5	1.1
cis-1,2-Dichloroethene	79.1	33.4	319	316	113	25.6
Trichloroethene	2.4	127	61.8	60.2	17.7	5.0
Tetrachloroethene	3.6	3.1	97.2	85.5	25.9	2.9
Chlorobenzene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Dichlorobenzenes	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Benzene	23.1	0.7	< 0.3	< 0.3	< 0.3	< 0.3
Toluene	0.1	0.2	< 0.3	< 0.3	0.4	2.5
Ethylbenzene	< 0.1	< 0.1	< 0.3	< 0.3	< 0.3	< 0.3
Xylenes	0.2	0.1	< 0.3	< 0.3	< 0.3	< 0.3
Styrene	< 0.1	< 0.1	< 0.3	< 0.3	< 0.3	< 0.3
CB28	< 0.0004	< 0.0004	0.0006	< 0.0005	< 0.0005	0.0009
CB52	< 0.0004	< 0.0004	0.0008	< 0.0007	< 0.0007	0.0010
CB101	< 0.0004	< 0.0004	< 0.0005	< 0.0005	< 0.0005	< 0.0005
CB138	0.0009	0.0004	< 0.0005	< 0.0005	< 0.0005	< 0.0005
CB153	0.0009	0.0004	< 0.0005	< 0.0005	< 0.0005	< 0.0005
CB180	0.0011	0.0006	< 0.0005	< 0.0005	< 0.0005	< 0.0005
PCB (sum)	0.0035	< 0.0025	< 0.0030	< 0.0030	< 0.0030	< 0.0030
Naphtalene	0.0757	0.0093	0.0063	< 0.0020	< 0.0020	0.199
Acenaphthene	0.0093	0.0034	< 0.0020	< 0.0020	< 0.0020	0.030
Fluorene	0.0065	0.0035	< 0.0020	< 0.0020	< 0.0020	0.039
Phenanthrene	0.0240	0.0082	0.0019	< 0.0005	< 0.0005	0.020
Anthracene	0.0011	0.0004	0.0004	0.0005	< 0.0002	0.010
Fluoranthene	0.0058	0.0015	< 0.0020	< 0.0020	< 0.0020	0.110
Pyrene	0.0028	0.0008	< 0.0010	< 0.0010	< 0.0010	0.977
Benz[a]anthracene	0.0010	0.0007	< 0.0010	< 0.0010	< 0.0010	0.714
Chrysene	0.0007	0.0002	0.0005	< 0.0005	< 0.0005	0.209
Benzo[b]fluoranthene	0.0007	0.0005	< 0.0020	< 0.0020	< 0.0020	0.127
Benzo[k]fluoranthene	0.0004	0.0002	< 0.0005	< 0.0005	< 0.0005	0.013
Benzo[a]pyrene	0.0005	0.0002	< 0.0010	< 0.0010	< 0.0010	0.037
Dibenz[a,h]anthracene	< 0.0002	< 0.0002	< 0.0010	< 0.0010	< 0.0010	0.390
Benzo[ghi]perylene	0.0013	0.0006	< 0.0040	< 0.0040	< 0.0040	0.461
Indeno[1,2,3-cd]pyren	< 0.0002	< 0.0002	< 0.0020	< 0.0020	< 0.0020	0.023
PAH (sum)	0.1300	0.0295	< 0.0200	< 0.0200	< 0.0200	3.360

PT – pumping test

Tab. 2. Chemical analysis of soil samples from borehole HP-3 (2001)

Depth (m)	0.5	0.9	1.8	3.5	5.0	6.5	7.0
	(mg/kg)						
TPH	39	< 6	242	18	6	9	11
Trichloromethane	< 0.002	< 0.002	0.002	< 0.002	< 0.002	< 0.002	< 0.002
Tetrachloromethane	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
1,1-Dichlorethane	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
1,2-Dichlorethane	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
1,1,1-Trichlorethane	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
1,1,2-Trichlorethane	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
1,1,1,2-Tetrachlorethane	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
1,1,1,2,2-Tetrachlorethane	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
1,1-Dichloroethene	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
trans-1,2-Dichloroethene	< 0.002	< 0.002	0.003	< 0.002	< 0.002	< 0.002	< 0.002
cis-1,2-Dichloroethene	0.005	0.006	0.022	0.025	0.002	< 0.002	0.002
Trichloroethene	0.018	0.014	0.047	0.013	0.011	0.003	0.003
Tetrachloroethene	0.005	0.008	0.012	0.005	0.003	0.002	0.002
Chlorobenzene	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
Dichlorobenzenes	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
Benzene	< 0.002	< 0.002	0.003	< 0.002	< 0.002	< 0.002	< 0.002
Toluene	0.002	0.003	0.008	0.012	0.011	0.004	0.002
Ethylbenzene	< 0.002	< 0.002	0.002	< 0.002	< 0.002	< 0.002	< 0.002
Xylenes	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
PCB	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010

PCB – sum of congeners No. 28, 52, 101, 138, 153 and 180

Some more samples were taken from V-3a, V-4a and HP-5a boreholes this year in order to assess the extent of changes in contaminant contents throughout a period of time.

Water sampling

Groundwater samples were taken partly from the existing boreholes HP-1 (in the hall No. 115), HP-2 (in front of the hall No. 115) and ST-121 (well in the building No. 121),

partly from newly built borehole HP-3. Water samples from the existing boreholes were collected using VV-3 sampling cylinder (Geospol, Ltd.). Newly built HP-3 borehole was utilised for zonal groundwater samplings at depths of 2.0 m, 5.0 m and 7.0 m in order to trace the vertical zonation of contamination. A preclusive hydrodynamic test was available for collection of groundwater samples before the initiation of the pumping test and, consecutively, before the termination of the 4-hour pumping.

During the subsequent stage, several groundwater samples were taken from boreholes HP-3 and HP-1. The samples from HP-3 were again collected as zonal samples so that vertical spread of contamination in the groundwater body and changes of contaminant contents in time could be evaluated.

Chemical analyses

All organic composition analyses of the collected samples were accomplished in the laboratory of the Czech Geological Survey, Brno branch. Collections, sample modification and even the actual final analyses were carried out in full compliance with standard laboratory procedures.

Tab. 3. Content of TPH in soil samples (2001)

Sampling site	Date	TPH mg/kg	Sampling site	Date	TPH mg/kg
V-1/0.5m	17. 07. 01	<6	V-4/0.3m	17. 07. 01	104
V-1/1.0m	24. 07. 01	6500	V-4/1.3m	23. 07. 01	287
V-1/2.0m	24. 07. 01	1750	V-4/2.6m	23. 07. 01	10300
V-1/3.2m	24. 07. 01	680	V-4/3.6m	23. 07. 01	10600
V-2/0.2m	17. 07. 01	14300	V-5/0.5m	17. 07. 01	1010
V-2/1.0m	17. 07. 01	6	V-5/1.6m	23. 07. 01	60
V-2/2.3m	24. 07. 01	58	V-5/2.5m	23. 07. 01	7470
V-2/2.5m	24. 07. 01	47	V-6/0.5m	17. 07. 01	32
V-2/3.0m	24. 07. 01	24	V-6/1.6m	23. 07. 01	223
V-3/0.5m	17. 07. 01	67000	V-6/4.0m	23. 07. 01	8100
V-3/1.5m	23. 07. 01	7350	V-6/10.8m	23. 07. 01	440
V-3/2.6m	23. 07. 01	18140			
V-3/5.0m	23. 07. 01	5260			

Tab. 4. Chemical analysis of soil samples (2002)

Sampling site	V3A						V4A						HP5A						
	0.5 m	1.0 m	2.0 m	3.0 m	4.0 m	7.5 m	0.2 m	0.5 m	1.0 m	2.0 m	3.0 m	4.0 m	4.5 m	0.5 m	1.0 m	2.0 m	3.0 m	4.0 m	8.0 m
	mg/kg												mg/kg						
TPH	7220	5250	6820	7170	5140	1040	-	149	12	6200	8030	20100	-	28	286	3770	26400	35300	-
CB28	0.0003	<0.0002	<0.0002	0.0004	0.0003	<0.0002	-	<0.0002	<0.0002	<0.0002	0.0003	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.0013	0.0015	-
CB52	0.0020	0.0003	0.0008	0.0003	<0.0002	<0.0002	-	<0.0002	<0.0002	0.0002	<0.0002	<0.0002	0.0002	0.0004	0.0002	<0.0002	0.0003	0.0003	-
CB101	0.0027	0.0009	0.0012	0.0016	0.0016	0.0003	-	0.0006	<0.0002	0.0004	0.0004	0.0008	0.0007	0.0003	0.0003	0.0008	0.0011	0.0013	-
CB138	0.0071	0.0031	0.0032	0.0028	0.0022	0.0005	-	0.0007	0.0002	0.0009	0.0008	0.0012	0.0014	0.0003	0.0006	0.0020	0.0014	0.0014	-
CB153	0.0063	0.0028	0.0028	0.0031	0.0020	0.0004	-	0.0005	0.0002	0.0008	0.0007	0.0016	0.0018	0.0003	0.0004	0.0017	0.0015	0.0015	-
CB180	0.0064	0.0028	0.0030	0.0025	0.0019	0.0002	-	0.0003	<0.0002	0.0007	0.0005	0.0011	0.0012	<0.0002	0.0006	0.0020	0.0013	0.0011	-
PCB (sum)	0.0248	0.0099	0.0113	0.0104	0.0080	0.0014	-	0.0021	<0.0012	0.0030	0.0027	0.0047	0.0055	0.0013	0.0021	0.0065	0.0069	0.0071	-
Trichloromethane	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001
Tetrachloromethane	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,1-Dichloroethane	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,2-Dichloroethane	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,1-Trichloroethane	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,2-Trichloroethane	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,1,2-Tetrachloroethane	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
adjustright1,1,2,2-Tetrachloroethane	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,1-Dichloroethene	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
trans-1,2-Dichloroethene	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
cis-1,2-Dichloroethene	-	-	-	0.006	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.016	<0.001	<0.001
Trichloroethene	-	-	-	0.013	0.009	0.009	<0.001	0.006	0.001	<0.001	0.001	0.001	0.001	0.133	0.207	0.380	0.007	0.009	<0.001
Tetrachloroethene	-	-	-	0.001	0.001	0.001	<0.001	0.004	0.001	0.001	0.001	0.001	0.001	0.009	0.015	0.007	0.001	0.001	<0.001
Chlorobenzene	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	0.003	<0.001	<0.001	<0.001	<0.001
Dichlorobenzenes	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Benzene	-	-	-	<0.001	<0.001	<0.001	<0.001	0.003	0.001	<0.001	0.001	0.001	0.001	<0.001	0.001	<0.001	0.001	0.001	<0.001
Toluene	-	-	-	<0.001	<0.001	<0.001	0.001	0.002	0.002	<0.001	0.002	0.002	0.002	0.001	0.002	0.001	0.016	0.022	0.001
Ethylbenzene	-	-	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.001	<0.001	<0.001	<0.001	0.001	0.001	<0.001
Xylenes	-	-	-	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.003	<0.002

In the case of all solid samples, several compounds belonging to less volatile or nonvolatile proportion and extractable by organic solvents were analysed. Amounts of TPH were determined using infrared spectroscopy. A saturated hydrocarbon fraction, a fraction of aromatic hydrocarbons and a fraction of persistent organochloric substances were analysed using gas chromatography measurements. In some solid samples, VOC (halogenated and monoaromatic hydrocarbons) were also analysed.

Solid samples collected for the analysis of nonvolatile substances were dried at room temperature and then ground and sifted on a sifter (2 mm pinhole diameter). From samples prepared that way, TPH was extracted by chlorofluorocarbon and analysed on Perkin-Elmer 783 IR spectrophotometer.

The next fraction was subjected to an extraction by a mixture of dichloromethane and methanol (95 : 5 volume ratio). An aliquot part of this extract was then fractionated (column chromatography, silica gel) into a fraction of saturated hydrocarbons and a fraction of aromatic hydrocarbons. The distribution of individual hydrocarbons in both fractions was determined using Agilent Technologies AT 6890 gas chromatograph equipped with flame ionization detector (FID).

For the purpose of the analysis of persistent organochloric substances (especially PCB), a portion of the extract was again purified by column chromatography (on a column with modified silica gel) and analysed using Agilent Technologies AT 6890 gas chromatograph equipped with electron capture detector (ECD).

Water samples were tested on TPH, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and VOC. TPH analysis was again similar to the analysis of solid samples. PAH and PCB were first isolated by a micro extraction with n-hexane. In the case of PCB, gas chromatograph with ECD detector was used. For PAH analysis, liquid chromatography (Agilent Technologies AT 100 with fluorescence detector) was employed.

VOC were determined both in water and in solid samples by means of instrumental arrangements containing a "headspace" – a Tekmar-Dohrmann device for VOC isolation 7050 HT– connected to AT 5890 gas chromatograph equipped with FID and ECD detectors.

Results

Laboratory analyses of soil samples

The results of soil analyses shown in Tabs 2, 3 and 4 were compared with values given in "Systematic direction of the Ministry of the Environment of the Czech Republic for risk analyses of the contaminated sites" (31st July 1996). Tables 2. and 4. indicate that VOC contents did not yet at all reach the limits given by B-criterion (0.5 – 50 mg/kg). Our attention was therefore later focused especially on the contents

of NES (non-polar extractable substances). The above mentioned direction sets the following limits:

TPH (mg/kg of dry mass)	A	B	C _{res}	C _{rec}	C _{ind}	C _{gen}
	100	400	500	750	1000	500

C_{res}, C_{rec}, C_{ind}, C_{gen} mean criteria for residential, recreational, industrial and general use of sites.

The stated criteria stand for limiting concentrations of the given compounds in soil and groundwater. By comparing concentrations determined during exploratory works with these criteria it is possible to roughly assess the extent of contamination and to classify the contamination according to its magnitude. One of the most significant points of the appraisal is the intended utilization of the locality. Different requirements resulting from the intended locality utilization are taken into consideration by a division of C-criteria into several subsets: industrially commercial, recreational, residential and general.

A-criteria

A-criteria reflect approximately natural abundances of monitored compounds in the environment (in connection with customarily set sensitivity limits of the analysis). If A-criteria are not exceeded, the environment is not polluted and the monitored compound occurs in its common natural concentration. Exceeding of A-criteria is considered as a contamination of the given environment constituent, with the exception of localities with naturally higher abundances of monitored compounds. As long as B-criteria are not exceeded at the same time, the contamination is not so serious and it is not necessary to compile more detailed data for its assessment.

B-criteria

B-criteria are artificially introduced criteria, which roughly represent arithmetic averages of A- and C-criteria for the given compounds. Exceeding of these criteria is considered as pollution, which might have a negative impact on human health and individual constituents of the environment. Exceeding of B-criteria necessitates a preclusive evaluation of potential risks resulting from the existing contamination, a finding of source/cause of the pollution and, with respect to results, a decision of further exploration or initiation of monitoring.

C-criteria

Derivation of C-criteria was based on the evaluation of physical, chemical, toxicological, ecotoxicological and sensory properties of the given compounds. Exceeding of C-criteria represents a pollution, which can pose a significant danger to human health and individual constituents of the environment. The seriousness of the risk can only be proven by its analysis.

As shown in Tabs 3 and 4, limits of $C_{\text{industrial}}$ were exceeded significantly in all exploratory boreholes excavated in the hall No. 115 (V-1 – V-6, HP-4, HP-5, V-3A, V-4A and HP-5A). Maximal contamination was found in borehole HP-5 at a depth of 4.0 m (35,300 mg/kg). On the other hand, in HP-3, situated outside the hall, neither exceeding of B-criterion was observed.

Laboratory analyses of groundwater samples

The results of groundwater laboratory analyses shown in Tab. 1 were again compared with values given in the cited systematic direction for groundwaters, in accordance with the individual criteria. A groundwater contamination by VOC-Cl was also observed. Therefore, not only TPH parameters but also 1,1-dichloroethene, trans-1,2-dichloroethene, cis-1,2-dichloroethene, trichloroethene (TCE) and tetrachloroethene (PCE) were monitored. The aforementioned systematic direction presents the following limits for the given compounds:

	A	B	C
TPH ($\mu\text{g/l}$)	50	500	1000
1,1-dichloroethene	0.1	10	20
1,2-DCE (cis-, trans-)	0.1	10	20
trichloroethene	0.1	25	50
tetrachloroethene	0.1	10	20

When comparing the obtained results with the given limits, it was stated that C-criteria are exceeded in the case of 1,2-dichloroethene, trichloroethene (except for the sample collected before the pumping test, November 2001, and the sample from a depth of 7,0 m, August 2002) and tetrachloroethene (except for the dynamic sample collection before and after the pumping test, November 2001). Limits given by C-criteria are exceeded also in the case of 1,2-dichloroethane in the groundwater of borehole HP-1 and well ST-121.

In addition to groundwater analyses, contaminant samples taken from HP-1 (LNAPL oil phase thickness of 1.30 m) and from waste reservoir in the hall No. 115 were also analysed. The nature of contamination corresponds to cutting emulsions (see Fig. 5).

Tab. 1 presents results of laboratory analyses of groundwater taken from borehole HP-3. It shows properties of samples collected before the initiation of, during, and closely before the termination (4 hours after the initiation) of the pumping test. At the same time, it shows the results of analyses of groundwater, which was zonally collected from depths of 3.0 m, 5.0 m and 7.0 m this year with the purpose of determination of contaminant progressions in time.

Discussion

Achieved results

The examined locality (its soils and groundwaters) was found to be significantly contaminated, especially by TPH and, to a smaller extent, by VOC-Cl. The most serious contamination by TPH is retained in soil under foundations of the machinery hall No. 115. Contamination by chlorinated hydrocarbons appeared in groundwaters, a higher contamination in borehole HP-3, and a lower one in HP-1.

The nature of the contaminant (see Figs 5 and 6) indicates that the pollution by TPH comes from two different sources. The first seems to be cutting oil, which has a similar hydrocarbon profile of aliphatic and aromatic fractions as both HP-1 oil phase and liquid from the waste reservoir. Most of this oil contamination is spread over the whole area of the hall No. 115. The second source seems to be a naphtha-like degreasing agent. The presence of this contamination is documented by chromatograms of the extractable proportion of a soil sample collected in borehole V-2 from a depth of 0.2 m (see Fig. 6). Characteristic distribution of paraffinic hydrocarbons around $n\text{-C}_{17}$ was observed.

As far as the areal distribution of TPH is concerned, it can be stated that the contamination is relatively evenly distributed over the whole hall No. 115. However, vertical contaminant distribution differs. It is obvious that most of the contaminants are retained by loamy soils under the water table. The contamination at the locality seems to be relatively stable and does not change in time. Collections realised in the immediate vicinity of the original boreholes (V-3, V-4 and HP-5) about a year after initial analyses indicate no remarkable changes in contaminant contents. With respect to the fact that this contamination has a nature of chronic threat, it does not possess significant mobility and is held by soil sediments under the floor of the hall No. 115. Results of analyses of groundwater from the vicinity of the hall imply that no spread of contamination outside the hall takes place, and the groundwater at the locality of interest is not at risk.

Nevertheless, the situation in the case of VOC-Cl content in groundwater is somewhat different. VOC-Cl were found in groundwater taken from borehole HP-3, located outside the hall No. 115. The source of contamination is apparently a storage of paints, situated in the neighbourhood of HP-3. It is worth mentioning that zonal water sample collections from HP-3 did not prove theoretical estimates of vertical distribution of DNAPL-type compounds (denser than water). Theoretically, the maximum contamination should appear at the aquifer base, especially in case of chronic contamination (see the ratio of PCE, TCE and DCE), where DCE predominated (DCE is a product of TCE and PCE decomposition). Here, the vertical distribution is influenced by the presence of relatively impermeable soil sediments, forming hanging wall aquitard of the groundwater body and affecting remarkably the sediment migration capabilities in the vertical direction.

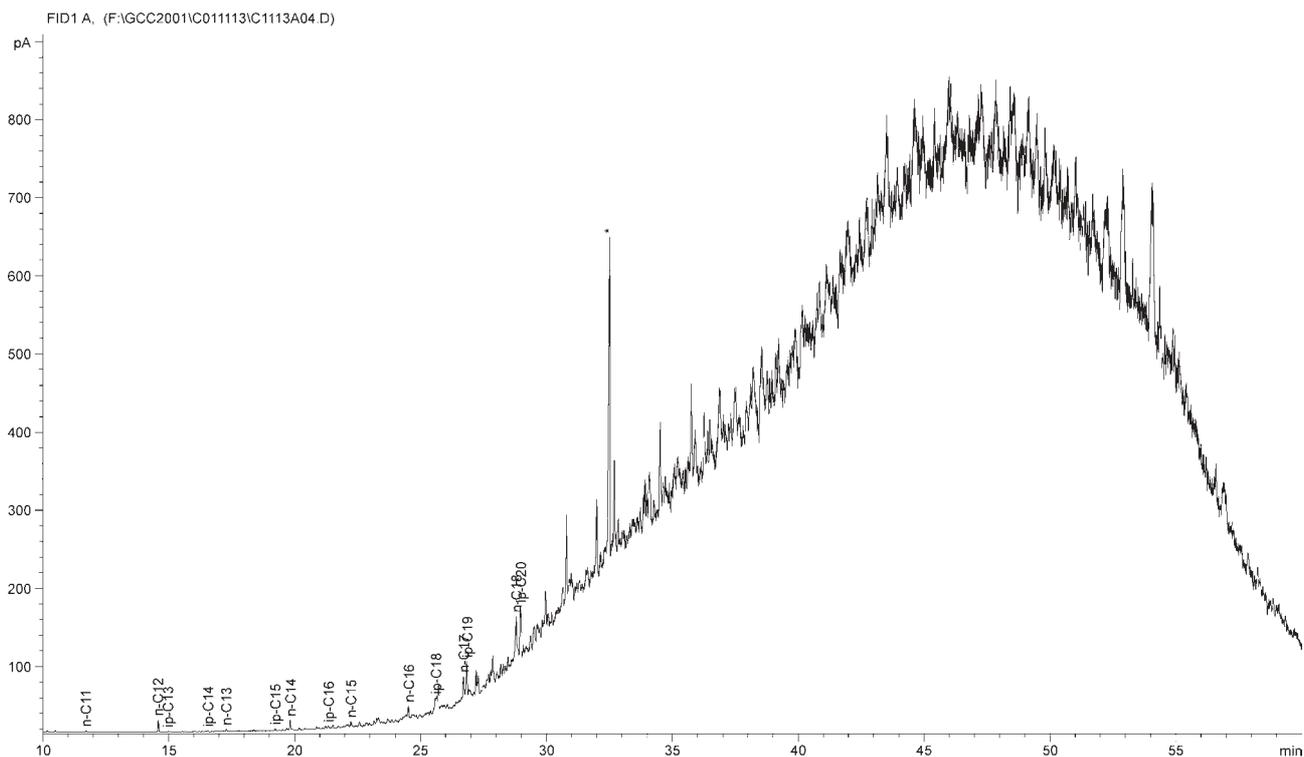


Fig. 5. Saturated hydrocarbons in oil contaminant.

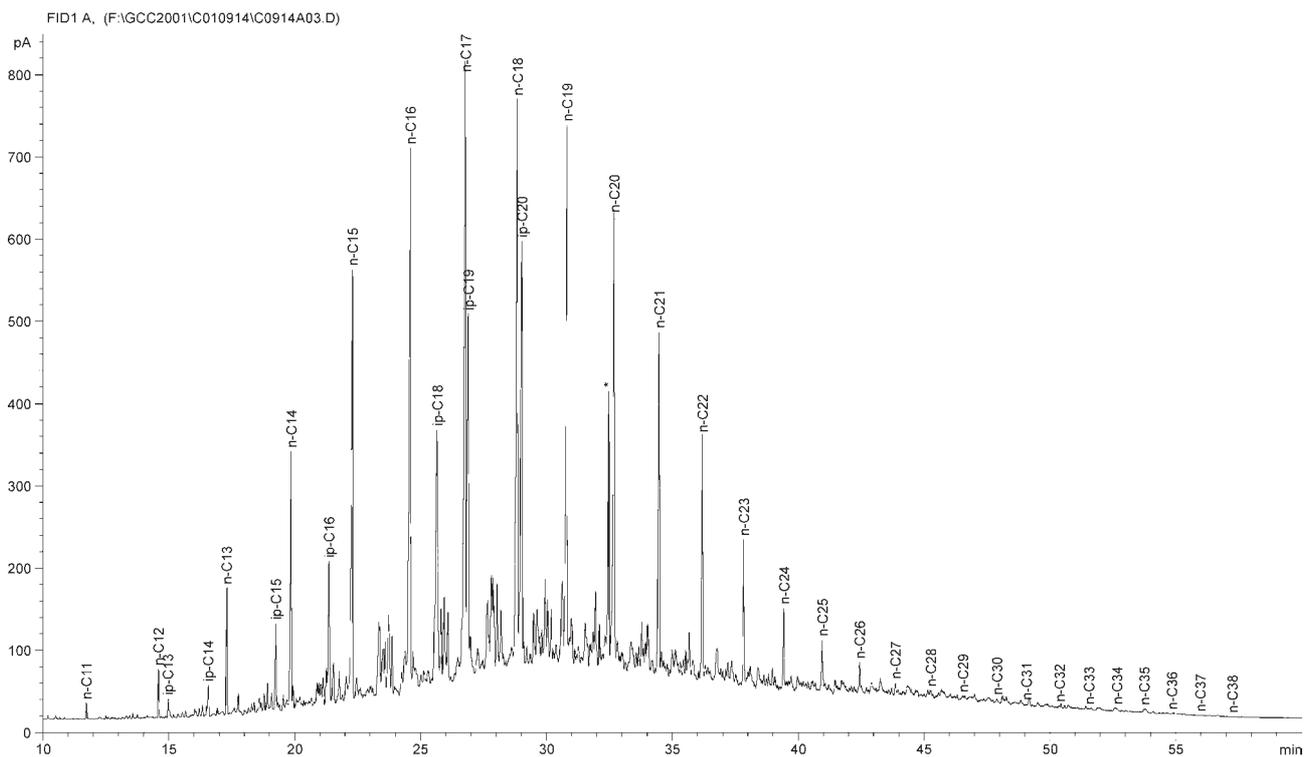


Fig. 6. Saturated hydrocarbons in soil sample V2/0.2 m.

It can generally be stated that the findings obtained during exploratory field works at the chosen locality and from the laboratory analyses are in agreement with the information gained from the literature. It appears that TPH contamination of loamy sediments is relatively stable, especially if infiltration of atmospheric precipitation is hindered (roofed

hall). The contaminant mobility is negligible. This statement can be evidenced by results of HP-1 groundwater analysis, where as little as 90 µg/l of NES was identified. The given value demonstrates minimal solubility of the oil contaminant, whose thickness in this borehole ranges from 1.11 to 1.30 m.

It can be deduced from the obtained results that TPH is not suitable for the contamination monitoring at the localities affected by chronic threat. TPH includes a great deal of compounds, which possess, due to their different physical and chemical properties, different distribution, means and rates of migration in soils and groundwater. From the viewpoint of monitoring of organic pollution in rocks and soils, the most suitable classification of NAPLs (non-aqueous phase liquids) seems to be a division into two individual groups, according to the specific gravity, known as DNAPL (denser than water) and LNAPL (sparser than water).

TPH parameter is also unsuitable for the evaluation of risks, resulting from the presence of contamination at the given localities. Since it is often an undefined mixture of compounds, it is not possible to specify migration capabilities of the given pollution and not at all to determine its toxicological characteristics. Resulting from the nature of TPH analysis, it is not possible to distinguish the quality of pollution, i.e., the toxicity of such pollution cannot be determined. The TPH analysis can therefore cover anything from the occurrence of insignificant amounts of natural compounds to one-species contamination by benzene.

TPH contamination should rather be evaluated as contents of individual specific compounds (e.g., individual aromatic or polyaromatic hydrocarbons) or as particular qualitative types, in case that their physical, chemical and toxicological properties are known. From this point of view, it is necessary to focus more on the methodology of estimation of risks caused by contamination by actual fuels and greases.

Conclusion

By comparing theoretically obtained data with the data obtained during field exploratory works, information was acquired, which led to a better understanding of processes, taking place at the contaminated localities and significantly affecting the possibility, effectiveness and cost of potential remediation works. During the examination of the model locality, it was proven that localities affected by similar

contamination under similar geological and hydrogeological conditions do not pose significant risk of areal contamination spread and jeopardy of individual environmental units in the neighbourhood.

The results achieved by the solution of this partial project section may prove useful in the estimation of the remediation intervention effectiveness and purposefulness of the spent financial resources at analogous localities.

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