Possible effects of soil contamination by light non-aqueous phase liquids (LNAPLs) on soil water parameters and their consequences*

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A b s t r a c t. In central Germany a loess derived site contaminated with very different light non-aqueous phase liquids (LNAPLs) emanating from production of mineral oils, was evaluated with respect to soil water retention to form an idea on the conditions and possibilities of deep percolation. At 4 subsites, undisturbed cores (100 cm^3) were sampled from profile depths ranging between 2 and 9 m. The water retention characteristics and bulk density were determined. Results indicate that in most cases > 50% of the pore volume (PV) is occupied by water held at matrix potentials of $\leq$ -15000 hPa and only about 10% of PV may be occupied by quickly draining water (matrix potential > -60 hPa). LNAPLs strongly decrease the surface tension γ to values ranging from 20 mN·m^{-1} to 45 m·Nm^{-1} and increase the angle of contact α to 20-45° (from literature) as compared to values of 72.75 mN·m^{-1} and 0° for pure water. Thus it is almost impossible to derive the correct pore size distributions of the material studied and other contaminated material from the water retention characteristics. The effect of the changed surface tension and angle of contact on the water regime (deep percolation, capillary rise) of contaminated profiles results in an enhancement of deep percolation and a restriction in capillary rise.

K e y w o r d s: water retention, pore size distribution, surface tension, angle of contact, LNAPL-contamination, soil water regime

INTRODUCTION

At places where oils, coal, lignite, or tar were or have been processed to produce fuels, colour pigments, lacquers, plastics and other products, it was in the past almost unavoidable that there was some contamination of the soil by these products. The group of light non-aqueous phase liquids (LNAPLs) comprises some of these contaminants. Because of their noxious effects, emphasis was placed on their chemical and biological behaviour in soils and profiles. National laws like the German Federal Law for Soil Protection (Bundes-Bodenschutzgesetz [BBodSchG]) [1] considers the avoidance and elimination of contaminations and the handling of contaminated materials mostly with respect to their chemical behaviour. Little attention, however, has been given to LNAPL transport. Movement of contaminants through the soil and the profile as the porous medium [35], however, is affected by both the porous system and the physical and physicochemical properties of the fluid. Water is normally considered to be the transporting fluid. Therefore, the properties of the fluid controlling its binding to the surfaces of, as well as the movement through, the porous material are assumed to be those of pure water. These properties, however, can strongly deviate from the surface tension $\gamma = 72.75$ mN· m^{-1}, angle of contact $\alpha = 0°$ and viscosity $\eta = 1.3$ mPa · s, which are normally assumed [13,14,36]. The contamination of soil by hydrocarbons like LNAPLs affects these fluid-soil properties to an extent depending on the concentration of the LNAPL, or surfactant, irrespective of their solubility in water [27]. Temperature is another factor to be considered. It is known that naturally occurring organic compounds present in soil organic matter decrease surface tension γ and increase the angle of contact α [2,11, 31]. Because a change of these properties must affect the water retention characteristics of soil and thereby some aspects of its moisture regime, a study was carried out on undisturbed subsoil samples from an LNAPL-contaminated site. The results are discussed with respect to modelling implications. The exact composition of the LNAPLs and their specific properties were of secondary importance within the context of this presentation and are reported by Totsche and Kögel-Knabner [30].

MATERIALS AND METHODS

The LNAPL-contaminated study site is situated at Rositz, Thuringia, in Germany. The parent material at this site is loess with under-lying loamy, fluvio-glacial material [3]. For more than 100 years, an industrial plant has produced, mineral oils and solvents [7,30]. More details about the site and sampling procedure are given by Haas *et al.* [7] and Totsche and Kögel-Knabner [30]. For determining the water retention characteristics, in most cases 2 undisturbed core samples (100 cm^3) per sampling depth were obtained from undisturbed soil columns after soil-coring to depths of 8 m at the 4 subsites code-named emc 33, GW2/99, GW3/99, and GW4/99. Following Hartge [8] and Hartge and Horn [12], each core sample was weighed and 2 undisturbed subsamples (each about 10 cm^3) were taken from each face of each core. The subsamples were placed on quickly draining filter paper and then placed on a ceramic plate for saturating overnight with distilled water. These were then drained for about 15 min by inclining the plate 10° before weighing. The water content corresponds then to 1 hPa water tension. Thereupon, these subsamples were subsequently equilibrated with increasing water tensions in a pressure chamber with pressures up to 1000 hPa using the same ceramic plate. They were regularly weighed. For higher water tensions the subsamples were equilibrated in a pressure-membrane chamber using a plastic membrane, and weighed after each pressure step. Times of equilibration ranged from 1 d at 20 hPa to 7 d at 15000 hPa. Finally, the samples were oven-dried overnight at 105°C. The separate filter paper for each subsample was necessary to avoid loss of soil during the moving of the subsample between the balance and the ceramic or plastic membrane. Even the loss of a very small particle of soil would simulate water loss. To consider the changing weight of the filter paper during water desorption, one filter paper without a sample was included per 'membrane' as a blank. Furthermore, one disturbed sub-sample was taken from each core sample, weighed, oven-dried overnight at 105°C and re-weighed for determining its bulk density. This data was used for determining volumetric water contents at different water tensions as well as for calculating the pore volume of the sample using Eq. (1) [8]. Eq. (2) corrected for the influence of organic matter according to Müller *et al.* [20]:

$$PV = \left(1 - \frac{\rho_b}{\rho_f}\right)100 \qquad (1)$$

$$\rho_f = 2.65 - 0.0115 \cdot om \qquad (2)$$

with PV - pore volume (vol. %), ρ_b - bulk density (g·cm^{-3}), ρ_f - density of solids (g·cm^{-3}), om - organic matter (wt. %) - C_{org} (wt. %) · 1.724 [1]. Due to the absence of the weight of the overlying soil, the subsamples adsorb more water during the initial saturation than corresponding to the pore volume determined (Eq. (1)). It is therefore necessary to correct the volumetric water contents determined according to Vogl [33]:

$$k = \frac{PV - PWP}{WC_1 - PWP} \qquad (3)$$

$$WC_{corr} = \left(WC_{det} - PWP\right) \cdot k + PWP \qquad (4)$$

with k - correction factor, PWP - permanent wilting point = water content at 15000 hPa, WC_1 - water content at about 1 hPa, WC_{corr} - corrected water content, and WC_{det} - measured water content [2].

RESULTS

Most of the samples were contaminated, some of them to high levels [30]. This was indicated by the fact that after opening the chambers for weighing, there was the characteristic smell of LNAPLs, or other hydrocarbons, even at 15000 hPa. This was most pronounced at site **GW4/99**. As this smell persisted for more than half a year when running the same procedure using uncontaminated samples, the ceramic membranes (plates) must also have become contaminated by these contaminated samples. Due to the numbers of core samples from each depth, the values of bulk density (ρ_b) and pore volume are presented as single values or as the mean of two values, whereas those of water retention at field capacity (*FC*) (300 hPa) and PWP are the mean of two or four values of the corrected water content (Table 1). The relatively flat or smooth course of the water retention curves have almost no pronounced air-entry value, as typified by those curves for the subsite **GW2/99**, except at a depth of 3.7 m (Fig. 1). This is typical for the deep subsurface material derived from loess and loam. Assuming contaminant-free water the differences between both *PV* and *FC* and *FC* and *PWP* represent the volumes of macropores (> 10 µm) and mesopores (0.2-10 µm), respectively, whereas *PWP* represents the volume of micropores (< 0.2 µm). It is evident from Table 1 that all layers at the 4 subsites have small total pore volumes with respect to the loessial to loamy material and relatively small amounts of macropores (15-22% of *PVs)* and very small amounts of quickly draining macropores (difference between *PV* and water held at -60 hPa; 3-16% of *PVs*). The latter are responsible for the relatively fast transportation of water and solutes to the groundwater assuming high continuity. On the other hand, water volumes held at *PWP* amount to 45-77% of *PVs*.

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[1]Eq. (2) is the result of regressions on 630 core samples from Lower Saxony [20].
[2]Assuming that (i) the water content by volume at 1 hPa (WC_1) corresponds to *PV* and (ii) the water content at *PWP* is not affected by the absence of overburden [33].

T a b l e 1. Organic carbon (C_{org}), bulk density (ρ_b), pore volume (PV), and amounts of retained water at different water tensions (hPa) at the contaminated site Rositz (Thuringia, Germany)

Depth (m)	C_{org} (wt. %)	ρ_b (g cm^{-3})	PV	60	300	15000
				(vol. %)		
Subsite **emc 33**						
2.8	0.76	1.716	35.2	29.5	28.0	21.8
3.2	0.76	1.723	34.8	31.6	28.5	19.0
4.2	0.76	1.732	34.6	30 .0	27.1	20.8
4.8	0.30	1.779	32.9	30.2	29.5	24.3
5.3	0.30	1.808	31.8	28.6	27.9	22.1
Subsite **GW2/99**						
2.4	0.49	1.600	38.0	35.9	34.9	28.5
3.7	0.19	1.721	35.1	25.7	22.1	16.4
4.4	0.32	1.760	33.6	29.6	27.9	25.3
5.5	0.23	1.852	30.1	25.5	24.4	23.2
6.2	0.22	1.826	31.1	26.9	24.5	15.5
7.3	0.07	1.818	31.4	28.8	26.6	22.3
Subsite **GW3/99**						
3.2	n.d.	1.529	40.9	35.4	32.7	22.7
3.8	n.d.	1.696	29.7	27.9	26.1	18.7
4.7	n.d.	1.764	33.4	30.1	27.5	19.1
5.5	n.d.	1.755	33.8	30.6	27.9	22.0
6.6	n.d.	1.873	29.3	26.2	24.8	20.0
7.7	n.d.	1.731	34.7	31.0	29.1	20.0
8.4	n.d.	1.826	31.1	28.4	26.8	19.2
8.8	n.d.	1.655	36.2	34.5	32.9	21.7
Subsite **GW4/99**						
0.8	1.12	1.570	40.8	34.6	31.3	21.6
1.2	1.12	1.523	41.3	36.4	33.3	22.1
1.8	1.12	1.464	41.1	35.3	32.6	21.6
2.4	1.12	1.644	37.3	32.6	30.2	16.7
3.5	1.27	1.745	32.7	32.2	31.1	19.1
4.6	1.27	1.709	33.7	32.8	31.2	19.1
5.5	0.50	1.761	34.0	34.1	32.0	22.3
6.6	0.50	1.779	32.9	31.5	28.4	17.1

n.d. = not determined.

DISCUSSION

All soil samples show relatively high to high bulk density values of 1.52-1.87 g · cm^{-3} (Table 1) even though they have silty to loamy textures [3]. These high values are due to the naturally occurring compacting effect of the overlying soil and profile material [9,10]. Due to their high bulk densities the samples have low pore volumes of about 29-41% (Table 1). Checking (or recalculating) the PV-values using Eqs (1) and (2) and the C_{org}-values (up to 1.3%) (Table 1), will result in about 0.5 vol.% higher values because of the C_{org}-values include the C-contents due to the contaminating hydrocarbons of the samples. Naturally occurring C_{org}-contents for these depths should be 0% or at least very close to 0%, because paleosols are absent at the

site [30]. Obviously, the highly contaminated profile samples of subsite **GW4/99** (3.5-6.6 m) show hydrophobicity because their water contents between 20 and 60 hPa (not shown) - although corrected - were higher by about 0.5 vol% than the corresponding pore volume, whereas the other soil samples had lower water contents by about 2-5 vol.% at these water tensions. The hydrophobicity was also indicated by the prolonged time necessary to water-saturate them, as compared to the other samples. Possibly, these samples had not become maximally saturated before starting desorption of water due to the often amphiphilic character of the surfactants [15]. As the water contents at 15000 hPa (*PWP*) make up 45-77% of the corresponding PV (Table 1) most samples possess only 3-16% of water (retained at ≥ -60 hPa matrix potential) which may be able to relatively quickly
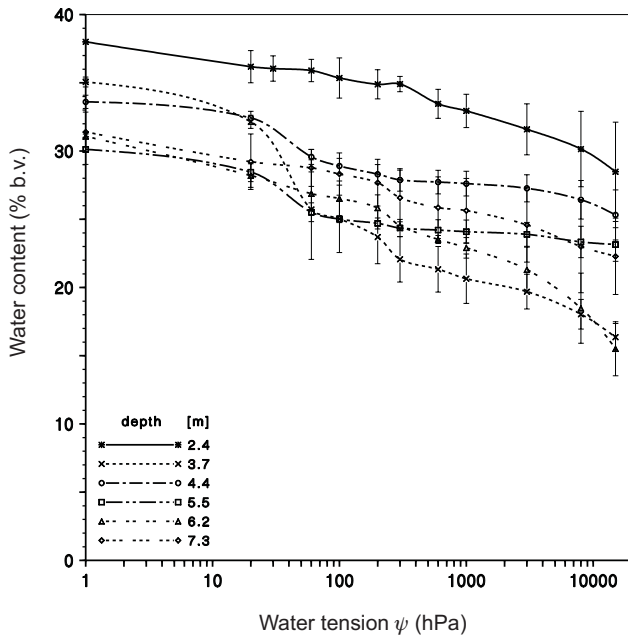
Fig. 1. Soil water characteristics for soil samples from different depths at the contaminated subsite **GW2/99**, bars indicate the standard deviations.

transfer soil solution including contaminants down the profile. Only some samples from depths of < 3.5 m show water volumes of > 15% held between 0 hPa and 15000 hPa. This finding leads to the soil water characteristics having only a gentle slope as demonstrated by Fig. 1. Keeping in mind the high bulk density and the low amount of water not stronger bound than -15000 hPa the pores filled with this water must have a very low continuity at any matrix potential. This possible condition will strongly restrict the movement of water and/or solute or any other liquid within and through a stratum of substrate. Nevertheless, there may be some enhanced flow due to the presence of fissures, which are typical for loamy material [27], or due to sedimentation differences as demonstrated by Miller *et al.* [19].

Presuming that water has a very low concentration of constituents affecting the surface tension γ and the angle of contact α of water, the pore size distributions (Table 1) were calculated from this water retention data using the well-known equation of capillary rise (Eq. (5)),

$$r = \frac{2 \cdot \gamma \cdot \cos \alpha}{h \cdot \rho \cdot g} \qquad (5)$$

with r - radius of capillary (or pore) (μm), h - height of capillary rise (cm), numerically identical to the absolute value of the corresponding matrix potential (hPa), ρ - density of water at 20°C, and g - acceleration due to

gravity (9.81 m·s^{-1}), and γ - surface tension = 72.75 mN·m^{-1} (at 20°C) and α - angle of contact = 0° [22].

However, there arises a strong problem (i) due to the soil temperature being 10°C or even less at profile depth and (ii) due to the contamination by LNAPLs. Both surface tension γ and angle of contact α are more or less affected by the different kinds of these contaminants and other hydrocarbons having contaminated the profile at the site. The hydrocarbons including LNAPL have very different physicochemical properties. They are either hydrophilic or hydrophobic, sometimes even amphiphilic [17,24,25,26], and reduce γ and increase α more or less depending on the mixture of compounds and their individual concentrations. According to Lide [18] and Egemen *et al.* [5], γ of individual hydrocarbon compounds ranges from about 20 to 40 mN·m^{-1}, and α varies for natural organic matter between 15 and 45° [2,31]. α depends on pH, too. Moreover, α shows a hysteresis due to draining or rewetting conditions [2, 11,29]. Unfortunately, α strongly depends on γ of the fluid composed of different LNAPLs of varying con- centrations, however not alone, but also on the kind of the 3-phase-system [34]. Thus it cannot be directly calculated from γ (e.g., Franke [6], Or and Wraith [22]). The aforementioned dependencies mean that the calculated pore radius (or pore diameter) decreases with decreasing γ and increasing α at the same matrix potential or water tension as compared to uncontaminated conditions. This deviation becomes increasingly more pronounced for $\alpha > 30°$ and $\gamma < 50$ mN·m^{-1} as demonstrated for pores of, e.g., 10 μm in Fig. 2. Assuming a mixture consisting of water and different concentrations of different hydrocarbon compounds at 10°C having in average $\gamma = 40$ mN·m^{-1} and $\alpha = 50°$, calculated pore diameters of 3.5 and 0.07 μm at 300 and 15000 hPa matrix potential result, respectively, as compared to 10 and 0.2 μm for 'normal' soil water. By roughly knowing or estimating γ and α, it is possible to estimate the pore size being probably emptied by the prevailing matrix potential as indicated by the same grey tones (or colours) within Fig. 3[3]. As a consequence, however, it is practically impossible to calculate correct pore size distribution from the water retention characteristics for any soil material contaminated by hydrocarbons as long as α and γ of the mixture at the prevailing soil temperature are unknown.

Considering the dynamic processes like solute transport, viscosity η must be taken into account, too. Viscosity is also affected by the mixture which shows two samples values of 6.6 and 6.7 mPa·s [30] as compared to that of water at 10°C of 1.3 mPa·s. However, η of individual hydrocarbon compounds varies between 0.3 and < 10 mPa·s [18]. Therefore, use of the Hagen-Poiseuille equation (Eq. (6)) [13,14, 23,36]:

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[3]By analogy to Eq. (5), the co-ordinates of the grid knots for the pore diameters specified were calculated with γ and α as independent and ψ as dependent variables. These matrices were imported into the graphic.
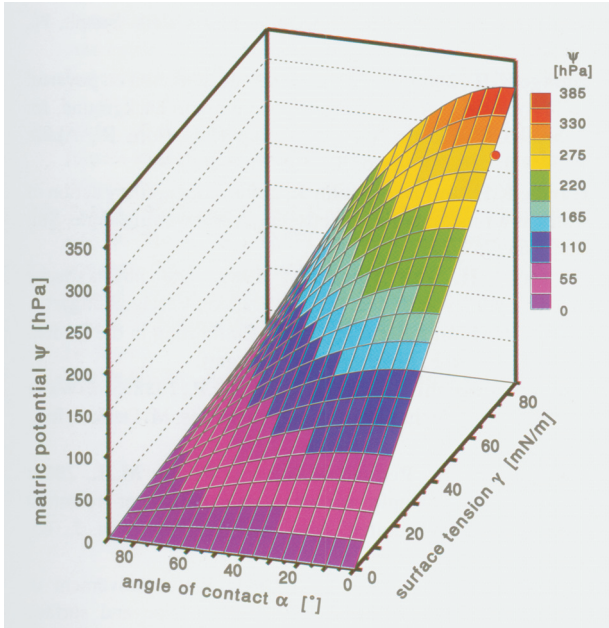
Fig. 2. Effect of surface tension γ and angle of contact α on the matrix potential ψ to empty a pore of 10 μm, black circle indicates pure water.
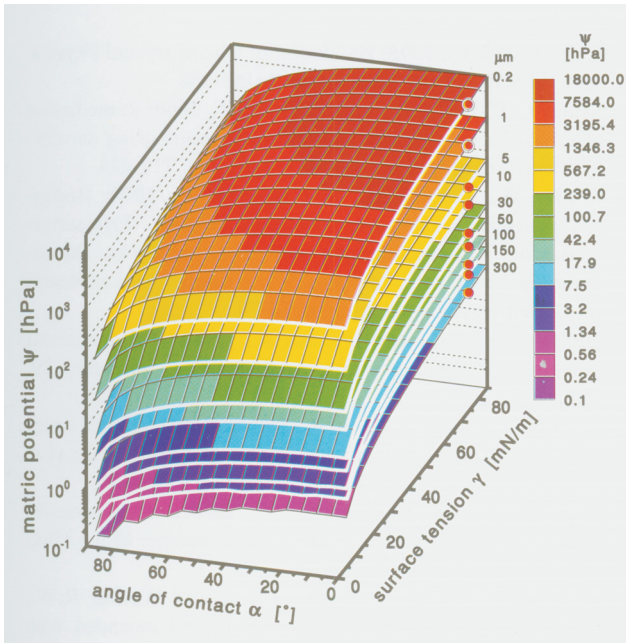

Fig. 3. Effect of surface tension γ and angle of contact α on the matrix potential ψ (logarithmical scale) to empty different pore sizes, black circles indicate pure water.

$$Q = \frac{\pi \cdot r^4 \cdot \Delta h}{8 \cdot \eta \cdot l} \qquad (6)$$

or similar equations to try to estimate or model the movement (velocity) of the contaminated fluid, is practically impossible, because r is very uncertain due to γ and α (see above) and η is more or less unknown for the mixtures. In

Eq. (6) Q - transferred quantity of water (cm^3), Δh - pressure or matrix potential difference (cm or hPa) along flow path, l - distance of flow (cm). With respect to site conditions, water as well as the contaminants (hydrocarbons) will move very slowly through the profile except for the preferential flow along some fissuring which cannot be detected by determinations of bulk density and water retention characteristics. On the other hand, the contaminants are often unevenly distributed within the pore space and the matrix, especially in fine-textured soils [4] like those presented. Thus, fingering of a moving front of solution due to fissures will be intensified [28].

As pointed out above, infiltration and deep percolation of soil water must be affected by organic contaminants. But at the same time, water supply to plant roots by capillary rise will be strongly restricted, too, because of the height of the capillary rise is reduced if LNAPLs are present [15,28,32]. Thereby, the effect of hysteresis of water retention, especially of coarse textured soils, is intensified [16]. Moreover, contaminated water having arrived at some critical depth will no longer be hindered by evapotranspiration to percolate deeper into the profile, thus possibly contaminating the groundwater more easily. As stated by Smith and Gillham [27], surface tensions for some organic compounds like methanol decrease linearly and 'slowly' with increasing concentration, whereas surface tension of other organic compounds (e.g., butanol) decreased nonlinearly with increasing concentration and levelled off near saturation concentration. But there exists a third group of organic compounds (long-chain ions like commercial surfactants) [27], the surface tension of which drastically decreases linearly with increasing concentration and, beyond a critical concentration (the 'critical micelle concentration'), no longer decreases, but rests on a very low level. The effect of methanol and butanol via their surface tensions on the behaviour of water infiltrating into sand under changing boundary conditions was simulated by Smith and Gillham [27]. No such simulations for fine-textured soils are known to the author.

It must also be kept in mind that landfill gases dissolved or not dissolved in water [26], and the other volatile and semi volatile decomposition products of landfill sites should also affect the surface tension of the water- (liquid-) -air interface [4,24] and thereby also the angle of contact within their top and bottom lining. This means that precipitation may percolate through a relatively dense top lining into the waste of the landfill. On the other hand, the capillary barrier [21] and/or the bottom lining may not work as expected, due to changes in surface tension and angle of contact. Being concerned with infiltration, deep percolation, capillary rise and/or the lateral movement of water or fluid at water-unsaturated, contaminated conditions especially when modelling, it is necessary to consider the hysteretic behaviour of the menisci and of the angle of contact, as shown by Steffy et al. [29] and Hartge and Bachmann [11].

CONCLUSION

At sites contaminated with organic compounds like light non-aqueous phase liquids (LNAPLs) water retention characteristics of undisturbed profile materials may be affected due to strong changes in surface tension (decrease) and angle of contact (increase). As the degree of these changes depends on the kind, the concentration and the mixture of organic contaminants, respectively, it is almost impossible, however, to derive pore size distributions for contaminated materials. Moreover, changes in surface tension and angle of contact enhance infiltration and deep percolation when the material is wet, and reduce capillary rise, thereby affecting the water regime of the profile material and increasing the hazard of groundwater contamination. There is a lot of work for soil scientists to do, to consider the effects of surface tension and angle of contact and for physico-chemists in the near future to consider soils and sites contaminated by organic compounds.

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