

Measuring and Estimating Pressure-Saturation Curves on Undisturbed Soil Samples by Using Water and NAPL

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The ever increasing use of hydrocarbons requires huge storage and transport facilities. The threat of pollution caused by the presence of such installations and the reported cases of soil and groundwater pollution by accidental spillage has prompted an increased interest in the fate of petroleum products in soil and water (RUBIN et al., 1998). The hydrocarbon pollutants are present in liquids that are immiscible with water rather than in aqueous phase or sorbed to solids. The 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 simulation of multiphase fluid flow in the subsurface of soil requires that the *pressure-saturation (P-S) relations* of the porous medium be known for all fluid pairs. The measurement of the relevant P-S curves for two fluid- and, especially, three fluid media can be very time consuming or difficult. Therefore there is a paucity of primary P-S data for drainage systems representative of contaminated soils or subsoils. (There is even less information available for the primary imbibition P-S functions characterizing these environments (DEMOND & ROBERTS, 1991)). Because of this, indirect methods – based on scaling and Leverett's assumption – are often used to predict P-S curves from data that are already available or can be measured more easily. Usually the P-S curves of air-NAPL system are obtained by scaling the air–water system (LENHARD & PARKER, 1987; FERRAND et al., 1990; BRADFORD & LEIJ, 1995).

The appropriateness of this approach for handling the effect of the variation in interfacial force on capillary pressure–saturation relationships has been debated in the literature. The first point of contention is whether Leverett's function needs to include a dependence on the contact angle (ANDERSON, 1987; BRADFORD & LEIJ, 1995; STEFFY et al., 1997). A second problem is whether

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Leverett's function is capable of predicting the change in residual saturation of the wetting phase as a function of interfacial forces. Current usage of Leverett's function sidesteps much of this ambiguity by replacing saturation with "effective saturation" (PARKER et al., 1987; DEMOND & ROBERTS, 1991).

Leverett proposed scaling P-S relations based on the assumption that the porous medium permeability and porosity are unchanged during the saturation with different fluids. It means that porous media are rigid and noninteracting (ideal porous medium). This assumption is not valid in clayey and/or in aggregated soils. Inadequate estimation of the NAPL retention may be a direct result of clay volume changes and soil aggregation changes when saturation with different fluids occurs (RUBIN et al., 1998; MAKÓ, 1999).

In light of problems that may be encountered in using Leverett's function, searches were made for alternative estimation techniques for P-S relationships. One of the possibilities is the *adaptation* of the widely used soil physical indirect method, in which the *water retention is predicted using easily measurable soil properties*.

GUPTA & LARSON (1979), SCHUCH & BAUDER (1986) used a statistical approach to find the correlation between particle size distribution and water retention characteristic curves. PUCKETT et al. (1985) were able to predict water retention curves successfully from textural data for soils covering large areas in the USA. AHUJA et al. (1985) tested a number of models that relate water retention to texture, structure, bulk density and organic matter content using published coefficients for their relationships. They found that the predicted water content values were generally higher than the measured ones, but that a great improvement could be obtained by including two measured water content values into the relationship. PUCKETT et al. (1995) pointed out that useful relations should only be expected for areas in which soils have similar mineralogy and genesis. A lot of other models exist describing the effect of soil texture, structure and other soil properties on water retention as well as hydraulic conductivity (e.g. NIMMO, 1999; ARYA et al., 1999).

On the basis of about 250 soil samples – mainly from the Great Hungarian Plain – RAJKAI et al. (1981) developed an evaluation technique for the calculation of water retention data from the texture and bulk density values of soils. This method was widely used in the categorization and mapping of hydrophysical properties and moisture regime of Hungarian soils (VÁRALLYAY, 1989).

The objective of this study was (1) to develop a technique for the routine measurement of the pressure-saturation curves of undisturbed soil samples saturated with NAPL; (2) to build a database using the measured P-S curves and the physical, chemical properties of the soils; and (3) to establish the dependence of NAPL retention on other soil properties.

Materials and Methods

35 horizons of 12 soil profiles in Hungary were investigated. Taxonomically, this soil database contained Luvisols (4), Cambisols (3), Regosols (1), Gleysols (1), Vertisols (1), Solonetz (1) and Phaeosems (1). The soil horizons encompassed a wide range of texture, porosity, humus and lime content (Table 1).

Undisturbed soil samples (100 cm³) were collected from each horizon in six replicates.

Table 1
The origin and properties of soil samples studied

Sample number	FAO names and name of the closest city	Symbol and depth of genetic horizons (cm)	Bulk density (g/cm ³)	Sand % (>0.05 mm)	Silt % (0.002-0.05 mm)	Clay + Fe-oxhydrates % (<0.002 mm)	Humus %	CaCO ₃ %
				Solid part of the soil (100 %)				
1.	Eutric Regosols <i>Zalakovár</i>	II. 20–33	1.71	45.57	35.30	17.95	1.18	0
2.		III. 33–63	1.68	50.33	35.77	13.22	0.68	0
3.		IV. 63–104.	1.60	52.37	31.86	15.31	0.46	0
4.		V. 104–122	1.63	51.29	29.76	17.23	0.82	0.9
5.	Dystric Luvisols <i>Heresznye</i>	A 0–39	1.66	22.23	59.39	17.18	1.19	0
6.		B 39–65	1.60	21.19	54.91	23.24	0.66	0
7.		C ₁ 65–105	1.63	15.35	50.69	33.60	0.36	0
8.		C ₂ 105–135	1.63	31.73	46.28	21.84	0.15	0
9.	Calcic Gleysols <i>Zalakovár I.</i>	A 0–20	1.15	21.80	24.35	37.20	5.66	11.0
10.		B ₁ 20–47	1.34	37.86	29.88	23.23	4.52	4.5
11.		B ₂ 47–76	1.38	35.46	31.67	29.96	1.21	1.7
12.	Dystric Luvisols <i>Zalakovár II.</i>	A 6–22	1.74	55.75	23.50	19.82	0.93	0
13.		B 22–43	1.75	46.37	21.03	32.23	0.37	0
14.		BC 43–54	1.62	38.03	30.69	31.02	0.26	0
15.		C ₂ 69–98	1.40	5.00	63.07	31.59	0.34	0
16.	Dystric Cambisols <i>Vízvár I.</i>	A 0–23	1.70	43.67	36.95	18.28	1.10	0
17.		B ₁ 23–39	1.74	39.51	38.32	21.59	0.57	0
18.		B ₂ 39–68	1.65	36.18	36.65	26.73	0.43	0
19.	Dystric Cambisols <i>Vízvár II.</i>	A 0–35	1.60	41.27	32.62	24.66	1.46	0
20.		B 35–57	1.67	44.29	35.73	19.46	0.53	0
21.		BC 57–79	1.60	43.55	32.16	23.97	0.31	0
22.	Orthic Luvisols <i>Nagyrecse</i>	B 20–35	1.51	6.91	54.64	36.72	1.72	0

Table 1 continued

Sample number	FAO names and name of the closest city	Symbol and depth of genetic horizons (cm)	Bulk density (g/cm ³)	Sand % (>0.05 mm)	Silt % (0.002-0.05 mm)	Clay + Fe-oxihydrates % (<0.002 mm)	Humus %	CaCO ₃ %
				Solid part of the soil (100 %)				
23.	Orthic Solonetz <i>Karcag</i>	B 20–40	1.44	0.49	34.84	62.52	2.05	0.1
24.	Gleyic Calcic Vertisols <i>Kisújszállás</i>	A 0–20	1.50	0.42	40.48	55.39	3.71	0
25.	Eutric Cambisols <i>Keszthely</i>	A 0–25	1.73	35.58	27.88	34.81	1.73	0
26.		B ₁ 25–40	1.66	34.00	34.46	30.73	0.81	0
27.		B ₂ 40–62	1.52	31.66	37.31	30.21	0.81	0
28.		BC 62–87	1.51	29.64	39.97	29.87	0.52	0
29.	Calcic Phaeosems <i>Lovasberény</i>	A 0–45	1.40	19.71	42.60	22.50	3.19	12.0
30.		B 45–73	1.27	12.57	55.75	16.88	1.64	13.2
31.		BC 73–104	1.18	12.71	40.50	15.66	1.13	30.0
32.	Gleyic Luvisols <i>Magyarszombatfa</i>	A 0–21	1.59	5.59	55.07	37.81	1.53	0
33.		B ₁ 21–47	1.60	3.69	45.18	50.53	0.60	0
34.		B ₂ 47–79	1.61	4.18	43.05	52.45	0.33	0
35.		C 79–105	1.57	3.66	47.84	48.15	0.36	0

Particle size fraction percentages were measured by the conventional pipette method. The full desaggregation procedure was made according to the ISO/DIS 11277/1995 standard. Other soil characteristic determinations followed standard methods (BÚZÁS, 1993). (Dry bulk density was used and was assumed to be constant within the whole suction range.)

The P-S curves with water (pF curves) were measured according to the Hungarian standard at 8 suction values (VÁRALLYAY, 1973). At pF values of 0 to 2.5 100 cm³ water saturated soil core samples were exposed to suction in boxes containing sand and kaolin plates. pF 3.4 and pF 4.2 values were determined on resaturated soil pastes in pressure membrane apparatus with cellophane membranes. The pF 6.2 values were calculated from hygroscopic measurements applying a relative humidity of 34% above the samples (set using CaCl₂ · 6H₂O).

The P-S curves with NAPL were determined using a *modified pressure cell apparatus* (Soilmoisture Equip. Corp., LAB 023) (KLUTE, 1986; MAKÓ, 1999). The wetting phase was a non-aromatic hydrocarbon distillation product, namely DUNASOL 180/220 (Table 2).

Table 2
Characteristic physical and chemical properties of the liquids
used in the measurements

Fluid properties	Distilled water	NAPL: DUNASOL 180/220
Boiling point (°C)	100	179–217
Density [20 °C] (g/cm ³)	0.998	0.775
Viscosity [20 °C] (cP)	1.00	1.91
Aromatic compounds (m/m%)	0.00	0.00
n-alkanes (%)	-	60.3
Cyclic alkanes (%)		
– 1 ring	-	25.1
– 2 rings		12.0
– 3 rings		2.1
– 4 rings		0.5
Interfacial tension (fluid/air) [20 °C] (mN/cm)	72.6	25.0
Interfacial tension (NAPL/water) [20 °C] (mN/cm)	-	45.9

Since the NAPL/air interfacial tension decreases significantly with increasing temperature, the temperature was set at 20 °C. Two types of porous ceramic plates were used (1.0 bar and 5.0 bar air entry value for water, originated from Soilmoisture Equip. Corp.). Pressure cells were designed and constructed in the laboratory of our department using the porous ceramic plates and oil-resistant silicon rubber. The materials of all accessories were Teflon and glass. Five different gas pressures were applied during the measurements (0.002; 0.1; 0.2; 0.5 and 1 bar). For the examined samples a week equilibration time was found sufficient (Figure 1).

In order to compare the P-S curves measuring with different methods and fluids, the following three parameter functions were fitted to them (VÁRALLYAY et al., 1979):

$$\theta / \theta_0 = 1 / [1 + (X/X_0)^b] \quad (1)$$

where θ_0 , X_0 and b are experimental constants; θ is the fluid content (vol%); X is pressure (bar).



Figure 1

The modified pressure cell apparatus constructed by the author for the measurements of the NAPL retention

For the selection of the soil variables best correlated to the points of P-S curves measured with NAPL, backward regression analysis was used. After determining the independent variables best correlated to retained NAPL amounts the following regression function was fitted by multiple linear regression (RAJKAI et al., 1981):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_1X_2 + b_4X_1^2 + b_5X_2^2 \quad (2)$$

where $b_0 - b_5$ are regression coefficients; X_1 is explanatory variable at the first place; X_2 is explanatory variable at the second place.

Results and Discussion

The results of pressure-saturation measurements with different fluids were not comparable, because of the different pressure values used with the different methods. Therefore a three parameter function (Eq. 1) was fitted to the measured NAPL content values in order to compare the water and NAPL retention at a given pressure. The R^2 values (> 0.90) suggest that the applied function is suitable for the description of the pressure-NAPL content curves measured with water and NAPL. Due to that reason the calculated values using this function can be used successfully instead of the measured data in further statistical examination.

Figure 2 shows a plot of NAPL retention data versus water retention data. As the relationship between the NAPL and water retention is not too strong ($R^2 = 0.71$), a Leverett-type scaling of the water retention data can give – in some cases – inadequate estimation of the NAPL retention.

The results of backward regression and the applied multiple linear regression of (Eq. 2) are summarized in Table 3. It can be seen that in the low suction range (0.1 bar $>$) the silt content and the bulk density are the determining soil variables. In the higher suction range first the sand and clay content, then the sand and humus content are decisive.

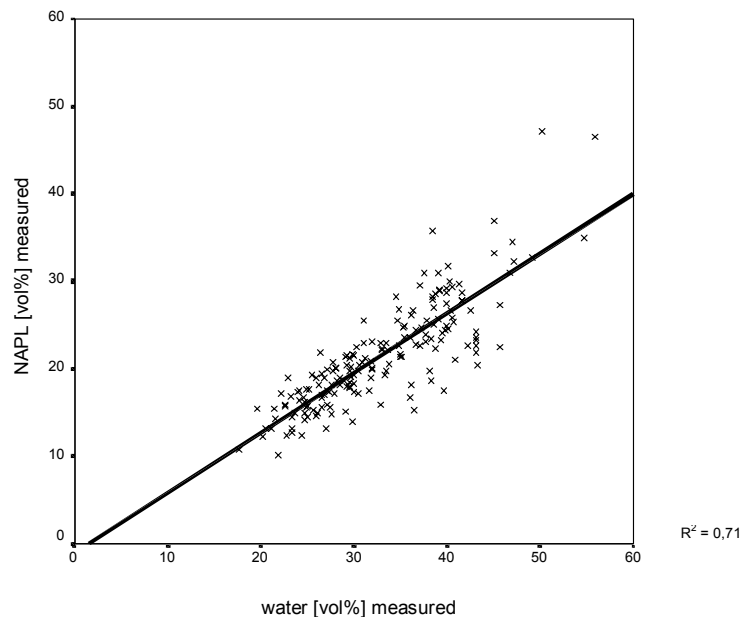


Figure 2
Relationship of measured (horizontal axis) and predicted (vertical axis) oil content retained by the soil samples

Table 3
Results of regression analysis of NAPL retention values and selected soil properties
(particle size distribution, humus content, bulk density)

$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_1X_2 + b_4X_1^2 + b_5X_2^2$										
Pres- sure (bar)	X ₁	X ₂	R ²	N	b ₀	b ₁	b ₂	b ₃	b ₄	b ₅
0	SI	BD	0.842	96	69.945	1.862	-68.831	-0.675	-8.620E-03	21.181
0.1	SA	CL	0.654	96	29.248	-0.300	-7.16E-02	-	2.160E-03	-
0.2	SA	HUM	0.706	96	25.940	-0.336	-0.742	3.401E-02	2.638E-03	-
0.5	SA	HUM	0.723	96	25.609	-0.400	-1.172	4.629E-02	3.616E-03	-
1	SA	HUM	0.711	96	25.375	-0.419	-1.140	4.723E-02	3.854E-03	-

Y: NAPL retention [vol%]; b₀-b₅: parameters of the regression equation; X₁- X₂: explanatory variables at the first and second place; R²: coefficient of determination; N: sample number; CL: clay%; SI: silt%; SA: sand%; HUM: humus; BD: bulk density, g/cm³

By the application of the linear regression equations of Table 3 the points of pressure-NAPL content curves can be calculated directly from the mechanical fractions, bulk density and humus content values of the soil in question. The

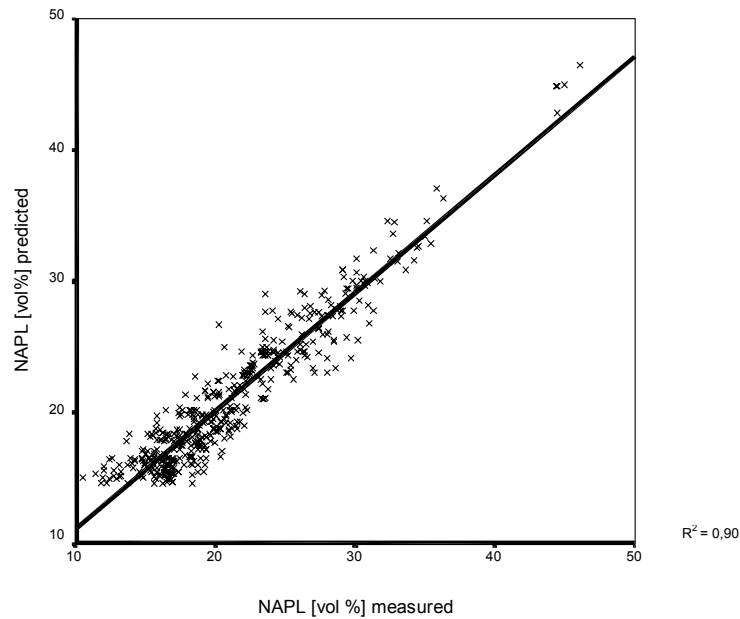


Figure 3
Relationship of measured and predicted NAPL content retained by the soil samples
Prediction: using the regression equations of Table 3

relationship of measured and calculated NAPL retention values is presented by Figure 3. As it can be seen from this plot, the measured and estimated NAPL retention data agree fairly well ($R^2 \sim 0.9$). This estimation method (after extending the database) can be useful for modelling NAPL fate and migration or mapping the organic contaminant sensitivity of the soils.

Summary

In order to expand the experimental data set of models describing the movement of organic liquids polluting the soils, a series of experiments was set up in which the fluid retention (pressure-saturation curves of the soils) were measured using water and NAPL (DUNASOL 180/220, a non aromatic petroleum product). Measurements were carried out on undisturbed soil samples originating from 35 different horizons of 12 characteristic Hungarian soils. The P-S curves with NAPL were determined in series, by a modified pressure cell apparatus – designed and constructed in the laboratory of our department – containing oil-resistant (silicon rubber, Teflon) components.

The applied methodology and the statistical analysis of the measured data are presented. The results show that the commonly used Leverett-type scaling of the water retention data provides inadequate estimation of the NAPL retention in some cases. This deviation may be a direct result of changes in clay volume and soil aggregation when saturation with different fluids was performed.

According to the analysis, however, with the easily measurable soil parameters (bulk density, particle size distribution and humus content) a better estimation of NAPL retention can be given. This estimation method (after extending the database) can be useful for modelling the fate and migration of NAPL or mapping the organic contaminant sensitivity of the soils.

Key words: pressure-saturation curves, NAPL, undisturbed soil samples, estimation, modelling

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