

# 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 Várvolgy (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).

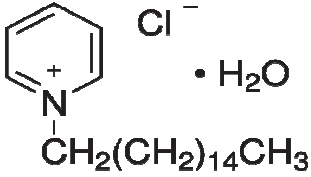
Table 1. Basic characteristics of soil samples

Sample	Depth (cm)	K <sub>A</sub> *	Organic matter (%)	CEC (mgeq/100 g)	pH (H <sub>2</sub> O)	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 <sub>21</sub> H <sub>38</sub> ClN•H <sub>2</sub> O	
Molecular weight (g/mol)	358.01	
Water solubility (g/l) (20 °C)	50	
Density (g/cm <sup>3</sup> )	0.37	
pH (10 g/l, H <sub>2</sub> O, 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<sup>3</sup> 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 <sup>3</sup> )	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.

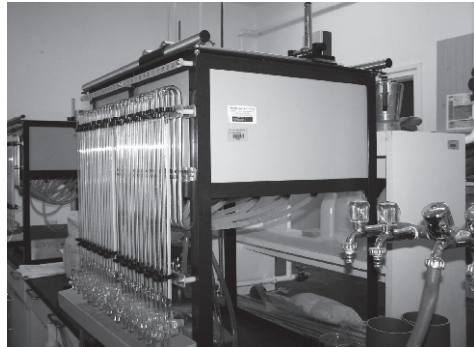
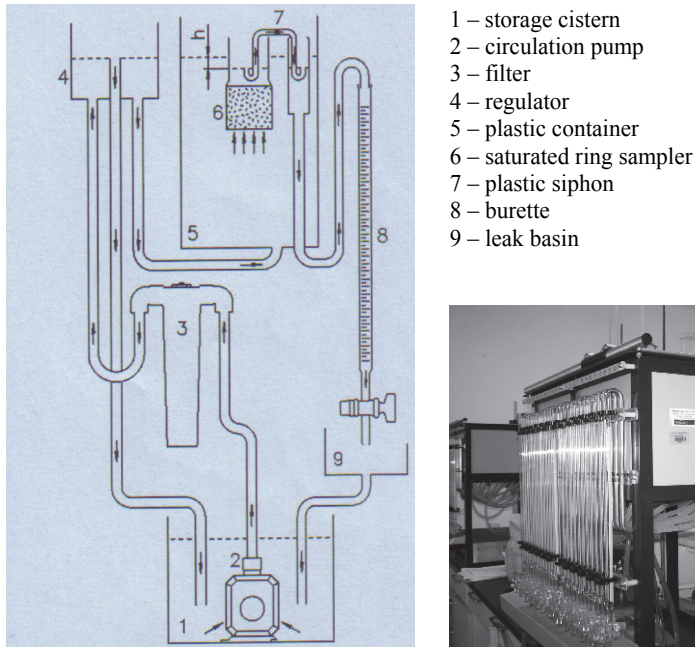


Figure 1. Eijkelkamp permeameter

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.

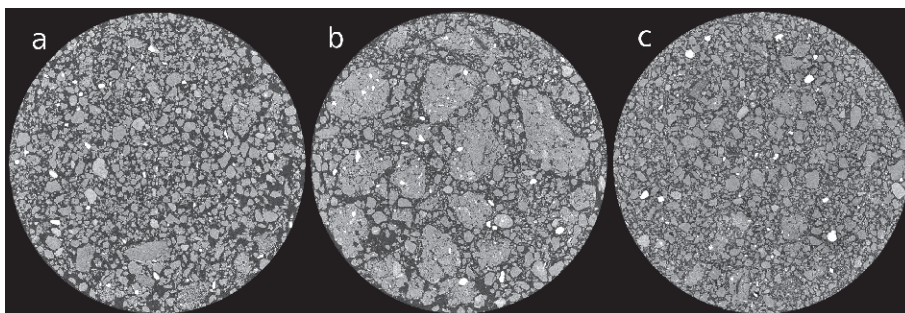
Computer Tomography (CT) analysis was performed using GE Nanotom S device. Theoretical basis of the analysis is described in the study of Taina et al. (2007). Artificial soil

columns were constructed from the samples in polyethylene tubes (5 mm in diameter). Voxel size was 2.5  $\mu\text{m}$ .

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: 1<sup>st</sup> quartile (Q1), median and 3<sup>rd</sup> quartile (Q3). The whiskers on the box plots extend to the most extreme data within the  $Q1-3 \cdot IQR$  and  $Q3+3 \cdot IQR$ , where IQR is an interquartile range equal to  $Q3-Q1$ . We also included the results from untreated, control samples for information purposes.



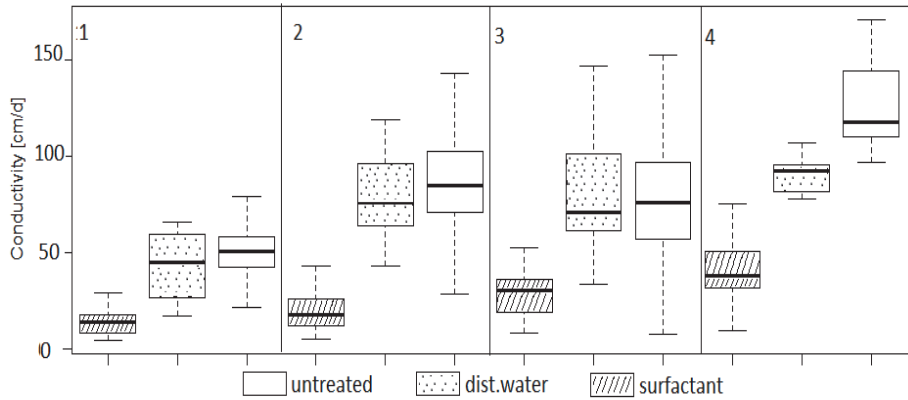


Figure 3. - Oil conductivity of the samples with various treatments

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  $\alpha=0.05$  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 have 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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