

GASOLINE PIPELINE ACCIDENT – MIGRATION OF MTBE, TPH AND BTEX IN A FRACTURED ROCK ENVIRONMENT

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In the beginning of the 1980's, the process of adding methyltertiary-butylether (MTBE) instead of tetraethylplubane to gasoline began. Using MTBE as a fuel oxygenate has become very popular due to its low price and excellent solubility in gasoline. Concentrations of MTBE in unleaded gasoline range between 10–15% of the volume. However, there are significant negatives related to its release into the environment. This contribution describes the behavior of MTBE, BTEX and TPH after the large accidental release of gasoline from product pipeline into the rock environment. Geological composition of the affected site shows the difference of behavior of the pollutants in fractured rock environment and the intrinsic permeability rock environment in time. Remediation process took more than five years and monitoring data were available for the study. By comparing the length of migration of MTBE components with BTEX and TPH components in the rock environment of the locality, the theory that MTBE component migrates faster in geological environment than BTEX components and TPH, has been confirmed. Movement of pollutants in fractured rock environment is several times faster than the intrinsic permeability rock environment on site.

MTBE; groundwater; migration; fractured rock environment; pollution

INTRODUCTION

In the beginning of the 80's methyl tertiary butyl ether (MTBE) started replacing tetra-ethyl lead as a gasoline additive worldwide. Production of MTBE started in the Czech Republic in 1981 and adding into unleaded petrol commenced in 2000. Utilization of MTBE as a fuel oxidant beside the other reactants (ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ethane (TAME) and diisopropyl ether (DIPE)) has become quite popular thanks to low cost and excellent solubility in gasoline. Commonly used concentration of MTBE in unleaded gasoline varies around 10% vol. However, there are also negatives connected with leakage into the environment.

An accident, resulting in leakage of gasoline occurred in June 2001 at the product pipeline in proximity of village Polepy, close the city of Kolin, Czech Republic, Europe. An illegal delivery device, placed on the product pipeline, caused the leak. The total spilled volume of gasoline was about 86,000 liters.

After an accident spillage, large contamination environment and groundwater occurred. The contamination ran through fractured rock environment and then due to the intrinsic permeability of the rock environment to the local watercourse. The pollutant spread mainly via diffusion of gasoline vapors (through unsaturated zone) and in the form of dissolved TPH, BTEX and MTBE by a hydrodynamic dispersion in Cenomanian aquifer (through saturated zone). In term of timing, the extremely fast response in a fracture system of unsaturated zone was detected. Here, spreading of gasoline vapors was detected in effective speed of up to 100 m in 24 hours.

MATERIAL AND METHODS

Site characteristics

The place of the accident is located in the district of Kolin, Czech Republic, Europe, approximately 1.5 kilometers south of the edge of this district town. The place of the accident is located about 500 meters south of the Polepy village community. The location of the leak to the rock environment is located 800 meters southeast from the local watercourse Polepka River.

Geology

From a geological perspective, the area represents a part of the Mesozoic filling of the Czech Cretaceous table. The bedrock is formed of the Kutná Hora crystalline complex that rises above the ground in several places nearby Polepy in the Polepka River valley. The crystalline complex is formed by gneiss. The cretaceous sediments in the surroundings of Polepy village occur as denudation remains of larger and more massive sediments originally lying on top of them. The sedimentation is mostly sandy – sandstone, cobblestone, fine sandy clays, sometimes calcareous sandstone or even limestone. Black claystone occurs in the basal part. The thickness of the Cenomanian sedimentation depends on the relief of the crystalline bedrock that influences the lithological character and sometimes even facial changes in the Cenomanian sedimentation. The average thickness of the sediments in the area is approximately 15 meters.

In most of the area, the Mesozoic sedimentation is covered by quaternary formations. They are especially loess, loess loams, and also relicts of stream terraces.

Tectonic structures on site

A geophysical survey in three 120-meter long profiles was conducted in June 2001 to determine the detailed tectonics on site.

The north–south direction of fracturing was found using the method of resistivity profiling. Besides this basic tectonic direction, the assessed area contains also lateral tectonics in northeast – southwest direction along the river plain of the Polepka River, which represents a drainage base of the monitored area.

Based on the concentration of the contamination of the hydrocarbons, we can suppose that spread of the contamination was taking place mainly along the main tectonic fault zone of the north–south direction (towards the community), from where the contaminant was distributed in the northeast direction to the groundwater extraction wells of house No. 18 through house No. 49.

Hydrogeology

Two aquifers are developed on the locality, at the place of accident. The first aquifer is associated with the fractured-semi-porous permeable sandstone (Cenomanian). Groundwater level is approximately 7 meters below the surface, the thickness of the aquifer oscillates between 1 and 2 meters, and based on survey results, the general direction of the ground water flow of this aquifer body is in the north direction, i.e. towards the local erosion base formed by the Polepka River. The sandstone permeability varies, and increases with an increasing volume of calcium. In areas of sandy limestone, where the fracture system has sometimes even a karst character, the increase in permeability is by one to two times higher than in the sandstone. This circumstance causes the establishment of preferential pathways that were indicated in the direction of the flow of the groundwater by the quick spread of the gaseous as well as liquid phases of the contaminant. There is the bottom-insulating layer developed by 1 to 3 meters thick bituminous claystone throughout the entire area.

The second aquifer is associated with the porous permeable crystalline complexes in depth approximately 14 meters below the surface. This aquifer has unconfined groundwater level in the surveyed area and it is located deep under the soil surface. Toward the Polepka River, in line with the contaminant movement, the fractured first aquifer wanes and the intrinsic second aquifer is developed in the community of Polepy village, approximately 800 meters far from the location of accidental gasoline release.

Spread of the contamination in the rock environment

The contaminant leaked on the soil surface at the place of the accident and consequently migrated through the unsaturated zone towards the water level of the groundwater. Because of the rock formation environment at the place of the accident, the sorption had a great impact on the surface of the rock particles – loess. When spreading through the unsaturated zone, formed in the top part by an 8-meter thick layer of loess loam, all accessible porosity was filled with gasoline. The concentration gradient (at the place of the release, the TPH concentrations amounted generally to higher tens of thousand of mg TPH per kg of solids in the soil) caused vertical diffusion of the contaminant towards the groundwater level. A contaminant plume was created in the area, wherein a significant part of the contamination to loess loam was fixed. A laboratory test was conducted on samples of non-contaminated loess loam to describe the potential of adsorption to the solid phase. Unleaded gasoline was used for the test and the resulting value of the capture to the solid phase (rock matrix) is 13.7 liters of the gasoline per m³ of the loess. At least 50,000 liters of the contaminant was accumulated in the body of the loess loam. Under the layer of the loess loam, a layer of ballast is developed at the place of the accidental release. The horizontal component of the spread of the contaminant through very permeable environment dominated in this layer. The advection flow of the gasoline phase through this layer reached approximately 100 meters from the contamination source, in the south–north direction.

The different thickness of the ballast layer (it wanes towards west) together with the concentration gradient probably caused the establishment of an elliptical body of contaminated ballast with the longer axis pointing from the place of the accident towards the northeast.

The layer of the ballast did not cause a more significant retardation of the contaminant because it has lower adsorption ability to the solid phase (in comparison with loess); it was this layer that caused the extended area contamination of the underlying sandstone.

The sandstone environment is fractured with double permeability. The contamination spreads primarily through the fractures – via preferential paths. At the same time, it penetrates through the diffusion process into the blocks with porous permeability. According to the results of the geophysical measurements, the preferential path is the north–south direction. The contamination spreads in this direction, especially through the unsaturated zone in the form of gasoline vapors, extremely fast. Already the fourth day after the accident, an indication of gasoline vapors took place in building No. 96, 400 meters away from the place of the accidental release. In case of the sandstone formation, in the saturated zone, the contaminant spreads via the preferential path at a significant speed due to hydrodynamic dispersion.

Progress up to now proves an existence of one preferential way – fractured system in Cenomanian sandstones in direction from place of accident through territory of former mining site towards north at slope by buildings

with Nos. 15, 16, 17, and 18. The contamination spreads mainly via diffusion of petrol vapors (through unsaturated zone) and as a dissolved TPH by hydrodynamic dispersion in Cenomanian aquifer.

In term of timing, the quickest response in a fractured system of unsaturated zone was detected. Here, spreading of petrol vapors was identified in effective speed of up to 100 m in 24 hours. Groundwater contamination migrates via preferential way in saturated zone with speed of up to 40 m a day.

Pollutants characteristics

During remediation works, TPH, BTEX and MTBE were detected and monitored in groundwater. Data collected during the monitoring process between June 2001 and April 2005 were used to compare migration speed of those substances.

Theoretical calculation (estimations) of TPH concentrations in soil air during vaporization off a free phase of oil product (at level of underground water or surface of elements) and off a product dissolved in water was conducted. For vaporization off a free phase of oil product, we started from derived Raoult's Law and state equation, while the estimation was based on a simplified model of benzene and pentane (molar ratio 1:1) presence. In case of vaporizing off from water level, in which the product is dissolved (tens of mg TPH per liter) we ran from Henry's Law and similar simplification as in case of the free phase. TPH concentration in soil air above the groundwater level reached almost 10,000 mg per m³.

From above, it is obvious that such a degree of soil air contamination cannot be caused by pollution spread via hydrodynamic dispersion. In terms of balance, phase crossing between contaminated water and soil air (Henry's Law) cannot be a source of such concentration. Source of such a vast contamination in preferential ways is crossing of free-phase / soil air (Raoult's equation).

The residual pollution after excavation of the contaminated soil was estimated at level of 5,000 kg of contaminated soils, groundwater rate of flow was 0.5 l/s (43 m³ per day). Most of the dissolved hydrocarbons were biodegraded; resistant parts (e.g. MTBE) were transported via collector drainage in valley of Polepka and trapped by groundwater pumping.

Data collection

The next step was the selection of objects suitable for data analysis. Two factors were taken into account at the selection. The first one was tectonic conditions and the second was the hydrogeology of the site. Based on those findings, a conclusion was achieved: the contamination itself spreads mainly on N-S direction tectonics. Fractured permeability of rock environment (Cenomanian sandstone) has a minimal significance for comparison of spread of contamination of MTBE and BTEX substances, main-

ly due to a short distance between objects. The selected objects and measured concentrations were charted into map and used in following analysis to compare speed of spread of MTBE and BTEX substances. As object suitable for comparison, monitoring wells P-18 and the extraction well of No. 49 were selected. The distance of the objects was 400 meters. On those objects, monitoring of TPH, BTEX and MTBE concentration was conducted in groundwater for 5 years.

Pumped samples of groundwater on selected objects were collected (sample pump Gigant – Eijkelkamp) after the monitored physical and chemical parameters (temperature, pH, conductivity).

RESULTS

MTBE concentration in monitored objects gradually decreases along the increasing distance from the accident location. In comparison of MTBE migration and BTEX migration it can be said, that in mutual comparison of concentration of those substances, a clear evidence of faster decrease in BTEX concentration is obvious, while faster decrease in concentration occurs in shorter distances.

An outstanding influence on BTEX, MTBE and TPH substances occurrence out of accident has the environmental heterogeneity, here occurring mainly in tectonics structure of the territory by fractured permeability of the rock environment. The graphical outputs below show throughput of the contaminants in selected objects (P-18 and No. 49) between June 2001 and April 2005. Differences in reached maximal concentration of each contaminant in time are evident in the charts. Highly mobile MTBE substances migrated through the monitoring wells first, followed by BTEX and then also by TPH. High migrating capability of MTBE is caused by high MTBE water solubility. MTBE is approximately 30-times more water-soluble than the other dangerous fuel additives (benzene). It does not fix directly to soil; it is chemically stable and moves quickly in groundwater.

Very interesting is impact of environment's heterogeneity on contaminant's maximal concentration in time. In case of monitoring well P-18, placed immediately in the tectonic structure connecting the point of accidental spillage and point of natural drain, the delay of reaching maximal concentration of MTBE and TPH is 5 months. For extraction well No. 49, it reaches as much as 12 months. This fact is caused by position of this object, situated in proximity of natural drain point, in alluvial plain of Polepka River, in porous environment.

DISCUSSION

Due to environmental characteristics, very fast spread of contaminant via preferred ways occurred, not only in liquid phase, but also in vapor phase (hydrocarbon vapors – up to 100 m per day). Fast pollution spread occurred also due to contaminated groundwater (up to 40 m per day).

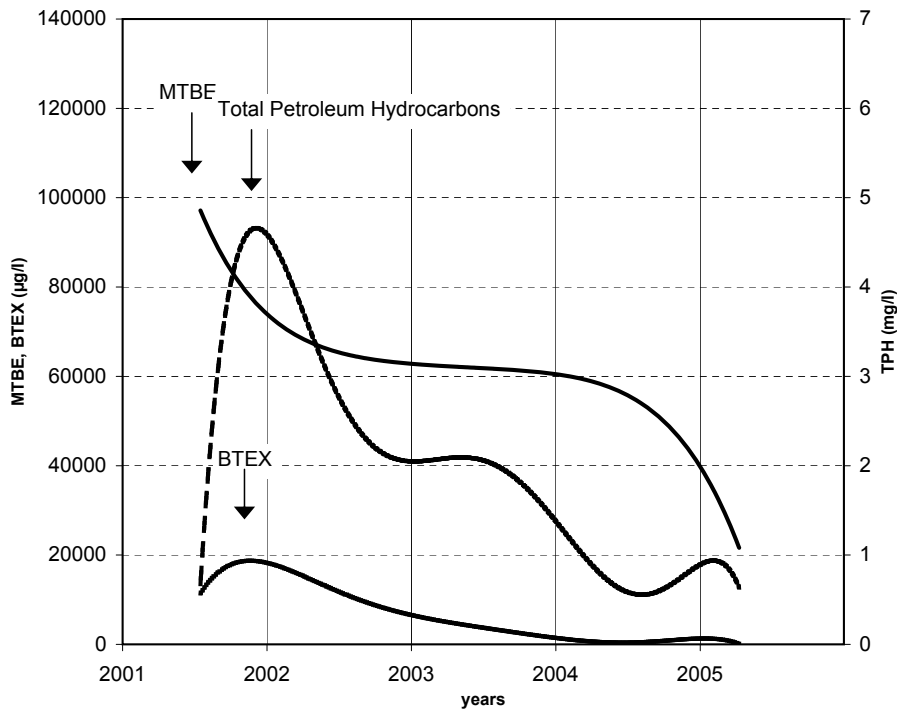


Fig. 1. Concentration of the contaminants (monitoring well P-18) in time

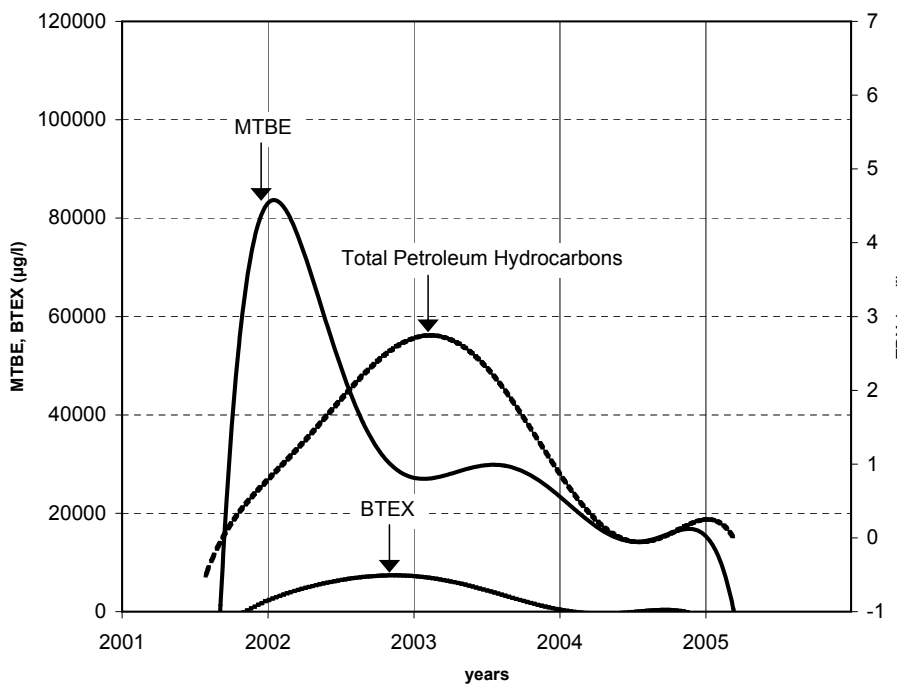


Fig. 2. Concentrations of the contaminants (monitoring well at building No. 49) in time

The highest amount of contaminant remains fixed to unsaturated zone at the point of the accident. Velocity of contamination transport by diffusion depends on difference in concentrations fixed in the rock environment and dissolved in groundwater.

Contaminated soil from this part of site was excavated and disposed off site.

The most dangerous part of contamination was soil-air pollution with hydrocarbon vapors. It is highly mobile fraction of pollution formed by evaporation from the free phase of liquid hydrocarbons. Up to 30,000 liters of hy-

drocarbons could be flowing through the preferred ways. Remediation of soil-air was conducted using soil vapor extraction method, which was very effective on site. Remediation works were supplemented by pump and treat of the first aquifer groundwater with the help of controlled biodegradation. The pump and treat remediation method was focused at the centre of contamination in Valley of Polepka River (home extraction wells). Approximately 84,000 liters of the 86,000 liters totally spilled contaminant were removed from the rock environment by the mentioned methods in total, i.e. 98%.

CONCLUSIONS

Large accidental release of hydrocarbons into the soils and groundwater presents significant damage of local environment. Composition of commercial hydrocarbons like gasoline requires specific attention for design of appropriate and effective remediation action.

Detailed knowledge of local geological/hydrogeological conditions and contaminant attributes are essential for successful problem solution. Fractured rock environment speeds up the velocity of plume several times in comparison with intrinsic porous rock environment on site. Hydrocarbons in the soil gas are detected three times faster than the liquid phase occurred. The velocity of high mobile contaminant (MTBE) is several times higher than the other compounds. The maximum concentrations of MTBE and TPH in the monitoring well No. 18 (fractured rock environment) were reached with a short delay of few months in comparison with the monitoring well No. 49 (intrinsic rock environment) where the delay of the maximum concentrations of MTBE and TPH were detected in one-year period.

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Migrace MTBE, ropných uhlovodíků a BTEX v puklinovém prostředí – následek havárie produktovodu.

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Přidávání metylterciálního butyletheru (MTBE) do automobilových benzinů bylo zahájeno kolem roku 1980 z důvodu náhrady sloučenin olova (tetraetyl a tetrametyl olova). Použití MTBE je velmi populární, protože MTBE je relativně laciné a výborně se v benzínu rozpouští. Obvyklé množství MTBE v benzínu je mezi 10 až 15 objemovými procenty. Bohužel existují i negativní stránky použití MTBE, zejména pokud dojde k úniku do životního prostředí. Tento příspěvek popisuje chování MTBE, BTEX a lehkých ropných uhlovodíků po havarijním úniku z produktovodu do horninového prostředí. Geologická skladba postiženého území ukazuje rozdílné způsoby migrace znečišťujících látek v puklinovém a průlinovém prostředí v čase. Výrazný vliv na rychlost pohybu látek BTEX, MTBE a TPH od místa úniku má heterogenita prostředí, která zde vystupuje především v tektonické stavbě oblasti a tím i puklinovou propustností horninového prostředí. MTBE migruje na větší vzdálenost než látky BTEX (benzen, toluen, etylbenzen a xyleny) a TPH. Neváže se přímo na zeminu, je chemicky stálý a v podzemních vodách je to vysoce mobilní kontaminant. Pohyb kontaminantů puklinovým systémem je také několikrát rychlejší než průlinovým prostředím. Sanační práce trvaly více než pět let a výsledky měření byly k dispozici pro zpracování tohoto článku.

MTBE; podzemní voda; migrace znečištění; puklinové horninové prostředí

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