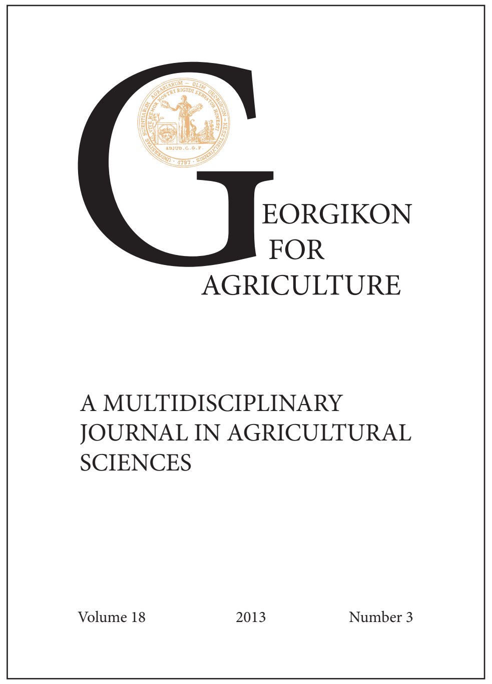

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SCIENCES

Volume 18 2013 Number 3

Content

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NATURAL OIL AS SOIL POLLUTION SOURCE: GENESIS, EXPLOITATION AND PROCESSING

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Abstract

In this paper, the actual problems of oil geology and technology are presented, mainly for specialists in environmental sciences. After a short historic introduction, the genesis of natural hydrocarbons, the process of oil and gas accumulation, the conservation in traps and the geological and geophysical methods of the discovery of the productive structures and their exploration are discussed. The terms like mother rock, reservoir rock, hydrocarbon trap and gas or oil productive structures are explained, too. After presenting the methods and the tools for drilling the oil and gas wells, the way of oil from the production well to the consumers of the oil products – fuels, chemical products – is described: the well head installations, the pipelines, the separation parks, the refineries and the deposits of the oil-derived products. Finally, the "hot spots", where the oil and the oil-based products may cause soil contaminations are discussed.

Key words: mother rocks, reservoir rocks, traps, drilling engines, crude oil, paraffin, soil pollution

Összefoglalás

A tanulmány az olajkutatás jelenlegi állapotát vázolja, főleg a földtan szempontjából, a földtani tudományokban kevésbé jártas környezeti szakértők számára. Rövid történelmi áttekintést követően a természetes szénhidrogének keletkezését mutattuk be, abból kiindulva, hogy ezek képezik a Föld (rég)múltjában bolygónkat érő napenergia szénben és hidrogénben “konzervált” anyagát. Követtük a szerves anyagokat tartalmazó üledékek anyakőzetként való betemetését, a betemetést követő átváltozásokat, amelyek során, megfelelő hőfokot elérve a komplikált szerves molekulákból szubmikroszkópos méretű olajcseppek és gázbuborékok keletkeztek. Ezek vándorolnak (migrálnak) előbb ki az anyakőzetből, majd a pórusos vagy üreges-repedezett (karbonátos) tároló kőzetben, nem egyszer több száz kilométert, addig, amíg kedvező csapdát találnak. Ezekben, elegendő agyagos-márgás rétegek védelmében halmozódnak fel a szénhidrogének és itt keletkeznek a földgáz- illetve olajtelepek. A következőkben részletesen bemutattuk az olajfeltáró kutak fúrásának, és a kutak üzemeltetésének technológiáját, valamint a kőolaj-telep termelékenység szinten tartásának a módját. A finomítókban a nyers olajból kinyerhető párlatok (desztillátumok) felsorolása után követtük az olaj útját a kúttól a felhasználóig és ezzel kapcsolatban rámutattunk a talajszennyezés szempontjából a lehetséges kockázatokra.

Kulcsszavak: anyakőzet, tároló kőzet, csapda, fúróberendezés, nyersolaj, parafin, talajszennyezés

Introduction

It is generally known that natural hydrocarbons such as oil and gas are the most important energetic and chemical raw materials. The modern life style is impossible without them. Therefore, their extraction, processing, transport and distribution in all developed countries represent an important branch of the industrial activity; while on the other hand, it also represents a serious environmental risk factor including soil level pollution.

That is why we believe that introducing some aspects of the genesis, the exploitation and the processing of natural hydrocarbons with their possible environmental consequences would be useful even for those who are not specialists of environmental problems.

1. Short history

The oil seeps and spontaneous gas emissions have been known from ancient times. Herodotos (484–425 BC) mentions the Mesopotamian naphtha sources and the holy fires of Colkhia (Caucasus). The Athenians used flaming naphtha against besiegers during the storming of the city (657 BC). The role of the Colossus of Rhodes was not only lighting the entrance of the port, but to burn the invaders’ ships with hot naphtha. In the ancient times and in the Middle

Ages such military use of natural hydrocarbons were common, but it does not exclude the "civil" uses of them; as medical potions, unguents or as cosmetics and — mainly in the Carpathian region – as cart-grease ("dohot").

By discovering petrol as lighting oil in the first half of the 19th century, research for natural sources started. The Carpathian, Caucasian, Middle Eastern and American oil fields were discovered and studied step by step. By the invention of the internal combustion engine and in the beginning of the 20th century by the serial automobile production the oil industry was busted. By the extension of the known fields, in newly discovered oil belts herds of oil wells appeared and now they invaded the offshore area. Giant refineries were built and the continents were enmeshed by thousand kilometers of pipelines. Now, the oil production is close to 10 billion barrels/year.

2. Oil in the history of Earth: genesis, migration and conservation.

Natural hydrocarbon accumulations along with coal deposits represent the "conservation" of ancient solar energy, hidden in C- (and H-) bearing natural substances. Over more than three billion years, the photosynthesis of some organisms has converted the carbon of the carbon-dioxide and the hydrogen of water into organic components such as hydro-carbonates, synthesized complexes such as N, S, P, K and Mg and other element-bearing macromolecules. After the death of the organisms, these compounds followed a reverse process: they were oxidized, mineralized and the process released CO_2, N, water and mineral salts; with the exception of the buried ones: under favorable P and T conditions natural hydrocarbon formation started in them.

2.1. Oil source rocks

As a consequence, the source of the gas and oil is the organic material that has been buried and preserved in sedimentary rocks. But which organisms are responsible for such a large mass of organic matter? In contrast to the terrific images of sci-fi stories, the main sources of C and H accumulation were microscopic unicellular organisms, e.g. the *Cyanobacteria* group, not Dinosaurs or other giants that were killed by catastrophic Earth events and volcanic eruptions. Now, in each cm^3 of the seawater thousands of such organisms are floating. In some black rocks, other Plankton rests as *Diatomaea, Radiolaria, Infuzoria, Flagellata* etc. (Photo 1) were identified – just like fish scales, bones and whole skeletons as well. The latter is present only as few pieces, without notable contribution to oil genesis, only as "gifts" for oil researcher paleontologists.

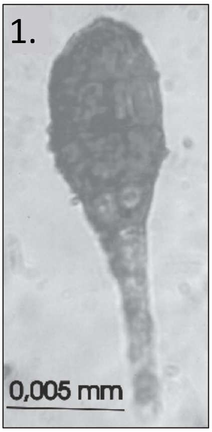

Photo 1.

Photo 2.

The most common organic-rich sediment is “black mud” on the bottom of isolated, anoxic basins (e.g. in the Black Sea below 200 m depth). By the burial and by a wide range of bacterial and diagenetic processes, these sediments were transformed into black shales (disodyle schists, hot shales, phtanites, Photo 2), i.e. as the mother rocks of the oil. These rocks contain hydrocarbons in the form of submicroscopic drops (Figure 1) and bubbles. The content of the CCl_4-soluble organic matter varies between 0.1–5%. Exceptionally, it can reach 15–20% (e.g. Anina-Steierdorf Liassic oil shale in Romania, exploited between 1930–1957 for polar oil extraction (Bucur, 1975)).

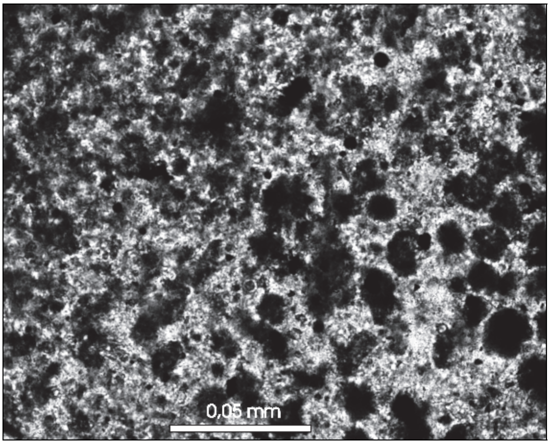

Figure 1.

In the subsurface region, the temperature is the most important factor for turning organic matter into oil. The minimum temperature for breaking the complex hydrocarbon and protein molecule, i.e. for the formation of oil components is ca. 65°C in the depth about 2800 m (Figure 2). Oil is generated from there and is down to about 150°C and up to 5500 m depth of burial. If the source rock is buried deeper, where the temperature is higher than 150°C, the remaining organic matter generates natural gas (Hyne, 2001).

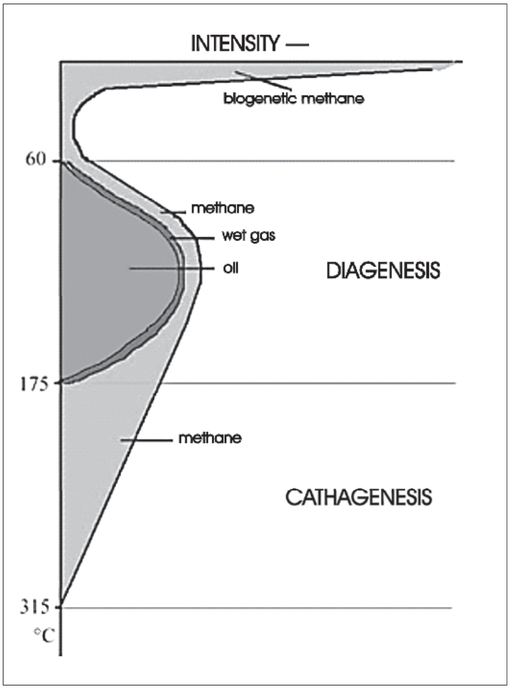

Figure 2.

2.2. Migration: the "birth-way" of the hydrocarbon deposits

The heat-generated hydrocarbon drops and bubbles may follow three ways: (i) by the tectonic and erosion processes the back shale rises to the surface and its organic content oxidizes; (ii) the shale sinks to deeper regions, to metamorphic zones and recrystallizes as mica-schists or black quartzites with a part of carbon being converted into graphite; and (iii) in the optimal zone (see 2.1. sub-chapter) the fluid content of these rocks migrates. At first, it leaves the mother rock, following the submicroscopic pores, micro-fault tracks, strata surfaces, crystal imperfections and dissolution voids. For the second step of the migration permeable rocks are required: sands, porous sandstones, spongeous or vacuolar limestones etc. In these rocks, the hydrocarbon particles unify, forming mobile drops and lenses (Figure 3), which percolate between the voids of these rocks. The mobility of them is assured (i) by the motion of the groundwater in which they are floating; (ii) by the ascension force due to the difference between the density of the water (γ=1.00–1.05) and the oil (γ=0.63–0.86); and (iii) by the "pumping" effect of associated gas. The way of migration can vary from a few hundred meters to hundred kilometers (e.g. from the Tanezuft Silurian hot shales, South Sahara to the Cretaceous sandstones and chalk in Sirte Basin, (Lüning et al., 2000)).

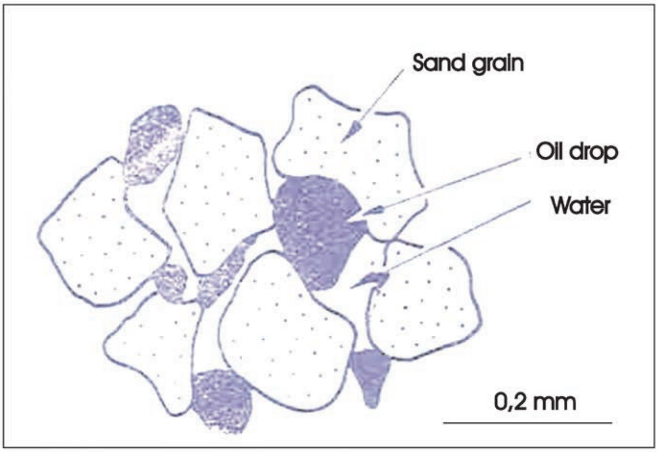

Figure 3.

During its migration, the oil can change its composition and rheological properties, it can loose some undesired compounds (as sulphur), or getting close to the surface, loose the light fractions, resulting in natural wax (ozokerite) and/or pitch (bitumen) seal of the outcropping sandstone level (Derna, NW Transsylvanie; Matița, Eastern Carpathians, Romania).

2.3. Conservation of hydrocarbons in traps

The hydrocarbon deposit, following a more or less long way in permeable sediments as reservoir rocks can be conserved for our use only in case it meets a favorable, closed geological structure, in which it can be accumulated for million years without notable losses (Selley, 1998).

The main property of the reservoir rocks is the permeability both for hydrocarbons and water. We can distinguish two reservoir rock types: porous and vacuolar rocks. To the first category different (dunar, shortline, river and delta) sands, sandstones, less frequently gravels (Figure 4), pyroclastic rocks (Farmos) or weathering crust breccias (Algyő, Ásotthalom, Szank, Hungary; Berettyószéplak – Suplacul de Barcău, Romania (Nicorici, 1974)) belongs.

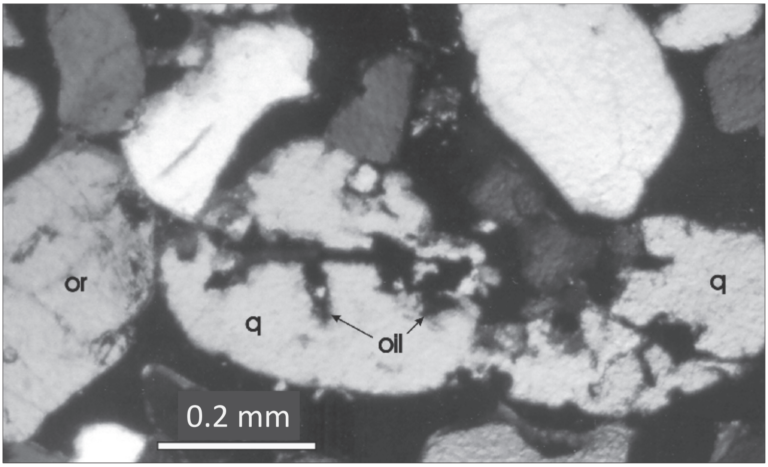

Figure 4.

To the second category mainly carbonate reservoir rocks belong: old reefs, limestone platforms, buried karst, chalk and dolomite deposits, oolitic limestones. They are the most productive reservoirs: the oil fields in Texas, Alberta – Canada, North Sea, Middle East and Indonesian – and in Hungary, the Pusztaföldvár, Hahót and Nagylengyel deposit belong to these rock types.

The main condition of the traps is the presence of an impermeable level that protects the upward hydrocarbon-bearing reservoir rocks (Figure 5). The structure must be closed downward, too with an impermeable bed or by the water table.

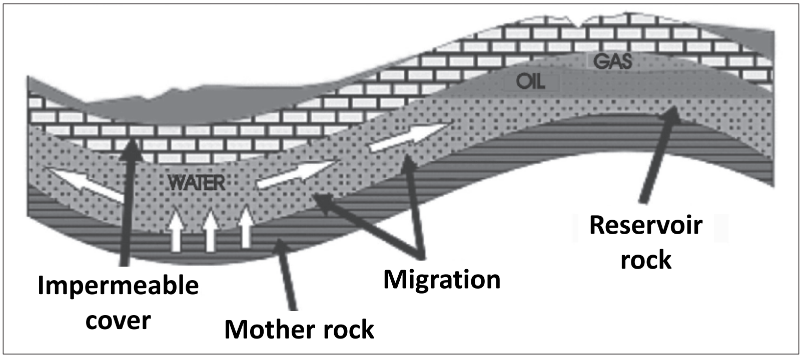

Figure 5.

By surface mapping, by geophysical (mainly seismic) measurements and by the interpretation of well logs, a few hundred trap types were justified. They are classified into three main types: structural traps, stratigraphic traps and combined ones (Chapman, 2004). In the Carpathian area, mainly structural trap types were recognized. Out of the Carpathian belt, the anticline structures, often with diapir salt plugs appear in which the oil and the associated gas are located in Pliocene, Miocene and Oligocene sand and sandstone reservoir rocks. In the Pannonian Basin, large anticlines (with or without fault lines) contain small oil and gas accumulations in Miocene (mainly Pannonian) sandy deposits. Triassic and Miocene carbonatic reservoir rocks and breccias of the Proterozoic-Paleozoic basement (Nicorici, 1972), protected by thick Pannonian marls and clayey levels (Dank, 1985) occur in the Transdanubian, Northern Slovenia (Peklenica) and Eastern Romania (Érábrány, Selénd, Nagyszalonta, Pécska) areas (Figure 6).

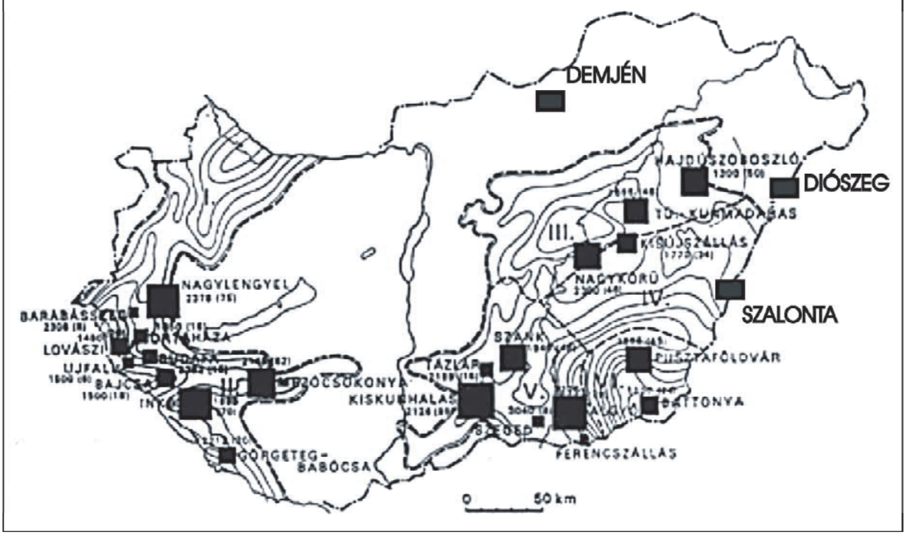

Figure 6.

3. Identification and extraction of oil from the depths

3.1. How were hydrocarbon-bearing structures discovered?

For put in exploitation, the first step is to localize the presumed hydrocarbon accumulation and to estimate their quantitative and qualitative parameters (Emmons, 1931).

As we presented in Chapter 2.3., the hydrocarbon accumulations are situated in structural and/or stratigraphic traps. Because these geological bodies are often hidden under thousand meter thick sedimentary rock formations, geophysics measurement is the main tool for their identification.

The gravimetry method that is based on the density of natural rocks mark the so-called gravimetric anomalies where the gravimetric field of the Earth is smaller (–) or greater (+) than the normal value in the given area. The negative anomalies mark presence of light rocks (e.g. salt domes or diapir plugs), while the positive ones mark increased density, for example when older, heavy rocks rise from the depth, i.e. in nuclei of an anticline structure. Hungarian geophysics played a pioneer role in this matter: the first application of the torsion balance that was invented by Loránd Eötvös indicated the structures of Transdanubia, where industrial oil accumulation was found later.

The position of the strata and the geometry of the presumed structure is determined by the interpretation of seismic profiles. Seismic methods are based on the reflection and/or refraction of elastic deformation waves along lithological boundaries (as stratification, faults etc).

Because the geophysical methods mark favorable structures without any information about their hydrocarbon content, they are combined with geochemical measurements. In air samples that were collected in shallow pits, the presence of volatile hydrocarbons (mainly methane) could be detected by gas chromatography. By this method, a large gas field was contoured by Soviet geochemists in Emba Basin (Northern Russia).

The positive result of the first exploration wells are the justification of the productivity of the proven structures. The presence of hydrocarbons is justified by borehole geophysics and by open well joint tests.

The well geophysics is a system of measurements of some geophysical parameters along drilled wells. The results are presented in geophysical (electric, radioactive, thermal) logs.

The most common logs are the electric ones: a long, depth proportional diagram where in the left side the spontaneous potential, while in the right side the continuous line of resistivity and the dotted line of the gradient are represented. The interpretation of these values make it possible to distinguish the oil, gas or (salt and/or fresh) water content of the permeable rocks as well as the impermeable ones without fluid phase content.

Another method is the radiometric log. In this case the natural gamma activity, the induced gamma, the neutron-gamma and the neutron-neutron radiations are measured.

Because an essential component of the oil is the hydrogen, the spectrum of the neutron activation and the deflection indicate the presence (and the approximate concentration) of oil in the sediment.

The thermometric logs in barren wells put in evidence the inflow of hot or cold fluids, and the back of the casing, the level of the cement ring. Periodic temperature and pressure measurements are made during the exploitation of the oil. The P-T variation in time offers diagnosis about the "health state" of the well and its environment.

3.2. The way of the oil from the depth to the surface

In the beginning, the naphtha was gathered from natural sources (called seeps) or from shallow trenches. In the Extra-Carpathian oil zone, the first lighting petroleum refineries brought the crude oil from 10–30 m deep pits, with grooved pine board liner together with a horizontal oil gallery as it can be seen in Sărata Monteoru oil park, a unique productive oil mine in Europe (Photo 3).

Photo 3.

The first boreholes, drilled for American oil structures, were realized by the Pennsylvanian drilling system. In this engine the rock of the well was broken by a percutant bit and the debris was extracted by a tubular spoon. The protection of the walls was assured by sheet iron casing. Reaching the oil bearing level, the oil was expulsed to the surface by the gas pressure, and was collected close to the well in small trenches and pits. It is evident, that the use of this method involves large soil pollution and, not at least, a high risk of well fires.

Nowadays, for well construction, Rotary method is used. The rock of the structure is loosened by rotating bits, and the debris comes up by the stream of the drilling mud. All of the circulation systems is safe, their rapid closing is possible by an assemble of ventils and valves.

The Rotary drilling equipment consists of the derrick, the rotary table, the drillpipes and the bit (Man. ing. petrolist, III. 1954).

The derrick is a vertical lathwork that moves all the objects that are used by the drawing out procedure of the borehole: the drillpipes, the casing and the tubing of the well by a system of steel cables, pulley blocks and the mechanic winch.

The rotary table is an engine, which turns the drillpipes by the quadrate pipe. At the upper part of the quadrate pipe, the hydraulic head is emplaced, by which the drilling mud is pumped in the well.

The drillpipes are 5–12 m long, strong steel tubes, with rapid screw-thread to bind each other together. The role of the drillpipes is to transmit the drilling force to the bit and to the lead in order to pass the drilling mud towards the working space of the bit. The first drillpipes that are directly up to the bit are the drill collars: heavy, massive pipes with thick walls that assure the verticality of the well.

The oil wells are dug by various types of bits. The simplest bit has a shape of a fish tail, with two, opposite cutting blades, often reinforced by hard metal alloy pellets. It is used by relative soft rocks: clay, shale, marl or friable sandstone levels. These rocks are cut in snail-like slices and disaggregated by the mud jet.

For the traverse through harder rocks, the rolling bits are used, which crush the rock and mill them to fragments, which can be removed to the surface by the mud.

The drilling mud is a suspension of clay minerals, mainly composed of smectites, in which during the rotation of the drillpipes and the pumping engine the solid particles are transported towards the surface. It coagulates, when the flow stops, the particles rest in suspension. This feature of the mud is called tixotropy. To meliorate the tixotropy and other rheological properties, the mud is treated with chemicals. In order to traverse through high pressure oil or water levels, the density of the mud is increased by adding barite or iron oxide powder. The appropriate properties of the drilling mud have high importance; thus, inside the drilling unit, a complete mud and water laboratory functions.

The drilling of a well comprise two or more stages (Figure 7). First, the near-surface, 10–50 m thick, soft sediments are traversed, and the first casing column, 16–22” in diameter is fixed and cemented. It is called the anchorage casing column.

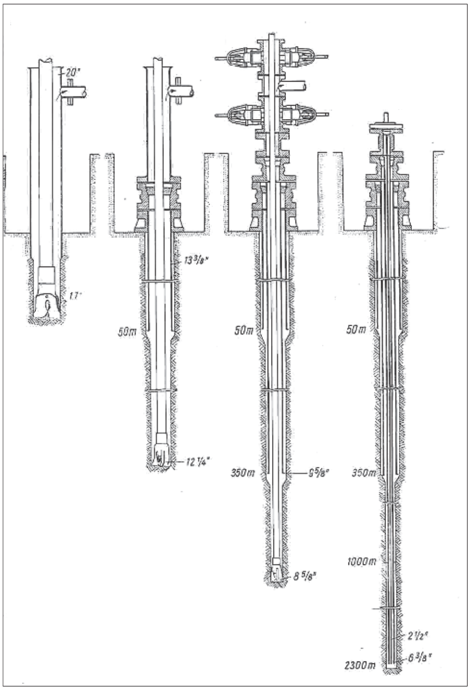

Figure 7.

The next stage is the drill until the head of the cover of the productive level. The hole is lined by a technical casing column, 8 5/8–10 1/2” in diameter and cemented up to the surface. At the head of this casing the prevention valve is assembled. By closing this engine around the drillpipes, the spontaneous eruption of fluids can be stopped in time.

The last stage is due to the traverse of productive levels. The well is lined by the production casing, 6 5/8–5 3/4” in diameter and cemented up to the foot of the technical casing.

In all of situations, the cement ring fixes the casing by filling the space between them and the wall rock. It also isolates the several fluid containing levels.

After the hardening of the cement ring, the casing is perforated in place of the traversed productive level(s), which was (were) established by geophysical logs. A column of tubing 2 1/2 –2” in diameter is introduced in the well, by which the mud is replaced by water. Decreasing the pressure, the oil or the gas (or the salt water) begins to flow towards the surface, in a so called controlled eruption.

In case of low pressure strata, or at the advanced stage of the exploitation, the uplift of the oil must be helped, pressing gas in the space between the casing and the tubing: the oil and/or the water flows out, like soda from the siphon-bottle.

During the exploitation, the pressure of the oil reservoir decreases in time. For a predictable and continuous oil production, it is important to "break" this loss of pressure using recovering procedures. In the gas cap, for the shallow deposits, methane gas, steam, carbon dioxide or thermo-central coal smoke injection is made – or to fluidize the heavy oil, it is heated by electric resistance (like tea electric kettle) or by the local burning of the oil with air injection (Berettyószéplak, Romania).

After the natural reservoir drive has been depleted, water flood and enhanced oil recovering can be attempted to extract some of the remaining oil. The recycled salt water is pumped under pressure down to the injection wells to force a part of the remaining oil through the reservoir towards the producing wells. At the Ţicleni oil field (Romania), the pumping of salt water into a depleted block of Helvetian 1 level, (three wells, called 74 SRP, 75 SRP and 76), the first line produced 500–600 m^3/day/well fluids with 3–5% oil content, in fact total 75 t/day crude oil (and 10–25 thousand m^3 wet gas). It seems, that the injected salt water "cleaned out" the pores of the sandstone, so all of the mobile oil drops could be extracted.

Photo 4.

Step by step, the natural pressure decreases and the hydrostatic level sinks under 500–800 m in depth. In this case, only the pumping of the oil is a rentable method for the extraction (Photo 4). The deep pump is fixed at the end of the tubing column and it is moved up-down by pumping pipes, 1 3/4 – 1/2" in diameter. At the surface, the pumping unit is formed of an electric motor, which actions the balanced fly-well, a pair of slide-bars, moving the balance bar ended by a parabolic piece called horse head. The pumping pipes are fixed to the horse head by a pair of short steel cables, called "horse traces". Traveling to Eger along the highway No. 25, leftwards, between the vineyards, two small pumping units may be seen. They produce oil from Oligocene sandstone, which forms the reservoir rock of the small Demjén structure. From the weakly oil production, two tank cars are filled.

After a well has been depleted, it is plunged and abandoned. Cement must be poured down the well to seal the depleted reservoir and to protect any subsurface fresh water reservoirs. Now, the appropriate sand levels of the abandoned wells are re-utilized as commercial gas reservoirs – or as fresh water sources.

3.3. From the well to the refinery

All fluids from the depth reach the surface through a complicate assemble of taps, pipes and measuring instruments, called “Christmas tree”. The main piece of the Christmas tree is the block valve, a steel or ceramic cylinder, with a calibrated orifice (from 5 mm to 1.2 cm in diameter). The debit and the pressure of the gas, oil or water stream is regulated by the block valve.

An other important piece is the pipe through which the paraffin crust is scrapped out from the tubing. It is known, that when the paraffinic (waxy) crude oil is in the subsurface reservoir where is very hot, the wax occurs as liquid. As it is being brought up by the well, it cools and the waxes solidify. This clogs the tubing in the well and the flow (mixture) lines on surface. The well and the pipeline than has to be shut in for a moreover to clean out the wax – an important oil-based raw material for lubricants, lacquers and paraffin candles.

Several pieces of the Christmas tree are heated with steam or with electric hot oil heaters because of cooling by gas détente and during cold weather.

The fluid from the exit tap of the Christmas tree is collected by a tank in case of exploration wells while for the productive wells it flows towards the separator park through a so called mixture pipe (4–8” in diameter). There is a short cylinder at their heads, which permits the paraffin scraper to be introduced into the mixture pipe called “godevill-car”.

The fluid which is flowing out from the wells is a multi-phase system, a mixture of gas, oil, water and sand particles. They are separated in an installation called separator park. Here the mixture is jetted to a ceramic plaque, which disperses them into small drops. Thus, both the solved gas and the salty water is separated: the “wet” gas is collected in gas pipes or burned, the oil and the salty water is pumped in tanks in which the water and the mineral particles are released by the bottom taps and the pure, crude oil is pumped into the main pipeline of the oil field.

The crude oil of the entire oil field is collected in a central park from which is transported toward refineries. The production of a few tone/day is transported by tank cars or by railway tanks. Three wells had produced four tank wagons of oil each month till 1957 from the Oligocene sandstones in Săcel-Iza field (Maramureş county, Romania). They were transported and discharged in Câmpina refinery. Afterwards, to finish the pipeline of 8” in diameter, all of the oil of Țicleni field (6–7000 t/day) was transported by long oil tank wagon trains to Ploieşti and Pitești. Thus, the Bărbăteni charge station close to Gilort river was the main pollution source for the whole hydrographic basin.

There are many hundred – a few thousand km long oil pipelines, traversing mountainous and desert regions as the pipelines between the Persic Gulf and the Eastern Mediterranean Coast or the newly lied pipeline of 36” in diameter, from the giant Elefantina oil field (Murzuq Basin) to Adjabiya refinery, Libya, crossing Sahara.

3.4. From the refinery to the consumers

The crude oil is not useful: containing light fractions, it is highly inflammable and containing heavy ones, it is improper to be used as motor fuel. It is necessary to separate these components by fractionated distillery (Man. ing. petrolist, IV.1954).

Five types of crude oil may be distinguished: *paraffin bearing*, *aromatic rich* and *asphaltic based crude oil*. The fourth category is represented by *heavy, oxidized oil*, which had lost the volatile components. It is characterized by high content of lubricant and electric (polar) oil fraction. Last, but not least, some oil wells produce a *colorless, volatile product* with pleasant, aromatic smell: it is the so called casing head gasoline, the natural condensed light fractions of the deep situated oil bearing zone.

All of these oil types must be refined for obtain commercial oil products. From lighter to heavier ones, in increasing order of the boiling temperature, these fractions are the following:

1. Low pressure gas. It is obtained by conditioning of the crude oil first to introduce in the fractionation column. It is ~90% methane, about 5% other hydrocarbons, water (steam), nitrogen and carbon dioxide. It is the main fuel for heating the furnaces of the distillery columns.

2. Light fraction: from C2 to C4: the LPG or PB gas. It is obtained mainly in the treatment of the wet gas, in so called degasolinizer stations, by adsorption on porous charcoal pastilles and desorption with steam. In refinery, it is a by-product of low pressure gas.

3. Gasoline (“benzin”) fraction: from C5 to C10 one, having as main component the octane C8H14. The Octane Number of the gasoline-type fuels is the main characteristic of their quality.

4. Kerosene or lighting petrol fraction (C10–C16) gives the fuel of planes and of reactive engines; in the past, it was the fuel of the old, nostalgic paraffin lamps.

5. The Diesel fraction (C16–C24) is the fuel of powerful trucks, locomotives and ships. Now, the Diesel oil-rich crude oils are the most useful ones, because the price of this fuel is increasing continuously.

6. The “black oil” (up to C25) is the liquid fuel of central-heating, and in the past, for steam locomotives (“pacura”). Now, it is the raw material for synthetic (cracking) fuel: by pyrolize, with or without hydrogen injection, the long hydrocarbon ranges are brooked to obtain lighter, useful oil fractions. The paraffin (see Chapter 3.3.) and the black bitumen for running cover of the sealed ways are also obtained from this heavy fraction.

The different fractions of refineries are transported out of the localities by pipelines toward fuel deposits in cylindrical or spherical tanks, with high level of security. Other pipelines, floats of tank-cars and tank wagons serves the consumers: gasoline stations, railway terminals, airports and chemical plants. The long way of hydrocarbons ends in the cylinder of the internal combustion engine or in reaction tanks of certain synthetic lacquer plant.

4. The hot-spots of oil pollution

Under optimal conditions, the oil and its products do not see the blue sky only as exhaust pipe smoke — but the reality is much worse: there are a lot of escape points though which they can invade the environments, including the fertile soil levels. Following the way of the oil from the depths till the consumers, we suggest these “hot points” (Figure 8).

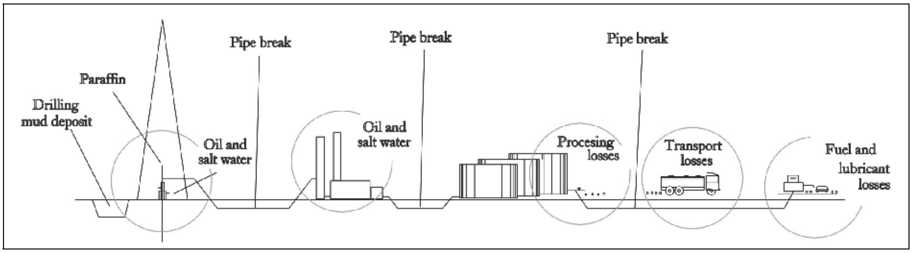

Figure 8.

4.1. The well

Drilling of oil, gas or water wells bear the risk of pollution.

During the drilling operation, the mud is the main pollution agent. The natural, clay containing mud is rather a fertilizer, having high content of smectite clay minerals and silica-gel, with neutral or slightly basic pH. But introducing some chemicals (tensio-active and/or anti-coagulants), and as well barite powder, the mud becomes pollutant. Therefore, the abandoned mud-filled trenches pollute the soil, mainly those having traversed productive levels with oil content or water-bearing levels with high salt concentration.

The successive essay of the presumed oil or gas-bearing strata in the exploration wells is another pollution source: the spreading of the oil-gas-water mixture, before it is transported to the tanks or pipes. Finally, in the depleted oil fields, in case of improper cementation of the casing system, the abandoned wells may lead to local pollution by oil or salt water escapes.

As for the stage of exploitation, the main sources of oil pollution around the wells are the oil jets that escape during such interventions as temperature and pressure measurements, valves and tapes changing of Christmas trees and the deep pump of pumping wells, as well as the launch of the paraffin scrapers into the tubing and into the mixture pipeline. These “small” amounts of the pollutants accumulate in the course of time: in 30–50 years or more, the whole area of the oil field became a semi-desert environment, with rare, sick vegetal cover and sterile soil level (Photo 4).

The uncontrolled, “free” well outbreaks that spread oil and salt water on large areas present major catastrophic pollution events affecting hundreds of hectares and in case the jet goes up in flames (Figure 9), the whole vegetation of the affected area can be burned down.

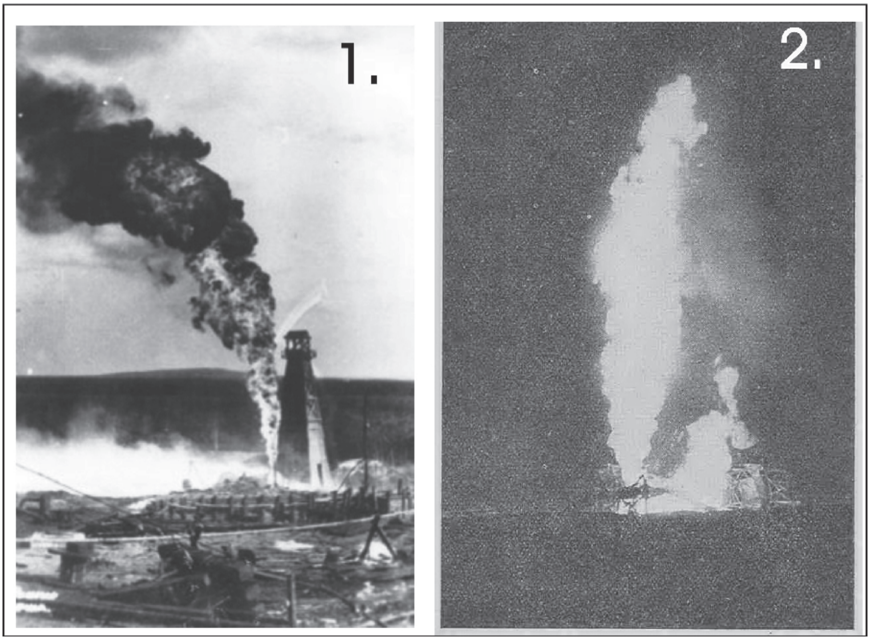

Figure 9.

4.2. The separator parks and the pipelines

In the separator parks, the whole courtyard is insulated by concrete cover. Unfortunately, there is no absolutely impermeable or fissure-free concrete. As it has already been mentioned, during the exploitation of the oil field, even half a century later, small quantities of oil and salt water can filtrate into the soil of the surrounding areas.

Despite the anti-corrosive (cathode) protection, the steel pipelines may be perforated over time. The fluids can escape through the records and the damaged soldering seams. Landslides, as well as unauthorized excavations on the track of the pipelines can crush the pipes so that the fluid content gets into the environs.

4.3. The refineries and the deposits

In these industrial objects, the soil is protected against the filtering of the oil products by thick concrete floor and by high earth and concrete walls. High level of fire safety and counter-terrorist measures assure their protection. However, unexpected natural events (typhoons, earth quarks, tsunamis) and technical accidents may occur followed by serious environmental consequences. For example, in 1978, in a high-pressure cracking unit of the Piteşti refinery (Romania), due to an inadequate pressure control an all-destroying explosion occurred. Hundreds of workers lost their lives and the environment was highly polluted.

4.4. Fuel pipelines, truck tanks and deposits

Apart from the risks presented for crude oil (and gas) pipelines (chapter 4.2.), the fuel pipelines are presumed pollution sources, not because of the natural or technical damages, but because of the fuel stealers. In despite of active, air borne and land patrols, in despite of sensible pressure and debit measurements, they dug long subsurface galleries and “milk” hundred tones of fuel from the pipeline, without problems of environmental pollution.

During the transport of the fuel and other oil-based chemicals, pollution may occur at the charging and discharging stations of the tank trucks and wagons, as well as in case of route and railway accidents.

Finally, some gasoline stations and other consumers release more or less hydrocarbons to the environment. For example, large areas of the former Soviet air bases show high level of kerosene pollution.

The detailed physical and chemical processes within polluted soil particles and in their pore space will be presented in the next papers of this volume.

Conclusions

In order to recognize the origin and the nature of oil pollution, we presented the genesis, the evolution and the geological condition of oil (and gas) accumulations. We described the mother rocks, the reservoir rocks and the hydrocarbon-bearing stratigraphic and structural traps, the diagenesis of the organic matter, the migration of hydrocarbons within the mother rock and out of them through porous or fractured rocks till they accumulate in productive structures.

The geologic research and the technical means to find an oil field and to start its exploitation are described, too. The well drilling techniques and tools, the phase of the exploitation of oil fields and the way of the crude oil from the well to the fuel consumers are shown, pointing out the “hot-spots” of oil pollution along this way. The risk factors of the oil pollution of the soil level involve natural (geological), technical and antropogene, accidental ones.

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PAH DEGRADING CAPABILITY OF MICROBES ISOLATED FROM HYDROCARBON CONTAMINATED SITES

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Abstract

The polyaromatic hydrocarbons (PAH) are occurred in petroleum, petroleum derivatives, or its products and come off from the incomplete combustion of organic matters. These compounds are hardly degradable (persistent) in the environment. Human health risk of PAHs caused by their mutagenic, teratogenic and endocrine distrupting effects. Seven PAH compounds were identified as human carcinogenic by WHO, IARC and US EPA. The aim of our work was to look for microorganisms, which can be applied for biodegradation of PAHs.

Bacteria were selected from the microbial culture collections of SZIU, Department of Environmental Protection and Environmental Safety. These microbes were previously isolated from soil and groundwater samples of Hungarian hydrocarbon (TPH, BTEX, PAHs) contaminated sites. The PAH degrading ability of chosen microorganisms were tested in three steps. In the first step, the method of Chinese researchers (Zhao et al., 2009) was used for screening the collection with three compounds [benzo(a)pyrene, benzo(a)anthracene, fluoranthene] to select possible degrading strains. In the second step PAH containing shaking cultures were used to verify degrading ability of the selected strains *in vitro*. Strains were paired for increasing degradation rate because, by the results of scientific references, a mixture of strains generally have improved degrading ability. Prior strain pairing tests were performed to analyze the multiplications of selected microbes together in mixed cultures. The third step was a degradation and soil respiration test (OxiTop, WVR International Inc.) with PAH and TPH polluted soil sample from a Hungarian contaminated site. The intensification of respiration and PAH degrading were compared between the control, and inoculed (with strain pairs) ones. Our results could lead to the creation of a PAH degrading inoculum, which can be used in contaminated sites, *in vivo*.

Keywords: polycyclic aromatic hydrocarbons (PAH’s), PAH degrading microbes, biodegradation

Összefoglalás

A poliaromás szénhidrogének, mint szennyezőanyagok, kőolajokban, kőolajszármazékokban, illetve termékeiben előforduló, valamint szerves anyagok tökéletlen égése során keletkező vegyületek, amelyek nehezen lebonthatóak, perzisztensek. Környezetvédelmi jelentőségüket növeli, hogy humán egészségügyi hatásaikat tekintve eddig hét PAH vegyületről bizonyosodott be humán karcinogén hatás, továbbá egyeseknek mutagén, teratogén, valamint hormonháztartást zavaró (EDC) hatásaik is ismertek. Munkánk célja olyan mikroszervezetek keresése volt, melyek okszerűen alkalmazhatóak PAH vegyületek biológiai lebontására.

Ennek érdekében a Környezetvédelmi és Környezetbiztonsági Tanszék törzsgyűjteményének felhasználásával olyan mikroba törzseket választottunk ki, amelyeket korábban kőolajszármazékokkal (TPH, BTEX, PAH) szennyezett területekről (talaj-,

talajvízmintákból) izoláltak. A kiválasztott mikroszervezetekkel több lépésben bontási kísérleteket végeztünk, amelyek során degradációs képességüket vizsgáltuk. Az első lépésben kínai kutatók (Zhao et al., 2009) módszerét használtuk három PAH vegyület [benza(a)pirén, benz(a)antracén, fluorantén] esetében, hogy kiválasszuk a potenciálisan bontásra képes törzseket. A második szakaszban rázatott mikroba tenyészetet alkalmaztunk annak érdekében, hogy a törzsek PAH degradációs képességét elemezzük *in vitro*, folyékony közegben. Ehhez törzspárokat állítottunk össze, amelyekkel a kísérletet megelőzően együttszaporítási vizsgálatokat végeztünk, mivel az irodalmi adatok azt bizonyítják, hogy a törzskeverékek általában nagyobb bontási képességgel rendelkeznek PAH vegyületek esetében. A harmadik munkaszakaszban OxiTop talajrespirációs vizsgálatot végeztünk két ismétlésben PAH, és TPH szennyezett kárhelyről származó talajmintán. Eredményeim megalapozzák egy olyan oltóanyag kialakítását, amely PAH vegyületekkel szennyezett kárhelyeken *in vivo* használható.

Introduction

Total Petroleum Hydrocarbons (TPH) are one of the most common group of organic contaminants in the environment, originated from crude oil. These contaminants contain only hydrogen and carbon atoms linked with aliphatic covalent bonds. The group members have 5-40 carbon atoms, which can be divided into two groups. One of these groups has 5-10 carbon atoms, which are VALPH (Volatile Aliphatic Petroleum Hydrocarbons) compounds, and the rest of the group is non-volatile EPH, (Extractable Petroleum Hydrocarbons). The increase of the carbon atom’s number the bioavailability, and biodegrability reduce.

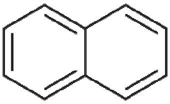

Figure1. Naphtalene

Polycyclic aromatic hydrocarbons, also known as poly-aromatic hydrocarbons (PAHs) which are included in petroleum, petroleum derivatives, or its products and occur during the incomplete combustion of organic matters. Nearly 200 compounds are belonging to this group. PAHs are built up with two, or more benzene rings, where these condensed aromatic hydrocarbon rings have common carbon atoms. The simplest polycyclic aromatic hydrocarbon is the only volatile PAH, naphtalene, which is built up with two benzene rings (Figure 1). Until three benzene rings PAH compounds are generally considered as well biodegradable. Above this number, the degrability, the water solubility, and the bio-avability are reduced. PAHs with more than three benzene rings are often referred in bioremediation literature as high molecular weight PAH's (Kanaly et al., 2000). Some of PAH compounds are belonging to POP (Persistent Organic Pollutant) compounds (http1). These hardly degradable materials in the environment could be accumulated in living organism (bioaccumulation). Human health risk of PAHs, caused by their mutagenic, teratogenic and endocrine distrupting effects (EDC), improve the environmental importance of these compounds. The possible degradation of PAH compounds is catalyzed by the microbial monooxygenase, dioxygenase enzymes.

Different groups of fungus, and bacteria use these proteins to degrade hydrocarbon compounds. Some of these bacteria are belonging to the Genus *Acinetobacter, Achromobacter, Pseudomonas, Bacillus*, *Rhodococcus*, (Anton, 2010; Haritash and Kaushik., 2009; Kim et al., 2007). Furthermore *Pseudomonas*, and *Sphingomonas* species are capable to degrade anthracene, fluoranthene, and benzo(a)anthracene (Mrozik et al., 2003; Schneider et al., 1996). Other researches have found that 85% of benzo(a)pyrene degraded by *Bacillus subtilis* (Lily et al., 2009). *Mycobacterium*, *Novosphingobium, Arthrobacter* strains were successfully used for degradation of poly-aromatic hydrocarbons (Willumsen et al., 2001; Kallimanis et al., 2009; Yuan et al., 2009). Most published research works have been shown, that microbial consortiums are capable to degrade high molecular weight polyaromatic hydrocarbons (Luan et al 2006, Yu et al 2005).

In our work microorganisms isolated from Hungarian hydrocarbons polluted sites were tested in our PAH degradation experiments. It was assumed that these microbes are able to stay alive in these contaminated matrixes, thus they have possible hydrocarbon degradation potential. These microbes are deposited in international strain collections, furthermore they are members of two different strain culture collections (SAFEREMED, INOSAFE) in the SZIU, Department of Environmental Protection and Environmental Safety (Table 1). The strain collections are made up of non-pathogenic, identified and taxonomical classified species. The degradation profiles of these microorganisms are well known, as well as tolerance against heavy metals. The biodegrading ability was verified in contaminated sites.

Table 1. The members of the strain collection

SAFEREMED	AK-35	*Rhodococcus erythropolis*
	AK-36	*Rhodococcus globerulus*
	AK-37	*Rhodococcus pyridinivorans*
	AK-38	*Rhodococcus gordoniae*
	AK-40	*Rhodococcus rhodochrous*
	AK-44	*Rhodococcus aetherivorans*
	CHB-15p	*Rhodococcus pyridinivorans*
	CHB-20p	*Chryseobacterium hungaricum*
	NCP-3	*Pseudomonas putida*
	NCAIMB-1494	*Pseudomonas putida*
INNOSAFE	TBF2/20.2	*Olivibacter oleidegradans*
	ZFM 23.1	*Rhodococcus erythropolis*
	S-8	*Rhodococcus ruber*
	OM-7.2	*Rhodococcus erythropolis*
	SZM5/4.2	*Pseudomonas mandelii*

The aim of our work, was to seek microorganisms from this two strain collections which can be applied for degrading high molecular weight polyaromatic hydrocarbons, such as benzo(a)pyrene, benzo(a)anthracene, and fluoranthene. Furthermore pairing tests were made for consortial use of these degrading bacteria.

Methods and Material

The TPH and PAH degradation capability of the members of these two strain collections was examined on compounds by an own improved experimental system. The steps of our system are demonstrated on the figure below (Figure 2.). As follows the figure is described in details.

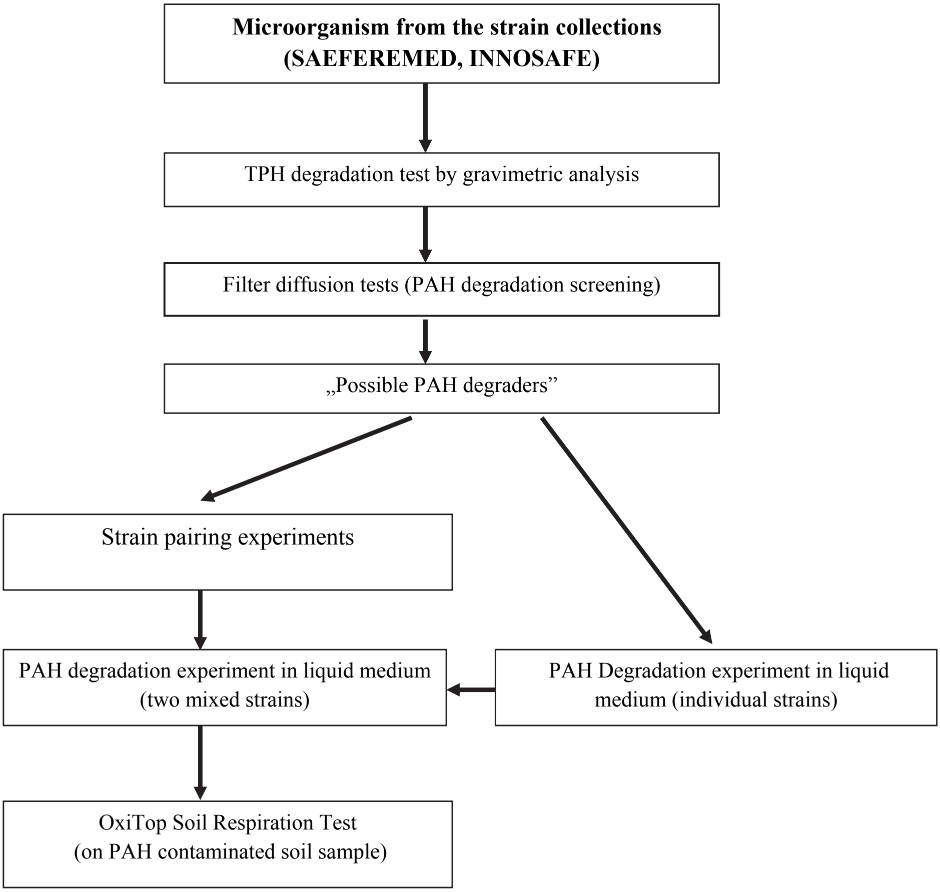

Figure 2. The elaborated experimental system for screening of degradation of PAH compounds

Gravimetric analysis

Individual bacteria were transferred from the collection to nutrient agar slant. After incubation time (24h) the prepared microbe colonies were washed into 50 ml liquid medium (LB medium) with sterile glass stick. The inoculated Erlenmeyer flasks were being shaken during 72 hours at 28°C with170 rpm. From these shaked cultures 5-5 ml of the suspension was placed into 100ml OIR-III liquid medium, [5.0 g $(NH_4)_2SO_4$; 1 g K_2HPO_4; 0.5 g KH_2PO_4; 0.5

g $MgSO_4 \times 7H_2O$; 0.2 g $CaCl_2 \times 6H_2O$, 0.01 g $FeSO_4 \times 7H_2O$, 1000 cm^3 distilled water, sterilization: 121 °C, 1 bar, 15 minutes]. 2 ml of a mixture of diesel and crude oil (approximately 1.7 g) was used as single carbon source that were put into the medium. Next to the inoculated samples the same gas oil – crude oil mixture filled OIR-III medium was applied with no bacterium suspension as control. The flasks were being incubated during 120 hours at 28°C and shaked at 170 rpm.

After the incubation the contents of the Erlenmeyer flasks were poured into glass shaker funnel. It was washed with organic solvents (petrol ether, chloroform) and the rest oil was separated. The oil quantity of the inoculated and the control samples were compared and the degradation percentage was described.

Filter Diffusion Test (PAH degradation screening)

The primary aim of this experiment was the selection of possible PAH degrading microbes from the strain collections. Chinese researchers (Zhao B. et al 2009) method was developed for this test. Degrading capability of the bacterial strains with three PAH compounds [benzo(a)pyrene (BaP), benzo(a)anthracene) (BaA), fluoranthene (Flu)] was screened.

As a first step four Millipore filters (d=2.5 cm) with 0.45 μm pore (MERCK Millipore cat. no. HAWP02500) were put onto OIR-III (1.5 v/v% agar) mineral medium (in Petri-dishes) with sterile clips. Three PAHs in 5000 ppm concentration were prepared in stock solutions, dissolved in diethyl-ether. 100 μl of the prepared PAH stock solutions were streaked onto the filter by sterile glass sticks. The fourth was the control treated by only diethyl-ether. After 5-minute drying in exhaust cabinet the solvent evaporated and then 100 μl of the bacterial suspension was streaked onto the four filters. Previously the individual bacterial suspensions had been inoculated on LB agar (10 g tryptone; 5 g yeast extract, 10 g NaCl; 18 g bacteriological agar; 1000 cm^3 distilled water). The suspension of the inoculum was set to OD_{600}=1 in the experiment. If bacterial colonies were formed on the filters that treated with the three different kind of PAHs that noted as “probably PAH degrading” strain.

Strain pairing tests

24-hour, pure cultures of individual bacteria from the strain collections were transferred on native agar medium slant. After the incubation (28°C), the prepared microbes colonies were being inoculated into 50 ml liquid medium (LB medium) with sterile glass stick. The inoculated Erlenmeyer flasks were being shaken during 72 hours at 28°C and 170 rpm. The suspension of the inoculum was set to $OD_{600=}$0,6 in every case. 2.5 ml of this suspension was injected into LB liquid medium then we determined the number of living cells with pour plate technique in every 24 hours. The Petri-dishes were incubated at 28°C and after 96–120 hours. The number of colonies were counted on the dishes by the presence of the different morphology.

PAH-degradation in liquid medium

Based on the screening analysis (PAH Filter Diffusion tests) another experimental system was started where those strains were examined in liquid medium which could form colonies on the filters. The incubation time was 21 days at 28°C and 170 rpm. In this case we used only individual strains to analyse the degradation. After the 14- and 21-day incubation times the samples were sent to analytical examination to an accredited Hungarian analitical laboratory (Wessling Hungary Kft.).

In the next section, two microbes in a mixture were shaken in liquid medium in order to analyse their PAH-degradation capability in liquor. Pairs of strains were selected by the results of above mentioned strain pairing tests. Stock solutions from the three PAH compounds, benzo(a)pyrene, benzo(a)anthracene and fluoranthene in 15 mg/ml concentration was prepared. In this case 300 mg from each compound have been dissolved in 20 ml acetone. Then 500 µl from each stock solutions were filled into 300 ml sterile Erlenmeyer flasks under exhaust cabinet. After the evaporation of the solvent it was poured up with 45 ml Bushnell-Haas medium (0.2 g $MgSO_4x7H_2O$; 0.02 g $CaCl_2x2H_2O$; 1 g KH_2PO_4; 1 g K_2HPO_4; 1 g NH_4NO_3; 0.05 g $FeCl_3$; 1000 cm^3 distilled water), that contained Tween80 detergent in 1 v/v%. 2.5 ml of each suspensions of the strain-pairs were injected into 45 ml Bushnell-Haas liquid medium contained all the three PAH compounds. Thus the PAH-concentration of the 50 ml medium has been 450 ppm (150 ppm of each Flu, BaP, BaA).

The incubation period was 14 days at 28°C and 170 rpm. Bushnell-Haas liquid medium contained only PAH compounds was used as control in equivalent concentration without any bacterium suspension.

Soil respiration and PAH degradation tests in OxiTop system

These experiments were carried out in OxiTop pots that are able to track respiration of soil.

The OxiTop is able to count the emission of CO_2. Since in the closed system the CO_2 derived from the soil respiration is consolidated in NaOH solution. As a result of this, micro-vacuum arises in the closed system and the registered reduction of pressure could show the activation of bacterial respiration of soil samples. In the closed system the changes of pressure is noticed by the head part of the instrument without disturbing the sample.

The soil sample was originated from a Hungarian hydrocarbon contaminated area (near Szank). The texture of the hydrocarbon compounds (TPH, PAH) contaminated soil was sand. 150 g of the soil samples were inoculated by the mixture of two strains. Strain pairs were selected by the results of strain pairing tests. Strains from 24-hour agar slants were put into 50 ml TGE-5 liquid medium (tryptone: 5.0 g; yeast extract: 2.5 g; glucose: 5.0 g; 1000 ml distilled water) with sterile glass stick. The inoculated medium was incubated during 48 hours at room temperature and mixed with 150 rpm. After this shaking period the cell density was set to OD_{600}=0.6 with sterile liquid TGE-5 medium. The homogenized, sandy, contaminated soil sample was inoculated with 2.5 ml of both strain suspensions separately. This OxiTop pots had two repetitions. The incubation period was 14 days. In this experiment AK-35 + AK-38 (*R. erythropolis* + *R. gordoniae*), AK-38 + NCP-3 (*R. gordoniae* + *Pseudomonas putida*) and CHB-15p + AK 40 (*R. pyridinivorans* + *R. rhodochrous*) strain pairs were applied. We had three repetitions and a control without any treatment.

Results

The results will be presented by the above shown steps of matherials and methods. The partition of sub-chapters is following the own prepared system of experiments (Figure 2.)

Gravimetric analysis, Filter Diffusion tests

As it can be seen in Table 2., the hydrocarbon degrading capacity of AK-35 *(Rhodococcus erythropolis*), AK-38 *(Rhodococcus gordoniae*), AK-40 *(Rhodococcus rhodochrous*), AK-44 (*Rhodococcus aetherivorans*), TBF2/20.2 *(Olivibacter oleidegradans)* are up to 50% by the gravimetric analysis. By the results of filter diffusion tests AK-35, AK-37 (*Rhodococcus pyridinivorans)*, AK-40, AK-44, and CHB-15p *(Rhodococcus pyridinivorans)* were able to grow on benzo(a)pyrene, benzo(a)anthracene, and fluoranthene treated filters from the microbial collection SAFEREMED. Only one microbe (TBF2/20.2) from the strain collection INNOSAFE was able to form colonies on the PAHs containing filters.

Table 2. The hydrocarbon (TPH) degrading capacities of tested strains and their growth on filters treated with PAH compounds (Filter Diffusion tests)
*: Average of 3 measurements
BaP: Benzo(a)pyrene, BaA: Benzo(a)anthracene, Flu: Fluoranthene

	Strains	**Species**	**TPH Gravimetric analysis ***	**Filter Diffusion tests**		
			Degrading capacity (%)	**BaP**	**BaA**	**Flu**
SAFEREMED	AK-35	*Rhodococcus erythropolis*	**65.55**	+	+	+
	AK-36	*Rhodococcus globerulus*	35.57	-	-	-
	AK-37	*Rhodococcus pyridinivorans*	26.96	+	+	+
	AK-38	*Rhodococcus gordoniae*	**73.30**	-	-	-
	AK-40	*Rhodococcus rhodochrous*	**69.25**	+	+	+
	AK-44	*Rhodococcus aetherivorans*	**53.40**	+	+	+
	CHB-20p	*Chryseobacterium hungaricum*	n.d			
	CHB-15p	*Rhodococcus pyridinivorans*	n.d	+	+	+
	NCP-3	*Pseudomonas putida*	22.11	-	-	-
	NCAIMB-1494	*Pseudomonas putida*	n.d	-	-	-
	DSM 7226	*Brevundimonas vesicularis*	n.d	-	-	-
INNOSAFE	TBF2/20.2	*Olivibacter oleidegradans*	**58.33**	+	+	-
	ZFM 23.1	*Rhodococcus erythropolis*	37.19	-	-	-
	S-8	*Rhodococcus ruber*	19.82	-	-	-
	OM-7.2	*Rhodococcus erythropolis*	37.80	-	-	-
	SZM5/4.2	*Pseudomonas mandelii*	n.d			

Strain pairing experiments

Until the end of our work 6 strain pairs were examined and just AK-35 + AK-38, AK-40 + CHB-15p, as well as AK-38 +NCP-3 strain pairs, were able to multiply, in mixed cultures with high cell numbers within 72 hours (Table 3.). Based on these results the degrading capacity of strain pairs on PAH compounds in liquid medium was examined in OxiTop soil respiration system.

Table 3. Results of strain pairing experiments after 72 hours (Cologny Forming Unit/ml)

Examined strain pairs	**CFU/ml after 72hrs**
AK-35 + AK-38 (*R. erythopolis +R. gordoniae)*	$10^9\backslash10^8$
AK-40 + CHB-15p (*R. pyridinivorans + R. rhodochrous*)	$10^9\backslash10^9$
AK-38 + NCP-3 (*R. gordoniae + Pseudomonas putida*)	$10^8\backslash10^9$
TBF2/20.2 + AK-35 (*O. oleidegradans + R. erythopolis)*	$10^5\backslash10^9$
TBF2/20.2 + AK-40 *(O. oleidegradans + R. pyridinivorans)*	$10^8\backslash0$
TBF2/20.2 + AK-44 *(O. oleidegradans + R. aetherivorans)*	$10^9\backslash0$

PAH degradation in liquid medium

By the results of this experiment AK-37, AK-40 and AK-44 were able to decrease the amount of PAH compounds individually, between 11–15% (Table 3.). The highest amount was 15% (AK-44) on fluoranthene. The strain pair AK-35 + AK-38 degraded the tested PAH compounds between 6–22%, in highest extent (above 20%) was in case of benzo(a)pyrene. The incubation was 14 days with individual strains and strain pairs, too. AK-35 was not able to degrade benzo(a)pyrene individually, but it could in AK-35 + AK38 strain pair.

Table 4. Results of PAH degradation in liquid medium with individual strains, and strain pair

	Average of degradation %		
Strains	**Flu**	**BaA**	**BaP**
AK-35	2.3	0.0	0.6
AK-37	7.8	0.9	**11.6**
AK-40	**12.2**	0.7	5.5
AK-44	**15.5**	1.1	**12.2**
CHB-15p	2.5	0.0	0.2
TBF2/20.2	0.8	0.0	0.0
AK-35 + AK-38	6.4	**14.2**	**22.1**

OxiTop soil respiration test

Based on the results of the strain pairing tests, a contaminated soil sample, originated from PAH and TPH polluted site, was inoculated with mixed bacterial cultures and their degradation ability was tested. The reason why these strains were used, that because they were able to grow together in appropriate living cell numbers, furthermore previous examinations showed that each strains had good TPH-degradation capability and AK-35 + AK38 had also PAH-degradation capability. An untreated (not inoculated) control was applied to compare degradation rates.

Table 5. Results of OxiTop respiration tests.

	Control average	**AK-38 + NCP-3**	**CHB-15p + AK-40**	**AK-35 + AK-38**
		Quantity of PAHs compare to Control (%)		
Sum of PAHs without naphtalene	**100%**	**75,5**	**81,5**	**63,8**

The results can be seen in Table 5. The quantity of PAH compounds in the contaminated soil was 299.6 mg/kg. After 14 days the strain pair AK-38 + NCP-3 degraded PAH compounds nearly 24%, CHB-15p + AK-40 18%, and the AK-35 + AK-38 was able to degraded poliaromatic compounds in highest quantity, 36%.

The respiration activity of the strain pair AK-35+AK-38 inoculated soil (RTK AK I., RTK AK II.) compared to the non inoculated control (Control 1, Control 2) can be seen in Figure 3. In the case of Controls soil samples the respiration values are low. By the end of the 14-days respiration test, the pressure decreased in the control samples to 12 hPa by the average of them. As the reason, the low values are caused by the presence of the sole indigenous microbial population. Compared to this the respiration activity of the inoculated soil samples were more intensive, and related with this the decrease of the pressure was more significant. On the 6th days the oxygen amount has been reduced because of the aerobic biological activity. Thus the OxiTop systems were opened once during the time of experiment and soil sample was rehomogenized.

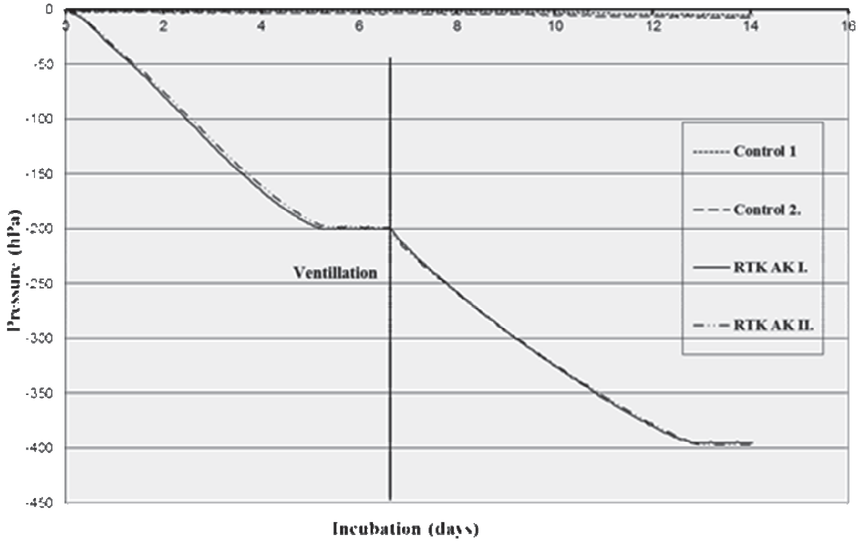

Figure 3. Respiration activities (pressure decrease) of two repetitives of AK-35+AK-38 strain pairs and controls

Discussion

The capacity of two microbial culture collection (SAFEREMED and INNOSAFE) was examined for degrading total petroleum hydrocarbons (TPH), and polycyclic aromatic hydrocarbons (PAHs). In the first step the capacity of collection strains for hydrocarbon degradation was examined with gravimetrical analysis. In the experiments hydrocarbon degrading capacity of AK-35 *(Rhodococcus erythropolis*), AK-38 *(Rhodococcus gordoniae*), AK-40 *(Rhodococcus rhodochrous*), AK-44 (*Rhodococcus aetherivorans*), TBF2/20.2 *(Olivibacter oleidegradans)* was up to 50%. These strains were selected based on their growth on PAH compounds, in filter diffusion tests. AK-35 (*Rhodococcus erythropolis)*, AK-37 (*Rhodococcus pyridinivorans)*, AK-40 (*Rhodococcus rhodochrous*), AK-44 *(Rhodococcus aetherivorans)*, CHB-15p (*Rhodococcus pyridinivorans)* and TBF2/20.2 (*Olivibacter oleidegradans*) were able to forming colonies on benzo(a)pyrene, benzo(a)anthracene, and fluoranthene diffused Millipore filters which were put on LB solid agar in Petri dishes. PAH degradation was tested with individual strains, based on the results of filter diffusion tests, in liquid medium as well. Individually AK-37, AK-40, and AK-44 strains were able to decrease the amount of fluoranthene between 7,8-15.5% and 5.5–12% on benzo(a)pyrene comparing to the uninoculated control. The strain pair AK-35+AK-38 was degraded benzo(a)pyrene in 22%. Based on these results OxiTop soil respiration tests were made with hydrocarbon contaminated soil sample in two replicates parallel to verify degrading ability. It was found, that the strain pair AK-38 + NCP-3 was able to decrease the amount of ∑PAHs (without naftalene) in 24% and CHB-15p + AK-40 was in 18% compearing to the untreated control. The AK-35 + AK-38 strain pair has reduced with 36% the amount of the same polyaromatic pollutants in the examined soil sample. The incubation period was only 14 days, however some of scientific references advise 30-40 days incubation period for degrading PAH compounds (Bishnoi et al., 2009., Kanaly et al 2000). Thus it is possible, that degradation efficiency of strain pairs can be higher in longer term experiments.

Acknowledgement

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COMPARATIVE ANALYSIS OF THE ORGANIC LIQUID CONDUCTIVITY OF SOIL SAMPLES TREATED WITH CATIONIC SURFACTANT

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Abstract

In our research we examined the saturated oil conductivity of soil samples originated from A and B horizons of two brown forest soils. The soil samples were treated with cationic surfactant Hexadecylpyridinium chloride monohydrate (CPC) or with distilled water. The conductivity measurements were performed in laboratory circumstances using Eijkelkamp closed system permeameter with Dunasol 180/220 (aromatics free distillation product). The surfactant caused the organic liquid conductivity to decrease. Based on the results of statistical analysis we could conclude that the type of soil and the type of treatment both influence the change in oil conductivity.

Keywords: soil, NAPL, surfactant, oil conductivity

Összefoglaló

Kutatásunk során két barna erdőtalaj A és B szintjének telítési olajvezető képességét vizsgáltuk laboratóriumi körülmények között. A talajmintákat hexadecilpiridinium-klorid monohidrát (más néven CPC) kationos felületaktív anyaggal és desztillált vízzel kezeltük. A vizsgálatokat Eijkelkamp zárt rendszerű permeaméterrel végeztük, a Dunasol 180/220 aromás komponensektől mentesített lakkbenzinnel. A tenzid hatására a szervesfolyadék-vezető képesség lecsökkent. A statisztikai vizsgálatok eredményei alapján elmondható, hogy mind a talaj, mind a kezelés típusa befolyásolja az olajvezető-képesség változását.

Introduction

Most petroleum derivatives fall into the category of non-aqueous phase liquids (NAPL). Based on the difference in densities light non-aqueous phase liquids (LNAPL, e.g. diesel oil) and dense non-aqueous phase liquids (DNAPL, e.g. chlorine treated carbohydrates) can be distinguished. Regarding the estimation of the transport and groundwater induced migration of petroleum distillates polluting the soils several mathematical models have been developed (among others van der Heijde, 1994; Weaver et al., 1994; Fagerlund, 2006), which are described in detail by Makó (1995; 2012). One of the most important input parameter of all these models is liquid conductivity.

Liquid conductivity, just as oil conductivity is influenced by the combined characteristics of the soil and the permeating liquid (Head, 1982; Makó, 1995; Dragun, 1998). Among the soil properties we will focus on the particle size distribution (silt and clay content), structure, pore size distribution, quantity and quality of clay minerals and humus content. Significant liquid properties are density and viscosity (Koerner et al., 1987; Schiegg and Schwille, 1991; Jarsjö et al., 1997). Also very important factors are the ambient temperature (Raisbeck and Mohtadi, 1974; Head, 1982), stratification and heterogeneity of the surrounding environment (Schiegg and Schwille, 1991). Schiegg and Schwille (1991), Khamehchiyan and colleagues (2007), as well as Rahman et al. (2010) have found that increasing oil content in soil caused the decrease of water permeability. Determining the liquid permeability can be performed with a variety of field and laboratory based methods and tools (Head, 1982; Klute and Dirksen, 1986; Buzas, 1993). The various experiments and modelling procedures performed in a controlled environment allow us to focus on specific physical and chemical processes, however they cannot reflect the versatility and spatial variability of the natural environment (Kueper et al., 1993).

Most of the models listed above estimate the soil's oil conductivity based on its hydraulic conductivity by taking into account the differences in viscosity and density (e.g. Raisbeck and Mohtadi, 1974; Koerner et al., 1987; Schiegg and Schwille, 1991; Makó et al., 2009). However, the most frequently used Kozeny-Carman equation can cause significant differences among the measured and estimated values (Makó et al., 2009), because that is only valid for ideal porous systems (sandy soils) (Koerner et al., 1987; Makó, 1995). In many cases – due to lack of measured data – hydraulic conductivity is also estimated using soil characteristics that are easier to measure based on pedotransfer functions (Pachepsky and Rawls, 2004). Significant correlations have been experienced between measured air permeability and oil conductivity of soils, thus the former can also be used in the estimation of the latter (Eijpe and Weber 1971; Makó et al., 2009; Dunai and Makó, 2011).

Surfactant materials are of dual characteristics: they consist of a hydrophilic head section and a hydrophobic chain, which is most often a long alkyl chain (made up of 10–20 Carbon atoms) (Patzkó, 1998). The hydrophilic component can contain cations or anions, has an electrical charge and is able to form hydrogen bonds. Surfactants reach the environment and the soil by means of waste water, but several pesticides and other agricultural chemicals also contain such compounds (assisting in the persistence of the active ingredients). By being adsorbed onto the surface of soil particles they can alter the physical, chemical and microbiological characteristics of the soil (Abu-Zreig et al., 2003). Among such affected properties are water retention (Karagunduz et al., 2001), oil retention (Csatári et al., 2013), aggregate stability (Piccolo and Mbagwu, 1989; Miókovics et al., 2011) and hydraulic conductivity (Allred and Brown, 1994). Surfactant agents are also being used in remediation and recovery of soils with oil pollution (West and Harwell, 1992; Lowe et al., 1999; Henry and Smith, 2003; Rashid et al., 2004). Upon entering the soil they reduce the interfacial tension in the oil phase, increase its solubility, etc. thus making it easier to remove (Ratherfelder et al., 2000; Henry and Smith, 2003; Rashid et al., 2004), while at the same time they can also facilitate the adsorption of insoluble organic pollutants (Brown and Burris, 1996). This can lead to the surfactant materials becoming co-pollutants themselves.

Most such studies were carried out by examining the movement of various NAPLs (e.g. Koerner et al., 1987; Abdul, 1988; Lenhard et al., 1993; Illangasekare et al., 1995; Candelaria and Matsumoto, 2000) in conjunction with surfactant materials (e.g. Abriola and Demond, 2000; Ratherfelder et al., 2000) within soils or modelling materials of sandy characteristics containing a water phase. There is much less research based on the behaviour of structured soils with variable clay ratios when exposed to surfactants and oil pollutants. The present paper attempts to provide some insight into the changes of saturated organic liquid conductivity (K_o) of various soils following treatment with cationic surfactants under laboratory conditions.

Materials and Methods

The A and B horizons of two different Hungarian soil profiles were chosen and sampled in order to perform the fluid conductivity experiments. One of them originated from Keszthely (samples 1-2; WRB classification: Hortic Terric Cambisol), the other profile was excavated in Várvölgy (samples 3-4; WRB classification: Cutanic Luvisol). The disturbed samples were air-dried, milled and sieved by 2 mm sieve. The most important physical and chemical properties of the samples were determined according the relevant Hungarian standards (Buzás, 1993), particle size distribution measurements was performed based on the ISO/DIS 11277/1995 standard (Table 1).

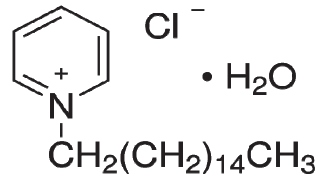
Table 1. Basic characteristics of soil samples

Sample	Depth (cm)	K_A *	Organic matter (%)	CEC (mgeq/ 100 g)	pH (H_2O)	Clay (%)	Silt (%)	Sand (%)
1	0–30	30	1.55	11.84	7.04	21.09	33.13	44.28
2	30–50	36	0.94	12.38	6.83	22.9	33.87	42.29
3	0–20	29	1.33	10.36	6.59	15.27	29.35	54.05
4	20–50	38	0.70	12.78	6.64	22.3	26.56	50.49

* Upper limit of plasticity according to Arany

The applied surfactant was Hexadecylpyridinium chloride monohydrate (CPC, distributed by Sigma-Aldrich) is being used mostly in the pharmaceutical and cosmetics industries because of its powerful antibacterial and anti-fungal properties. Its chemical composition and other characteristics are detailed in Table 2.

Table 2. Main characteristics of Hexadecylpyridinium chloride monohydrate

Empirical formula	$C_{21}H_{38}ClN*H_2O$	
Molecular weight (g/mol)	358.01	
Water solubility (g/l) (20 °C)	50	
Density (g/cm^3)	0.37	
pH (10 g/l, H_2O, 20 °C)	5.0 – 5.4	

The soils were treated with surfactants using the static equilibrium experiments (or "flooding technique"). We added a solution of surfactants to the soil with a concentration with which we assumed that at least monomolecular coverage can be formed around the soil particles thus rendering them completely hydrophobic. This concentration was determined by using adsorption isotherms measured by Varian Cary 50 UV-VIS spectrophotometer (Tóth, 2012; Földényi et al., 2013). During treatment we first added distilled water in 1:1 ratio then the samples were left to saturate for 72 hours in a cool, dark location, then the surfactant solution of the specified concentration were added. The final ratio of soil and surfactant solution became 1:10. The resulting suspension was left in place after careful stirring, for 48 hours stored in a cool, dark location. Samples were dried at 40°C, then milled and sieved through 2 mm sieve again.

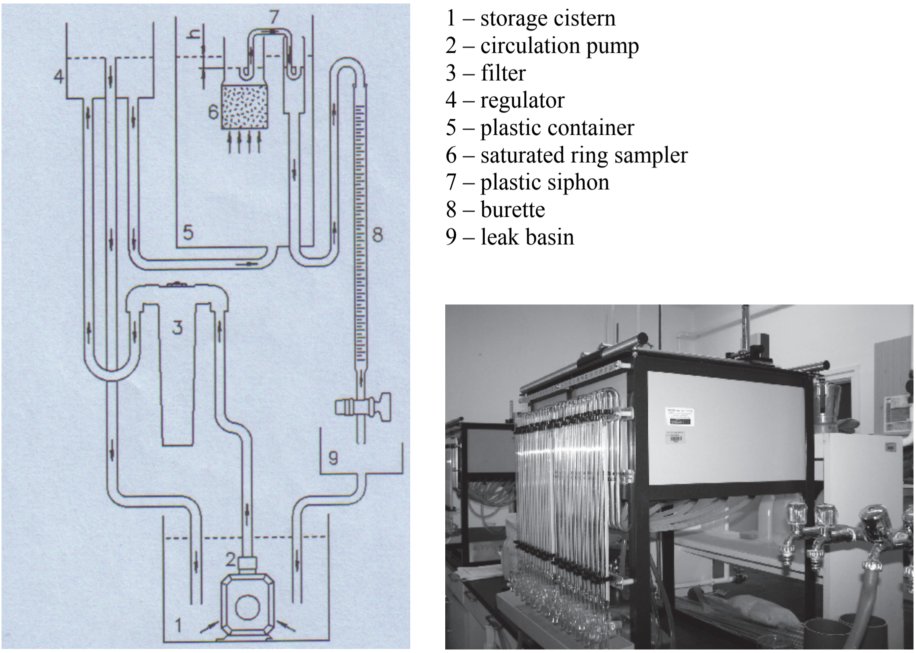
Artificial soil columns were constructed of approximately 90 cm^3 from the samples (diam.: 5 cm, height: 4.5 cm) in three parallel repetitions with identical bulk density in each treatment.

During the experiments a LNAPL called Dunasol 180/220 was used (referred to as Dunasol in the remainder of this paper) which is an aromatics free distillation product (source: MOL Hungarian Oil and Gas Plc., Százhalombatta). Main characteristics of the model organic liquid are summarised in Table 3.

Table 3. Main characteristics of Dunasol 180/220

Boiling temperature (°C)	179 – 217
Density 15 °C-at (g/cm^3)	0.775
Viscosity at 20 °C (cP)	1.91
Aromatic components (m/m%)	0
Interfacial tension (liquid-air) at 20 °C (N/cm)	25

Liquid conductivity can be measured using several methods both in the field and in the laboratory, we chose to use the laboratory based closed system permeameter manufactured by Eijkelkamp (Figure 1). The instrument required a few minor modifications to enable the measurement of oil conductivity. Organic liquid conductivity (K_o) was determined using the constant or falling head method, depending on the rate of flow.



1 – storage cistern
2 – circulation pump
3 – filter
4 – regulator
5 – plastic container
6 – saturated ring sampler
7 – plastic siphon
8 – burette
9 – leak basin

Figure 1. Eijkelkamp permeameter

Since we experienced disaggregation and structure failure within the samples following the static equilibrium surfactant treatments we decided to also perform the treatment of samples with distilled water among identical conditions. Thus we could compare the results of samples treated with two different liquids (evaluate the effect of surfactant adsorption) instead of using natural, untreated soils.

Computer Tomography (CT) analysis was performed using GE Nanotom S device. Theoretical basis of the analysis is described in the study of Taina et al. (2007). Artificial soil columns were constructed from the samples in polyethylene tubes (5 mm in diameter). Voxel size was 2.5 µm.

Statistical assessment was performed using R program, and normally distribution was tested with Shapiro-Wilk test.

Results

Microtomographic images in Figure 1. well demonstrate the disaggregation caused by the "flooding technique": the central image shows the sample without treatment, the right image shows the sample after surfactant treatment and the left one after "water treatment". We concluded that bulk density of surfactant treated samples was higher than that of samples treated with distilled water.

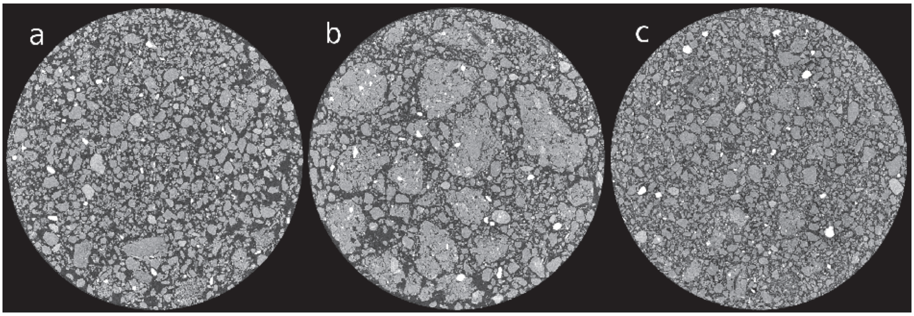


Figure 2. CT images of sample no. 1 (a – water treated, b – non treated, c – surfactant treated)

Figure 3 shows the results of the measurements of oil conductivity. Box plots presents statistics of parallel measurements: 1st quartile (Q1), median and 3rd quartile (Q3). The whiskers on the box plots extend to the most extreme data within the Q1–3*IQR and Q3+3*IQR, where IQR is an interquartile range equal to Q3-Q1. We also included the results from untreated, control samples for information purposes.

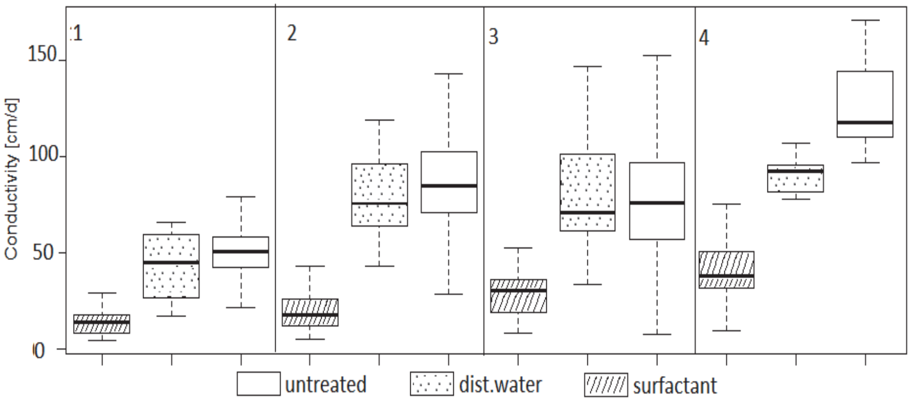


Figure 3. - Oil conductivity of the samples with various treatments

Boxplots suggest that measured oil conductivities for most samples are not normally distributed, they are skewed. To test it Shapiro-Wilk normality test was conducted which results are presented in Table 4. Based on the values of p-values for normality test and usually used value of alpha level equal α=0.05 one may state that only half of measurements for which p-value > 0.05 may be treated as normally distributed. For other samples we have to reject the null hypothesis of Shapiro-Wilk test about normally distributed samples.

Taking into account the non normality of measurement data and the fact that the number of measurements for each soil samples is not equal, one have to use Wilcoxon rank sum test to test for differences between subsequent datasets. The test was performed between each pairs of measurements for surfactant treated and distilled water treated soil samples. The results of this test are presented in Table 4. For each pair of soil samples p-value is far below significance level, which means that its distributions are shifted and differences in means are statistically significant.

Table 4. Statistical indicies for measured oil conductivities

Soil sample	Mean value of oil conductivity [cm/d]	Sample no.	p-value of Shapiro-Wilk normality test	p-value of Wilcoxon rank sum test
1- surfactant	12.4158	40	0.1107	5.621e-07
1- dist. water	37,4327	14	0.1532	
2- surfactant	17,4222	42	0.000157	4.787e-08
2- dist. water	17,6960	14	0.003591	
3- surfactant	26,3609	52	0.2232	1.306e-07
3- dist. water	77,5790	14	0.01977	
4- surfactant	38,2876	49	0.003737	2.159e-04
4- dist. water	83,6298	7	0.2117	

The organic liquid conductivity of the soil samples is verifiably influenced by both the characteristics of the sample (clay content, structure, etc.), and the applied treatment (distilled water, surfactant).

Oil conductivity decreased in the samples treated with surfactants, not only when compared to samples treated with distilled water, but also to untreated samples (Figure 2). In case of all samples there is significant difference between the NAPL conductivity of distilled water treated samples and the surfactant treated samples. The most remarkable difference was measured in sample no. 2 (level B of Hortic Terric Cambisol, which had the largest clay and smallest sand content). Saturated NAPL conductivity of samples treated with distilled water is measurably higher than that of samples treated with cationic surfactant.

Conclusions

CT images showed that the rate of macropores (being the main agents in liquid conductivity) and gravity pore space have also changed – both of which could have played important parts in the reduction of saturated oil conductivity. Porosity may has decreased during both treatment methods.

A further decrease in pore size could be found in the case of surfactant treated samples – in a single layer – caused by the amount of Dunasol, which can bind easier in the hydrophobic environment. This in turn could cause further conductivity reduction. Even though the differences in tentative set up, Rashid et al. (2004) experienced similar results when following the cationic surfactant treatment of an aquifer material. They found that its (water) conductivity has decreased in parallel with the increased binding of the organic pollutants.

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INVESTIGATION OF TRANSPORT MODELLING AND SOIL STRUCTURE INFLUENCING EFFECT OF BIODIESEL BY-PRODUCT IN AGRICULTURAL SOILS

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Abstract

Our investigations are parts of a complex research work which have been started by Department of Soil Science and Agricultural Chemistry of Szent István University. This research work focuses on agricultural application of biodiesel by-product as an alternative nutrient and its effects on the cultigens and on the environment (Kovács et al., 2011a, Kovács et al., 2011b, Tolner et al., 2011, Kovács et al., 2012). The safety use of this material requires the accurate knowledge of its behavior thence several experiments were performed.

The first step of our research was the transport modeling of the biodiesel by-product. The basics of models were column tests where the leaching of biodiesel by-product was investigated in presence of nitrate in different agricultural soils. During leaching tests the by-product was substituted by glycerol because of its decisive glycerol content. The second part of our research was the geotechnical investigation of soil parameters. In these experiments the soil structure modifying effect of glycerol was determined.

According to results of transport modeling the leaching of glycerol mainly depends on the soil type and on the presence of nitrate. The amount of washed-out glycerol is significantly high from sandy soils but it decreases by adding of nitrate. The soil structure influencing effect of glycerol was proven by geotechnical investigations. Changes of soil mechanical parameters were observed in cases where the soils were treated with glycerol.

Keywords: biodiesel by-product, leaching test, transport modeling, consolidometer test, shearing test

Összefoglalás

A bioüzemanyagok, mint megújuló energiaforrások egyre nagyobb teret hódítanak a világban, amit az is igazol, hogy a 2000 és 2007 közötti időszakban a világ bioüzemanyag termelése a háromszorosára nőtt (Coyle, 2007). Az üzemanyagok előállítása során azonban jelentős mennyiségben keletkeznek melléktermékek, melynek felhasználásáról, elhelyezéséről gondoskodni kell, ugyanis az üzemanyag előállítás növekvő trendjének következtében, ezek mennyisége is növekedni fog.

A biodízel előállítása során nagy mennyiségű melléktermék keletkezik, magas glicerin tartalommal. Ez a magas glicerin tartalmú melléktermék ugyanakkor növényi részekkel való szennyezettsége miatt a kozmetikai ipar számára nem felhasználható (Wilkie, 2008). Viszont épp emiatt a növényi tartalom miatt képzelhető el ennek alkalmazása a mezőgazdaságban, alternatív tápanyag-forrásként. A glicerin számos baktérium faj számára hasznosítható szénforrás, segítségével intenzifikálható a mikrobiális tevékenység a talajban, melynek következtében nő a humusztartalom és javul a talajszerkezet.

Vizsgálatink célja, hogy megismerjük a biodízel melléktermék transzportfolyamatát a talaj háromfázisú zónájában, valamint a talaj szerkezet módosító hatását.

Önmagában a glicerin migrációja a talajban főként az adott talajtípus hidrogeológia paramétereitől függ, mivel terjedése uralkodóan advektív transzporttal zajlik. Kísérleteink során viszont azt tapasztaltuk, hogy nitrát hozzáadásával a kimosódás intenzitása csökkenthető, ezáltal fokozható a gyökérzónában történő hasznosulása és csökkenthető a

talajvíz terhelése. A talajba jutatott glicerin azon túl, hogy terhelést jelenthet a felszíni vízadókra a gyors kimosódásával, a talaj szerkezetében is változásokat okozhat. A talajok geotechnikai vizsgálatait ezen változások megfigyelésére végeztük el, melyek során eltéréseket tapasztaltunk a glicerinnel kezelt és kezeletlen talajok fajlagos összenyomódása, kohéziója és belső súrlódási szöge között.

Introduction

Industry of biofuels is a part of renewable energy sources which gains ground by leaps and bounds. Between 2000 and 2007 global biofuel production tripled from 4.8 billion gallons to 16 billion gallons. The biodiesel production was about 3 billion gallons in 2007 and more than 50 % of this quantity was produced by EU (Coyle, 2007). By prognosis this process will increase which raises issue of by-product utilization.

During biodiesel production a huge amount of useable by-products are produced with high glycerol content. Outputs of biodiesel production largely depend on oil type and quality. Approximately for 100 liters of vegetable oil 25 liters of methanol and 0.8 kg KOH catalyzer are used to produce 75 liters of biodiesel and 25 liters of crude glycerol (Wilkie, 2008). In general the glycerol used by cosmetic and chemical industry but biodiesel by-product is contaminated by vegetal parts. But this „vegetal contamination” makes it perfect for use by-product like fertilizer on fields.

The glycerol is an easily available and adequate carbon source for micro-organisms (Lee et al., 2001; Tickell, 2003). It could intensify microbial activity of soils which can helps to increase availability of vegetal nutrients. Furthermore the microbes enrich organic nutrient content and organic part of soils which increase the humus content and result good texture.

The application of biodiesel by-product as a fertilizer in the agriculture could be an alternative way to utilize the huge amount waste of biofuel industry (Kovács et al., 2011b, Tolner et al., 2011). Before utilization the probable effect of by-product on environment must be ascertain. Our first research works were the mobilization investigations of glycerol in column tests which were simulated in a transport modeling program. The spread of glycerol was investigated alone and in presence of nitrate in two types of soil. The second work was the investigation of soil structure modifying effect of glycerol by oedometer and shearing machine.

Materials and Methods

The transport calculations were accomplished by VS2DT (Variably Saturated 2-D Flow and Transport Model) which module is integrated in software package of WHI UnSat Suite Plus. This module is a suitable tool to model transport of chemicals in unsaturated zone of soil. In porous media the components of chemical mass flow are advection, diffusion and dispersion. Furthermore the amount of chemicals in water phase are depend on adsorption and chemical, radioactive decay (Kovács, 2004). In this experiment the decreasing of glycerol amount were measured which were taken as a basis to compute the decay constant of glycerol. That was applied in transport calculations to simulate the microbial degradation.

The basic of models were the column tests. Two different soil types were applied in the experiment. Primary, one groups of columns were filled up with 1 kg of loamy sand soil while the other group with 1 kg of loam soil. The columns were treated with different concentration of glycerol and nitrate base solutions. (The concentration of glycerol and nitrate base solution was 8000 µg/ml and 2000 µg/ml, respectively.) The first solution only included glycerol while second solution included nitrate near glycerol. After treatment of soil columns with base solutions 3 days long resting period was left for microbes to degrade the nutrients. After the third day 100 cm^3 distilled water was filled in the columns to investigate the wash-out of the chemicals. The biodegradation of glycerol is only possible in aerobic conditions therefore after 15 minutes 100 cm^3 solution was exhausted from the columns. This procedure was repeated in every 18th hours until the end of experiment which was on the 11th days. The glycerol content of the exhausted solutions was analyzed by CARL ZEISS F1 refractometer and the nitrate content was determined by Parnass-Wagner distillation apparatus. The main parameters of soils are shown in Table 1.

Table 1. Initial parameters of modeling

Parameters of soils	**Loamy Sand soil**	**Loam soil**
Horizontal hydraulic conductivity (*m/day*)	2	0.25
Specific storage (*1/m*)	0.1	0.1
Porosity (*v/v*)	0.41	0.45
Residual moisture content (*v/v*)	0.07	0.11
Bulk density (g/cm^3)	1.6	1.6
Longitudinal dispersivity (*m*)	0.5	0.5

In the agriculture the good condition of soil structure is a decisive moment from point of view of plant develop. Oedometer tests and shearing tests were performed to determine the soil structure modifying effect of glycerol. The oedometer test gives information about compressibility of soil. In the shearing tests the internal friction (φ) and the cohesion (τ) are determined. The soils could be classified into two groups, the cohesive and the cohesiveless soils. In the cohesive soils (loam, clay) there are internal binding forces between grains about the high effective surface of particles so the value of cohesion (τ) is higher than 0 (at normal stress (σ) of 0) while in the cohesiveless soils (gravel, sand) these forces do not work, the cohesion is 0 (at normal stress (σ) of 0). The cohesive soils are characterized by low internal friction contrary to the cohesiveless soils.

During geotechnical investigations the used soil types were different in contrast with the column test ones. There was not a significant difference between geotechnical parameters of the soil types used in column test so the effect of glycerol could not be sensible after treatment and investigation. One of them was a sandy soil from seashore with low effective surface of grains which means lower cohesive reactions but it is an optimal material to observe the effect of glycerol on the internal friction. The second one was a clayey soil from a Hungarian agricultural field close to Cegléd. The high effective surface of grains could give a high surface reaction so the investigation of cohesive force changes is more significant than in case of sandy soil.

As we can see on the Figure 1 the grain size distributions of investigated soils are totally different. The clayey soil is a well graded material but the soil from the seashore includes same grain size particles. More than 85% of the grains are in interval of 0.1 to 0.08 mm.

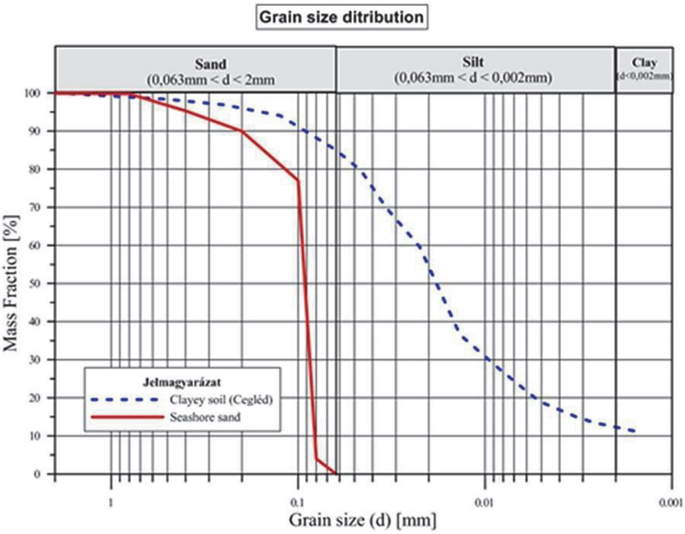

Figure 1. Grain size distributions of investigated soils

Two traditional soil mechanical methods were chosen to investigate the soil structure changing effect of glycerol. Before geotechnical investigations the soils were treated with the same glycerol base solution (8000 µg/ml) which was applied in column tests.

Oedometric measurements were selected to describe the compaction behavior. During this method the investigated material is filled into a rigid cylinder than it is pressed with a predefined normal stress from the axial direction. The normal stress is following a step by step increasing function and after the measurement we can calculate a specific compression value. These values could show the compressibility of the soil.

Other geotechnical parameter is the shear resistance which could characterize the effect of glycerol on soil structure. A torsion shear machine was used to investigate the changes of the cohesion and the internal friction. Torsional shearing (Figure 2) is a special shear method because it was developed to measure not only the maximum shear strength of different kind of soils but the residual shear strength as well. This machine consists of a standing upper part with two force gauges where the resistance forces are measured and a rotating bottom part where we can control the velocity of the displacements. An axial displacement sensor measures the changes of the sample height during all the test periods.

The oedometric and shearing tests were performed with two soil conditions. The first measurements were standard measurements with given moisture contents which was 10 % (m/m) and 14 % (m/m) in the sandy and the clayey soil, respectively. After that the soils were treated with the same glycerol base solution which was used during column tests to investigate the changes of geotechnical parameters.

Figure 2. Shearing apparatus

Results

The different characteristics of leaching processes in the two soil type are shown on Figure 3 and Figure 4. On the figures Line 1 shows the concentration distribution of glycerol after filling up of glycerol base solution. Line 2 is the concentration distribution after 3 days long resting period which is an equilibrium concentration distribution. The concentration of glycerol increased in the lower layers which were caused by flow of base solution. But this process is significantly slower in loam soil than in loamy sand one. The difference between Line 2 and Line 3 were caused by filling up of distilled water. The concentration decrease in loamy sand soil is experienced along the whole cross-section while in loam soil it is only observable to the middle of column. The Line 4 shows the concentration decreases after exhausting.

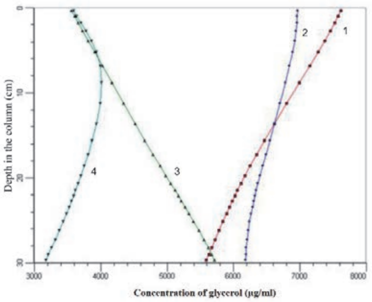

Figure 3. Concentration change of glycerol in loamy sand soil after first filling and exhausting of distilled water (the meanings of lines are explained in the text)

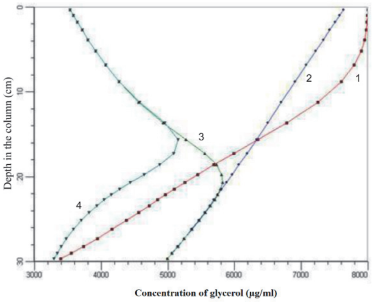

Figure 4. Concentration change of glycerol in loam soil after first filling and exhausting of distilled water (the meanings of lines are explained in the text)

Figures 5, 6 show the wash-out concentrations of glycerol from loamy sand and loam soils in lack of nitrate. The Figures 7, 8 show the leached glycerol concentrations in presence of nitrate. The figures (Figures 5, 6, 7, 8) present simultaneously the measured concentrations from labor experiments and calculated concentrations. To compare the results of measurements and calculations correlation was calculated. The values of correlation coefficients were higher than 0.85 in three cases (Figures 5, 6, 7) which mean high similarity. The effect of nitrate in loam soil was not calculated perfectly, the value of correlation coefficient was 0.71.

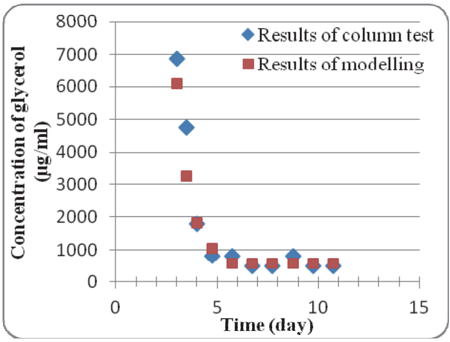

Figure 5. Concentration change of glycerol in lack of nitrate in loamy sand soil

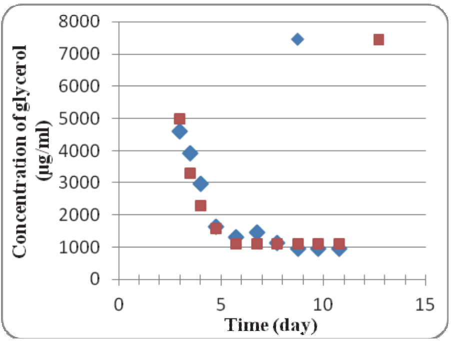

Figure 6. Concentration change of glycerol in lack of nitrate in loam soil

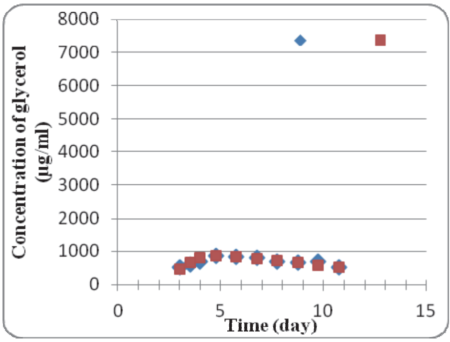

Figure 7. Concentration change of glycerol in case of added nitrate in loamy sand soil

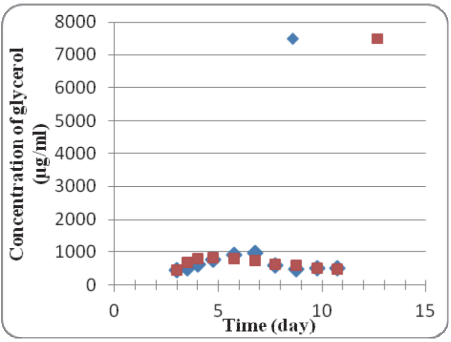

Figure 8. Concentration change of glycerol in case of added nitrate in loam soil

Figure 9 shows the different soils with different compaction characteristics. We found that the glycerol helps the consolidation of soils in both type of soils but the changes are not significant.

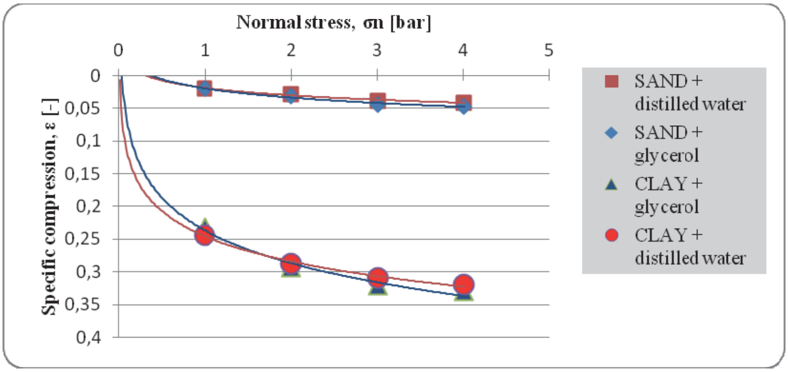

Figure 9. Results of oedometric measurements

In case of shearing measurements the changes are different. In the aspect of clayey soil we can see that only the cohesion of the soil was changed but the internal friction was the same. At zero normal stress (σ) the cohesion increased from 9.3 kPa to 23.4 kPa (Figure 10).

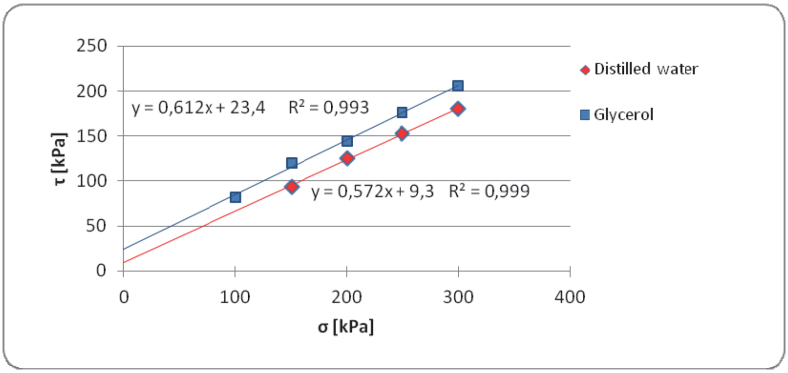

Figure 10. Results of shearing measurements (Clayey soil (Cegléd))

In case of seashore sand sample a small difference was observed. Differences between angular coefficients of lines (Figure 11) show decreasing of internal friction (φ) after glycerol treatment meanwhile the cohesion of the soil was not changed. (Figure 11).

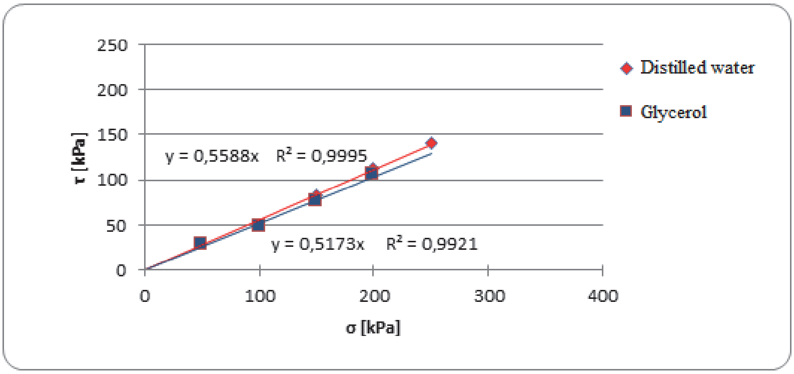

Figure 11. Results of shearing measurements (Seashore sand)

Discussion

The glycerol is a water soluble chemical so its adsorption is not significant on surface of inorganic and organic colloids in soils, therefore the migration of glycerol decisively advective transport. That means the wash-out of glycerol significantly depends on the hydrogeological parameters of soils which mainly determined by soil type. The intensity of leaching in sandy soils is higher than in loamy ones. But the nitrate can decrease the amount of leachable glycerol content of treated soils. The added nitrate as nitrogen source can intensify the microbial activity in the soil which increases the degradation of glycerol. The intensified biodegradation can cause lower leached glycerol concentrations.

Differences were experienced in geotechnical parameters of soils after treatment of glycerol. The specific compression increased which means the glycerol helps the consolidation in both type of soils. During shearing test of clayey soil the internal friction was not changed but the cohesion increased. It is easy to explain it because the high effective surface of the clayey soil we had a high reaction surface where the glycerol solution could build up stronger bond between grains. The sandy soil was cohesiveless before and after treatment of glycerol but the internal friction was decreased because the glycerol worked as a lubricant between the grains of soil.

Acknowledgement

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Figure Captions

Figure 1. Grain size distributions of investigated soils

Figure 2. Shearing apparatus

Figure 3. Concentration change of glycerol in loamy sand soil after first filling and exhausting of distilled water

Figure 4. Concentration change of glycerol in loam soil after first filling and exhausting of distilled water

Figure 5. Concentration change of glycerol in lack of nitrate in loamy sand soil

Figure 6. Concentration change of glycerol in lack of nitrate in loam soil

Figure 7. Concentration change of glycerol in case of added nitrate in loamy sand soil

Figure 8. Concentration change of glycerol in case of added nitrate in loam soil

Figure 9. Results of oedometric measurements

Figure 10. Results of shearing measurements (Clayey soil (Cegléd))

Figure 11. Results of shearing measurements (Seashore sand)

ASSESSING OIL RETENTION MAP WITH PEDOTRASFER FUCTIONS FOR A STUDY AREA AT KESZTHELY, HUNGARY

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Abstract

Oil spills are among the most common sources of soil pollution therefore, it is necessary to spatially assess the sensitivity of soils. Our goal was to develop a method which is suitable for such assessment. Oil retention at various pressures was determined in an earlier study and it was found that soil organic matter and sand content determine the oil retention at one bar. However, regular soil tests in Hungary do not include particle size distribution measurements hence sand content only liquid limit according to Arany is determined and generally, spatial density of recent soil tests is insufficient to perform spatial assessment. We have developed a method to estimate the most probable particle size percentages based on regular measurements and we used all available high resolution soil legacy data to derive spatial estimates of sand and organic matter content for a study area at Keszthely, Hungary. From these base maps, oil retention of the upper soil layer at one bar pressure was assessed. Because of the averaging nature of the used statistical methods (regression analysis, kriging) the values around the average (19.1 vol %) were frequent in the estimated map but large or small values which were present among the data used to develop the estimating equation were generally missing.

Keywords: oil retention, pedotransfer functions, digital soil mapping methods, liquid limit according to Arany

Összefoglalás

A talajok olajszennyezése a leggyakoribb talajszennyezések egyike. Bármely talaj, amelyet érint az emberi tevékenység és a robbanómotorok használata, ki van téve ennek a kockázatnak valamilyen mértékben, ezért fontos, hogy a talajok érzékenységét térképszerűen becsülni tudjuk. Célunk volt, hogy kifejlesszünk egy erre alkalmas becslési módszert. A talajok olajvisszatartó képességét egy korábbi kutatás során vizsgáltuk különböző nyomásokon, és megállapítottuk, hogy egy bár nyomáson a szerves anyag tartalom és a homoktartalom a legfontosabb befolyásoló tényezők. Azonban a szokásos talajvizsgálatok során Magyarországon nem határozzák meg a talajok szemcseméret összetételét, így homoktartalmát sem, csak az Arany-féle kötöttségi számot mérik. Továbbá a jelenlegi talajvizsgálatok térbeli sűrűsége sem elég nagy ahhoz, hogy azokból térbeli becslést lehessen végezni. Kifejlesztettünk egy módszert, amellyel a szokásos talajvizsgálati adatokból meghatározhatók a legvalószínűbb szemcseméret eloszlás arányok, és a múltbéli összes elérhető talajvizsgálati adatot felhasználva becslést készítettünk egy Keszthely melletti mintaterületre a talaj szerves anyag és homoktartalmára vonatkozóan. Ezekből az alaptérképekből kiindulva becsültük a talaj felső rétegének olajvisszatartó képességét egy bár nyomáson. Az alkalmazott módszerek átlagoló tulajdonság amiatt (regresszió analízis, kriging) az átlag körüli értékek (19.1 térfogat %) gyakoriak voltak a becsült térképen, de hiányoztak a

szélsőségesen nagy és kis értékek, amelyek pedig a becslőegyenlet kifejlesztéséhez használt adatbázisban szerepeltek.

Introduction

About 20 million tons of oil and petroleum products are used world wide each day. In Canada, 12 spills of more than 4000 L are reported each day while in the United States, 85 of such spills occur daily on land (Fingas, 2013). Expectedly, several hundreds of small spills occur each day in all countries most of them on land therefore, assessment of sensitivity of soils to this kind of pollution may have large environmental significance. The risk of oil spills in the vicinity of various activities may be vastly different. The probability of larger accidents is much higher along the major transportation lines (pipelines, highways, railways) but systematic spatial assessment of soil sensitivity is not known in Hungary for soils along these lines.

There is a general soil map for Hungary that enables to design policies at large scale (Várallyay et al., 1979, 1980) but detailed soil maps are missing to support fine scale intervention. Hungary is rich in legacy soil data and there are two soil maps and two thematic databases that can be used as potential sources to compile an updated and detailed soil map. However, systematic evaluation of the sources is largely missing (Sisák and Bámer, 2008) in spite of the fact that both Hungarian Soil Protection Strategy (Németh et al., 2005) and EU INSPIRE Directive (EC, 2007) require. Detailed sources are still partially digitized (Pásztor et al., 2010), or they are only in the initial phase of harmonization (Dobos et al., 2010). Additional drawback of the Hungarian soil maps that soil test methods are not always compatible with standard international methods thus, published procedures are rarely applicable directly e.g. for assessing water or oil retention of soils (Tóth, 2010; Hernádi, 2012; Tóth et al., 2013).

We had the objective to assess a detailed oil retention map for an area at Keszthely from usual soil test results with help of pedotransfer functions developed in earlier studies and in this study.

Materials and Methods

No. 5258/4 (Keszthely) sheet of the oldest soil map (Ébényi, 1942) was selected for our study to assess oil retention. The study area was 266 km^2 large and located at the western tip of Lake Balaton, Hungary. A quarter of the area is covered by forests of the Keszthely-hills where no soil sampling and mapping were done. Legacy soil surveys covered only the agricultural land with a non-uniform spatial distribution therefore only a nearly rectangular area of 175.2 km^2 with high and uniform point density was retained for final interpretation (Figure 1).

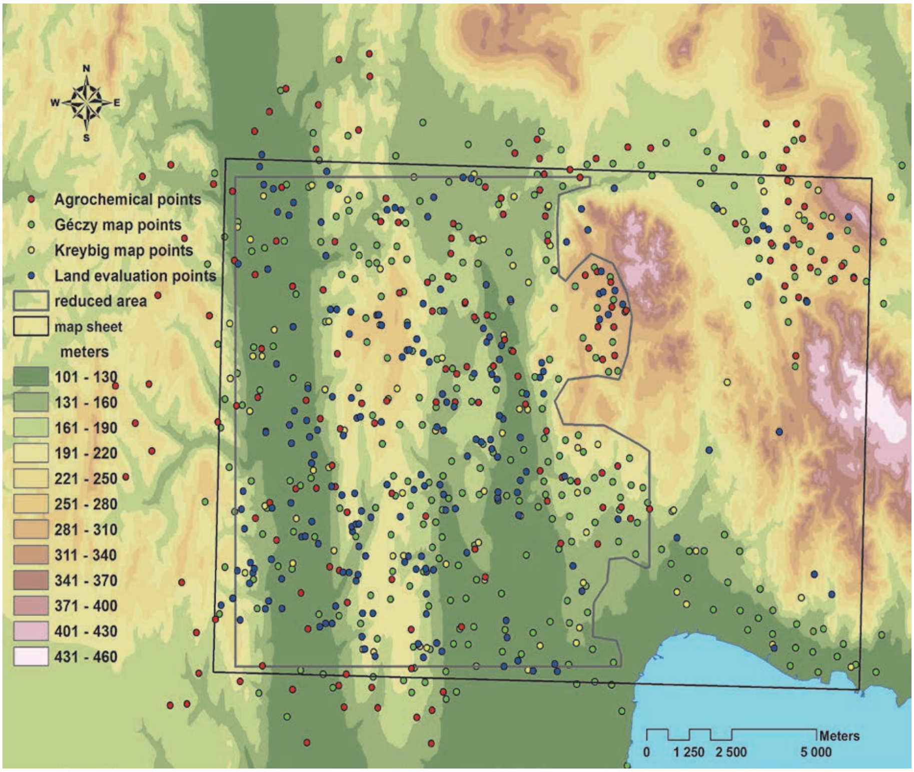

Figure 1. Study area, assessment area, location and source of legacy soil data

In a previous study, we assessed fine scale soil physical properties of the study area (Sisák and Pőcze, 2011). Four legacy data sources were used. 1.) Kreybig soil maps were among the first fine-scale national soil maps in Europe (Kreybig, 1937). The mapping went on between 1932 and 1952. Data on capillary rise of water (mm) for the surface layer were used. 2.) Géczy (1960) published principles of a soil survey. The mapping went on between 1958 and 1961. The purpose of the survey was to improve the data quality of the Kreybig soil maps. Data on field assessments of the texture classes and derived clay content in the surface layer were used. 3.) In the era of the collective agriculture in the 1970’s and 1980’s, large agricultural companies were obliged to investigate soils regularly for better planning fertilizer use. Data on liquid limit according to Arany was used from this agrochemical soil database. 4.) Research was started in the 1970`s to change the old land evaluation system in Hungary. Soil profile descriptions, laboratory investigation data of the soil samples and high precision coordinates of the reference sites are available. Liquid limit according to Arany for the surface layer was evaluated. We have assessed from these data sources (Sisák and Pőcze, 2011) liquid limit according to Arany for the surface soil of the study area, since this is the usual soil test in Hungary for soil physical properties (Figure 2). The basic method of analysis was main component kriging.

Soil organic matter data were only available for the last two sources (agrochemical and land evaluation database). Kriging was used to interpolate point results for the reduced study area. However, these sources insufficiently covered areas with natural vegetation, thus organic matter for large peat areas was inaccurately estimated. Therefore, we incorporated results from an earlier study (Sisák and Bámer, 2007) to correct recent estimates. The previous study used densely placed sampling points, polygon maps and inverse distance weighted method to assess organic matter in Histosols (Figure 3).

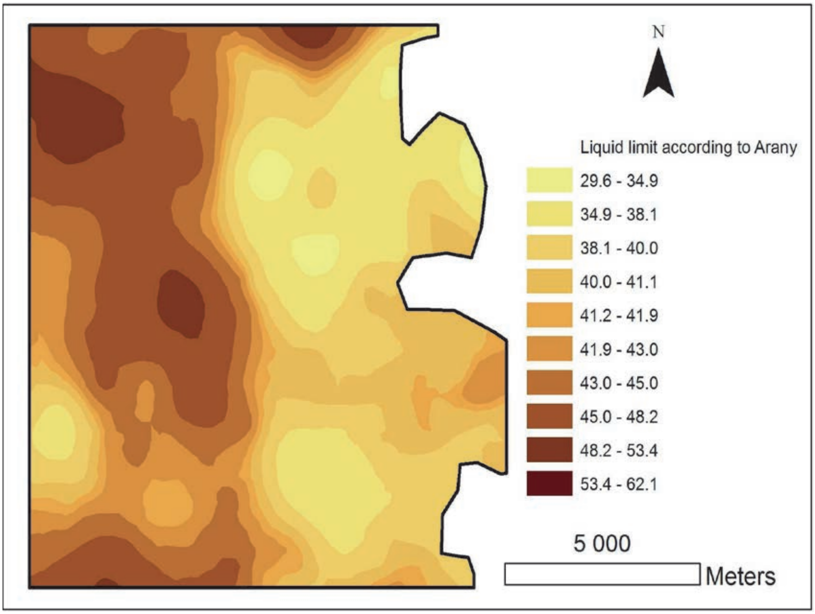

Figure 2. Assessed liquid limit values

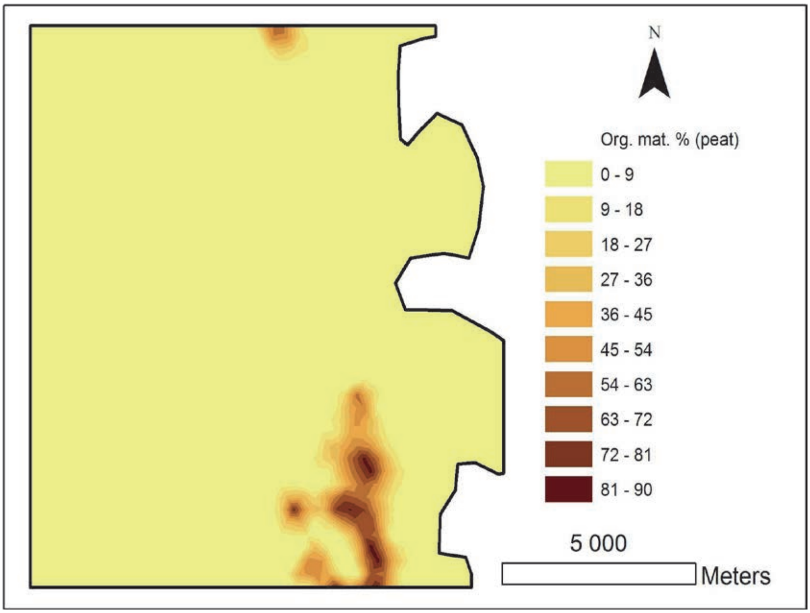

Figure 3. Assessed organic matter content of Histosols

Makó (2002) investigated soil samples from 35 horizons of 12 soil profiles collected in the region to establish relationship between oil retention and other soil properties. Later on he has refined his analysis (Makó, 2005) and calculated the following empirical relationship:

$$\mathbf{OilRet = 26.631 - 0.45{*}S - 2.231{*}OM + 4.49{*}10^{-2}{*}S{*}OM + 3.98{*}10^{-3}{*}S^2 + 0.208{*}OM^2}$$

$N = 70$ $R^2 = 0.771$,

where OilRet: oil retention vol % at one bar pressure; S: % sand content of soil; OM: % organic matter content of soil; N: number of samples; R^2: determination coefficient.

Sand content is not included in the usual soil tests. However, Makó et al., (2010) compiled the MARTHA soil physical database for Hungary which includes usual soil tests (e.g. liquid limit according to Arany and organic matter content) and also particle size distribution data among others. This database allowed us to calculate liquid limit distribution within the texture triangle and also the frequency distribution of data within the texture triangle. Having combined the two distributions, the most probable sand, silt and clay percentages could be determined for each liquid limit categories.

We have converted liquid limit map (Figure 2) to the most probable sand content map and we used sand and organic matter base maps to determine oil retention of the soil surface layer according to the method of Makó (2005).

At the end, we have compared the 50 m by 50 m pixel estimates with the original oil retention data measured by Makó (2002).

We used ArcMap 9.3 for all the spatial analyses.

Results

Liquid limit is generally a function of soil colloid quantity and quality (organic matter, clay minerals, oxides, calcium-carbonate). A modified liquid limit procedure was proposed by Arany (1943) to meet needs for information on soil physical properties. It is a cheap and quick method which became national standard in Hungary in 1978. Its value is equal to the mL of water in 100 g soil when the yarn test is positive (Sisák et al., 2001). It is not surprising that same liquid limit values can be measured on soils with various colloid content. We have determined its distribution within the texture triangle for soils which are similar to the soils in our study area: mostly Luvisols and Cambisols (Figure 4). Extreme sandy and clayey soils can be precisely determined based on the liquid limit according to Arany but one value may represent a wide range of soils with transitional particle size distributions.

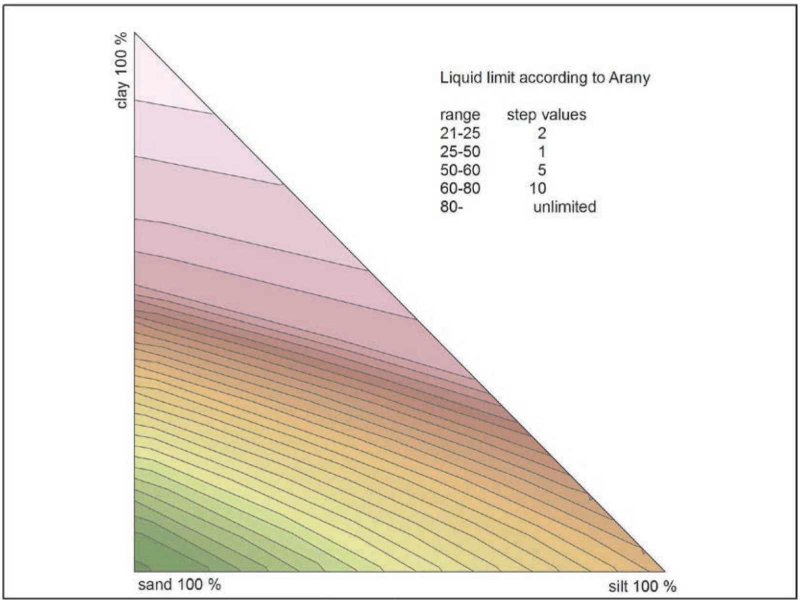

Figure 4. Liquid limit distribution within the texture triangle

However, the probability of the different sand silt and clay fractions are not the same. We have estimated the kernel density function of the data points within the triangle diagram for the same group of soils and we got Figure 5.

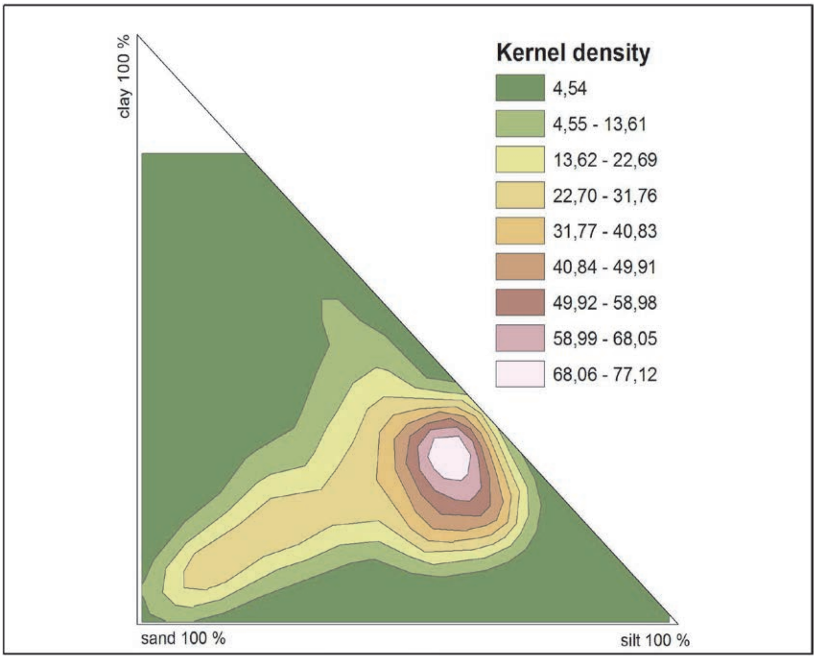

Figure 5. Data density distribution within the texture triangle

By combining the two distributions, we were able to calculate the most probable sand, silt and clay contents for each liquid limit categories (Figure 6.). We used this relationship to assess sand content map for the study area (Figure 7) based on liquid limit map from the earlier study (Figure 2).

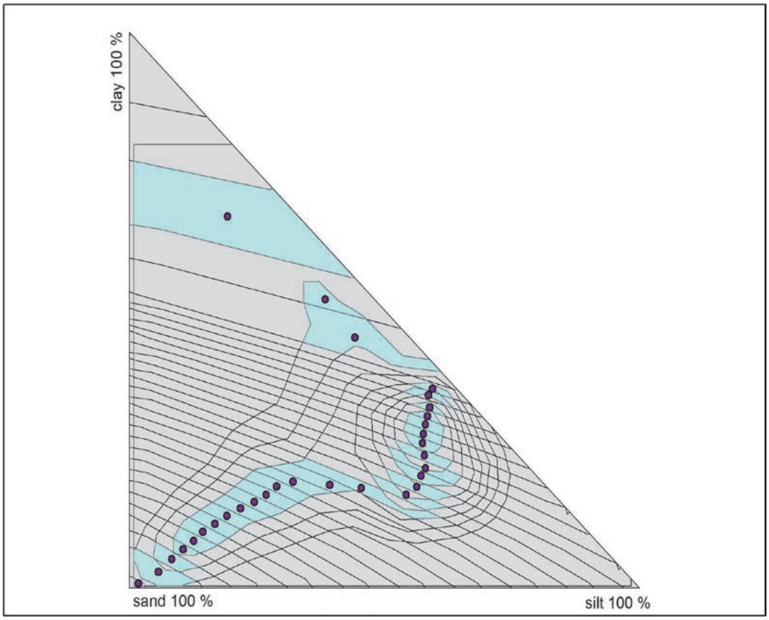

Figure 6. Intersection of liquid limit and data density and the most probable values

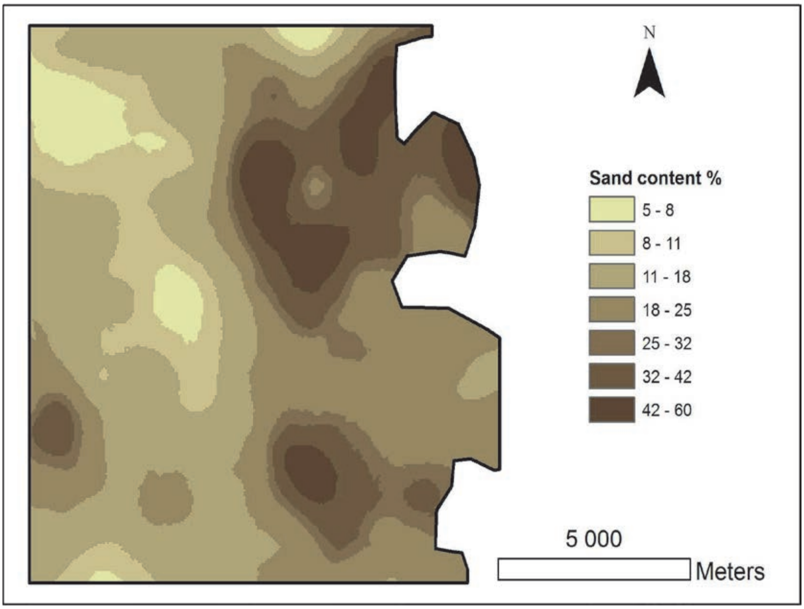

Figure 7. Estimated sand content map

Point data from the agrochemical and land evaluation databases were used to spatially assess organic matter content by kriging. Previous assessment (Figure 3) was superimposed to this map in order to accurately represent Histosols. The resulting map can be seen on Figure 8. The intervals of categories are strongly different in order to accurately depict both mineral and organic soils.

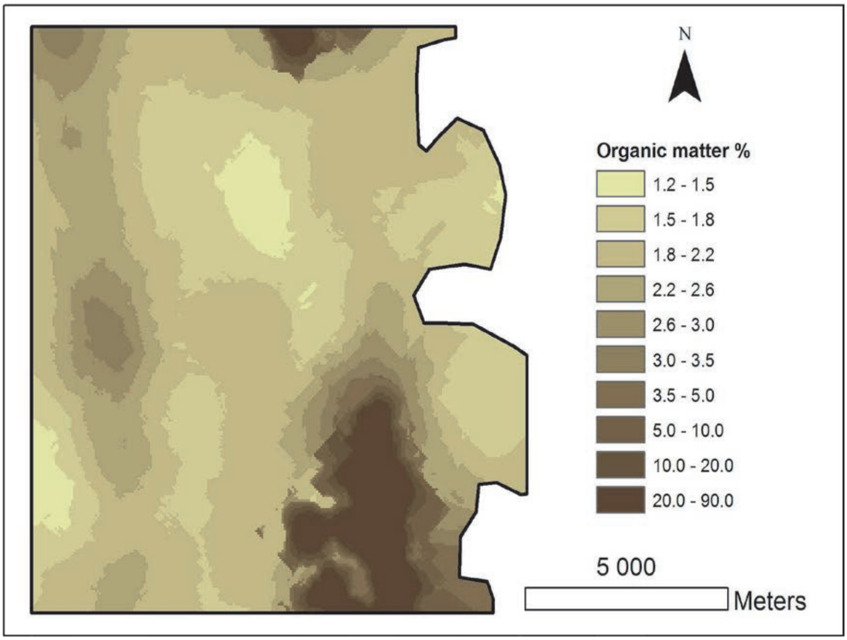

Figure 8. Estimated organic matter map

Organic matter and sand content maps (Figure7 and 8) were used to assess oil retention map for the study area (Figure 9).

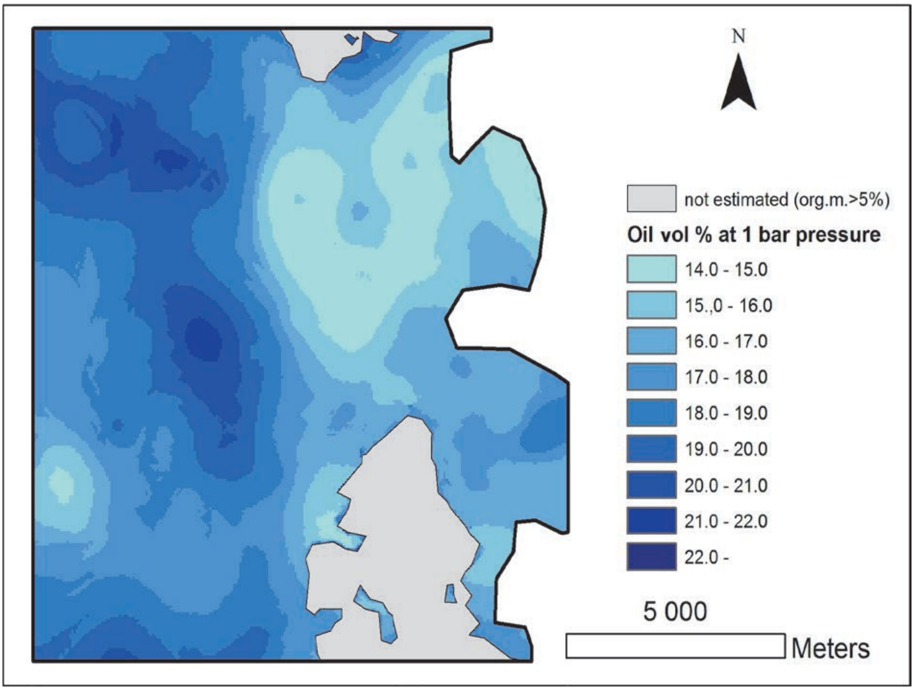

Figure 9. Estimated oil retention map

Discussion

Validity of assessments is always limited by the data which are used to develop relationships and equations. The original data set to derive oil retention equations (Makó, 2002) contained samples with sand content between 5 and 60 percent and with organic matter content between 1 to 5 percent approximately and the measured oil retention varied roughly between 8 and 42 percent. The soils in our study area had a sand content within the same range but organic matter content of Histosols far exceeded 5 % (Figure 7). Therefore, we excluded these areas from estimation (Figure 10). Organic material has high adsorption capacity for non-aqueous liquids and that favour oil retention but the very low bulk density and very high porosity of Histosols pose little barrier for any liquids. After excluding soils with excessive organic matter content, we had approximately the same ranges for the original data set and for our study area regarding sand and organic matter content. But this was not the case for oil retention values (Figure 10).

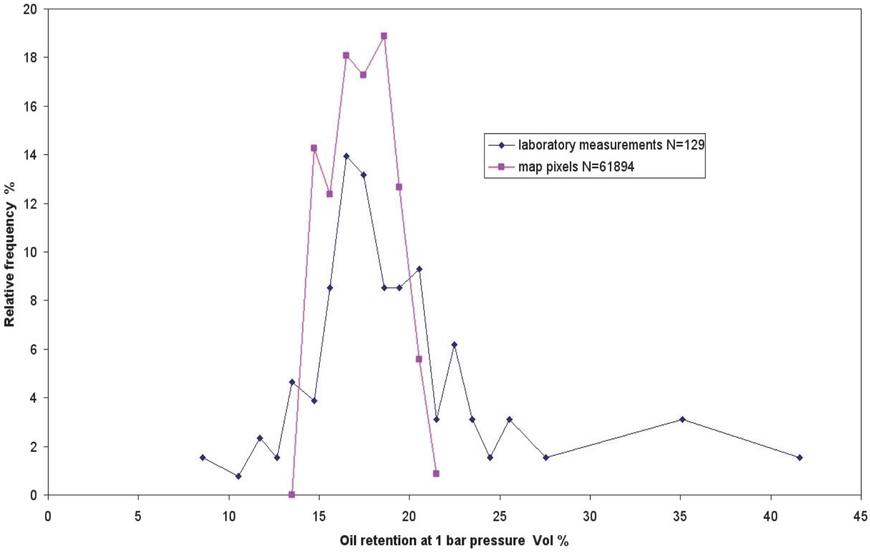

Figure 10. Distribution of original and estimated oil retention data

The average for the samples was 17.3 vol % (standard deviation: 5.5) while for the pixels of the estimated map, it was 19.1 vol % (standard deviation: 1.7). The range of the estimated data was much smaller than that of the original data set in spite of the large number of estimated pixels. The reason can be mainly attributed to the methods of estimation. Both regression analysis in the studies of Makó (2002, 2005) and kriging (Sisák and Pőcze, 2011) are oriented toward central tendency and handle extremities as errors. Recently developed methods which consider real distribution of inputs and produce expected distribution of outputs by Monte-Carlo simulation with subsets of data (such as Bayesian-method) may bring more realistic results in terms of the predicted liquid (oil) retention (Chiu et al., 2012).

Soils usually have three phases (solid, liquid and gaseous) and even dry soils contain bound forms of moisture. Water content of soils strongly influences wetting with non-aqueous phase liquids hence oil retention is reduced by the concurrent water phase (Makó and Hernádi, 2012). The measurements by Makó (2002, 2005) were done with air dry soils therefore, his results represent maximal oil retention and the same is true for our estimated map.

Liquid limit data must not only be influenced by individual colloid materials but by their interactions, too. Even if liquid limit according to Arany has been widely used in Hungary for the last half century this interaction is not well understood or at least not quantified. Further investigations must be done to clarify interactions which should help to build better prediction models to derive rarely measured sand, silt and clay contents of soils.

Generally, real fine scale spatial variability of soil properties including that of particle size distribution and organic matter content is insufficiently known. Digital soil mapping aims at better predict soil properties with help of ancillary variables (McBratney et al., 2003) but fine scale assessments are still far from satisfactory as evidenced by many studies including our own investigation (Sisák and Pőcze, 2011). Better understanding of spatial variability and better models for crucial soil properties are needed.

Acknowledgement

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ANDRÁS MAKÓ - HILDA HERNÁDI

PETROLEUM PRODUCTS IN SOILS: RESEARCHES IN SOIL PHYSICS

(BOOK REVIEW)

Slightly over the second part of the 20th centuries, parallel with the development of chemical industry and the spreading and widely use of engines, the pollution of subsurface environment had been turned up as those undesirable but attached attributes. Hazardous materials, such as petroleum products leaked out from the tanks and technological cables, might pollute the ecological systems like soils and groundwater which are essential environmental resources. The former offers the main part of victuals, the latter provide significance proportion of drinking water for the mankind - in Hungary this rate is over 90 per cent.

From the respect of thickness, upland is similar to a thin wax layer on the skin of an apple. Soils in this thin layer, formed as an interfacial zone by the geological, climatic and biological processes and by other factors, are essential for terrestrial life. In this dynamic equilibrium between inorganic and organic word, soils are considerably vulnerable. Soil formation and degradation processes, for example erosion, are continuously act and run nowadays, as well. Shift in soil formation processes, be it ever so small or short, might have significant effect and may change for thousands of years the present condition. To diminish the impacts of degradation processes is particularly important for mankind. We must ensure the protection of soils and their quality, as far as possible. Furthermore, we have to prevent soil from pollution and protect them, in time. Soil fertility is an individual characteristic feature; we could not substitute or replace it with anything else.

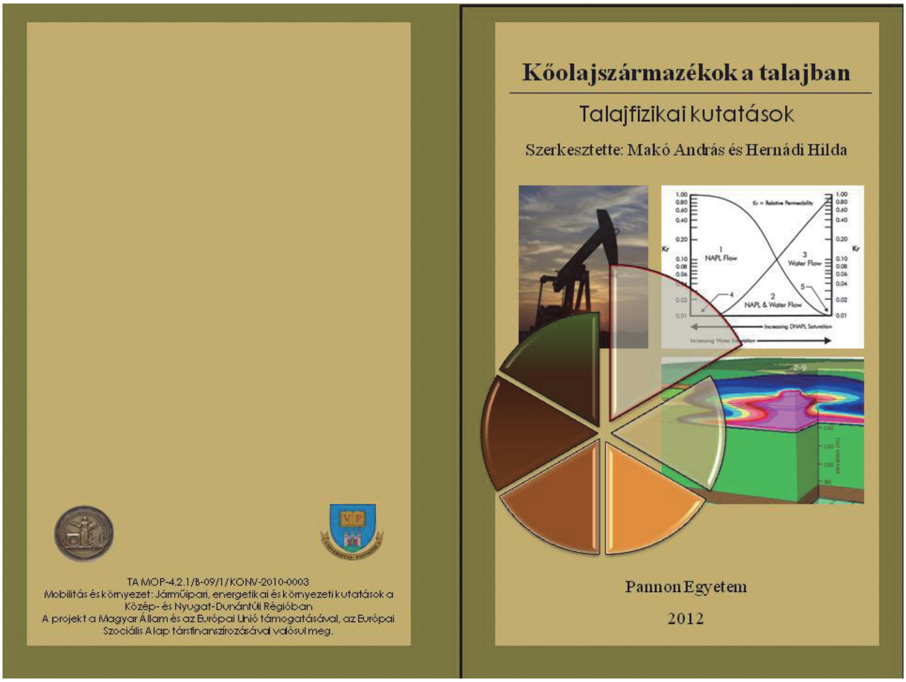
In a wider sense, the defence against pollution is an important scope of soil protection. Amongst the organic chemicals, which may contaminate the subsurface environment, petroleum products might cause the main part of soil pollution. Accidental surface release and improper disposal of petroleum products (e.g., jet fuel, refinery wastes, diesel, etc.) and volatile organic solvents are recognized as an increasingly troublesome threat to soils and groundwater.

Understanding the behaviour of these chemicals in the subsurface to limit their interaction, migration and the accumulation processes are indispensable to identify and asses the rate of pollution, and to develop cost-effective methods for remediating polluted sites. This claims interdisciplinary approach. Besides the knowledge of petrogeology, the experimental results of the connected disciplines, such as hydrology, chemistry, mineralogy and microbiology is required.

The hydrocarbon pollutants are present in liquids that are immiscible with water rather than in aqueous phase or adsorbed on solids. Accurate prediction of the movement of non-aqueous phase liquid (NAPL) as a separate phase in vadose and groundwater zones is a prerequisite to the development of simulation models describing the migration and fate of organic contaminants in the subsurface.

The advanced expectations and their contiguous severity in environmental protection and the widely use of petroleum products add increasing importance to the subject of this book, even now. The contents of this book range from topics in basic soil and fluid properties which might affect the migration, transport and degradation of NAPLs in soils, to the measurement and estimation methods of soil water and NAPL retention and conductivity. It deals with measurement of air permeability, as well as degradation processes and it contains a short issue on the recently used transport models, respectively.

The objective of this monograph, with the title "Petroleum products in Soils: Researches in soil physics", is to provide give introspection in soil physical concern of environmental pollution with organic liquids with special regard to petroleum products (Figure 1.). In this book you could familiarized with the environmental respect of soil pollutions caused by NAPLs.


TAMOP-4.2.1/B-09/1/KONV-2010-0003
Mobilitás és környezet: Járműipari, energetikai és környezeti kutatások a Közép- és Nyugat-Dunántúli Régióban
A projekt a Magyar Állam és az Európai Unió támogatásával, az Európai Szociális Alap társfinanszírozásával valósul meg.

Kőolajszármazékok a talajban
Talajfizikai kutatások
Szerkesztette: Makó András és Hernádi Hilda

Pannon Egyetem
2012

Figure 1. The book sleeve of the monograph

In Chapter 1, after a short presentation about the properties and attributes of petroleum products, the soil and fluid properties and environmental parameters which influence the NAPLs migration and adsorption are summarised. Moreover, subchapters entertain with the main processes that determine their fate and transport in soils.

In Chapter 2 the organic liquid vapour adsorption on soils is presented. Besides, the recently used measurements and the policy of this research field were shown, respectively.

Chapter 3, 4 and 5 deal with various methods to determine the organic liquid retention and conductivity of soils, that may be the most important soil properties as input parameters for organic liquid transport simulation models. In subchapters we could get acquainted with the theoretical and practical experiences in the first measurement and modelling researches as well as the application of the up-to-date technical achievements and their advantages and drawbacks. The authors are focusing on the tools and the scientific background of a quick, exact suitable estimation method for the determination of the above mentioned soil properties. In these days, parallel with the development of simulation models, growing necessity is experienced for these statistical approaches.

This book introduces a number of promising new methods like the application of pedotransfer functions and measured air permeability values in the course of prediction the oil retention or organic liquid conductivity of soils.

Chapter 6 makes ourselves familiar with the main types of soil pollution models. Furthermore, some of them used in home practice are mentioned (MOFAT /MOTRANS and HSSM model).

Last, in Chapter 7 the factors which have influence on chemical and microbiological degradation of NAPLs in soils were summarised. The bioremediation technologies and the application of microorganisms to remove NAPLs from soils is a really promising facility nowadays, as well as in petrol industry and in environmental protection. This chapter deals with the main microbiological degradation processes. Besides, in subchapters you could read about the species, that engage in the degradation of NAPLs and enzyme catalysed processes applied in remediation technologies in case of an oil pollution, respectively.

Microbiological processes by mean of changing the pollutants composition and the microbial produced biosurfactants may affect the physical and chemical properties of soils such as the organic liquid retention and conductivity, as well. Biosurfactants, and their environmental impact, which are nowadays more and more challenging topics, were also mentioned by the authors.

This monograph is not just a theoretical summary but also contains the experiences in scientific literature and the results of research carrying on over more than two decades, at University of Pannonia. Probably it may kindle the interest of scientists working in this fast improving scientific field of soil physics or in directly or indirectly connected other disciplines. Moreover, adumbrate collected studies of methods in measurement and estimation methods in soil physics. Scientific references might give a sight for the researchers and for enquirers on environmental protection and soil protection, as well.

Last, but not least we want to take this opportunity to present the table of contents of the monograph.

CONTENTS

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