

# Natural colloid mobilization and leaching in wettable and water repellent soil under saturated condition

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**Abstract:** The coupled transport of pollutants that are adsorbed to colloidal particles has always been a major topic for environmental sciences due to many unfavorable effects on soils and groundwater. This laboratory column study was conducted under saturated moisture conditions to compare the hydrophobic character of the suspended and mobilized colloids in the percolates released from a wettable subsoil and a water repellent topsoil. Both soils with different organic matter content were analyzed for wettability changes before and after leaching using sessile drop contact angles as well as water and ethanol sorptivity curves, summarized as repellency index. Hydrophobicity of the effluent suspensions was assessed using the C18 adsorption method. Water repellency level of the repellent soil decreased after leaching but remained on a lower level of water repellency, while, the wettable soil remained wettable. The leached colloids from the repellent soil were predominantly hydrophilic and the percentage of the hydrophobic colloid fraction in the effluent did not systematically changed with time. Total colloid release depended on soil carbon stock but not on soil wettability. Our results suggest that due to the respective character of transported colloids a similar co-transport mechanism for pollutants may occur which does not depend explicitly on soil wettability of the releasing horizon, but could be more affected by total SOM content. Further studies with a wider range of soils are necessary to determine if the dominant hydrophilic character of leached colloids is typical. Due to the mostly hydrophilic colloid character we conclude also that changes in wettability status, i.e. of wettable subsoil horizons due to the leachate, may not necessarily occur very fast, even when the overlying topsoil is a repellent soil horizon with a high organic matter content.

**Keywords:** Soil water repellency; Hydrophobic colloids; C18; Sessile drop; Repellency index.

## INTRODUCTION

Colloids (i.e. particles with effective diameters of around 10 nm to 10  $\mu$ m) in natural subsurface environments may have various organic and inorganic sources: i.e. silicate clays, sesquioxides (Fe- and Al- oxyhydroxides), mineral precipitates, humic materials, microemulsions of non-aqueous phase liquids and microorganisms including viruses and bacteria (Bradford and Torkzaban, 2008; McCarthy and Zachara, 1989). Colloid translocation by convective water flux in soil and sediments is an important environmental issue for the co-transport of organic and inorganic contaminants (Lazouskaya and Jin, 2008; Sepehria et al., 2014; Tufenkji et al., 2004) whereby mobile organic or inorganic colloids can serve as effective shuttles. Pollutant transport (i.e. heavy metals, radionuclides, pesticides, phosphorus, and pathogens) in natural environments may be accelerated by the complexation with mobile colloids (so-called colloid-facilitated contaminant transport) as shown by many others (Amrhein et al., 1993; Carstens et al., 2017; Guo and Chorover, 2003; Karathanasis, 1999; Motoshita et al., 2003; Totsche et al., 2006; Tufenkji et al., 2004). The extent to which these various colloid fractions are mobile in porous media affects also the mobility of associated contaminants.

Among various factors (McCarthy and McKay, 2004; Chen and Flury, 2005; Sen and Khilar, 2006), soil water repellency, or in extreme cases soil hydrophobicity, is an often overseen but important property that may principally affect colloid transport (Baumann and Niessner, 2006). In most studies using laboratory-scale columns under well-controlled conditions colloid transport is focused on injection of colloids to the wettable or nonwetable porous media to analyze chemical, physi-

cal and/or physicochemical interactions between pore wall and colloid (Goebel et al., 2013; Lazouskaya and Jin, 2008; Ochiai et al., 2006; Wang and Yoon, 2005). In these studies, either the transport of natural colloids (i.e. extracted water dispersible soil colloids) or of artificial model colloids (i.e. hydrophilic/hydrophobic carboxylic tubes) is conducted to identify main mechanisms that govern transport and retention of colloids through porous media (Auset and Keller, 2004; Crist et al., 2004; Keller and Auset, 2007; Keller and Sirivithayapakorn, 2004). Some results indicated that the transport of colloids in natural environments are affected by the respective properties of the organic matter components such as dissolved organic matter (DOM) or dissolved organic carbon (DOC) (Larsen et al., 1992; Nanny and Ratasuk, 2002; Wood et al., 2011). Therefore, a growing research effort aimed to develop an understanding of the impact of hydrophilic or hydrophobic organic components in leachates through different methods (Dilling and Kaiser, 2002; Egeberg and Alberts, 2002; Ghernaout, 2014; Lindroos et al., 2002; Nanny and Ratasuk, 2002).

Given that hydrophilicity is the inverse of hydrophobicity (Brown and Peake, 2003) it still remains unknown what the respective effects of wettable and water repellent soils on the specific colloidal translocation processes like mobilization, transport, retention (Goebel et al., 2013) and colloidal flocculation and stabilization processes (van Oss, 1995) are. Ritsema and Dekker (1998) found by using 3D-visualizations of water content and water repellency pattern that the dissolution of hydrophobic substances proceeded along flow paths which were formed by instability-driven fingered flow which rendered the soil within the pathways more wettable than the surrounding soil. In contrast, Dymov et al. (2015, 2017) concluded that

transport of hydrophobic components in water solutions might be the reason for an increase of subsoil water repellency.

To analyze such phenomena listed above, a method is needed to characterize the hydrophilicity/hydrophobicity character to the organic colloids. Determination of hydrophobic colloids in leachates using the C18-method (Octadecyl: micro-particles; 40  $\mu\text{m}$  diameter) is relatively new (Klitzke and Lang, 2007). Therefore, the current knowledge about mobilization and transport of natural colloids detached from repellent or wettable soil material in context with the hydrophilic or hydrophobic character of the mobile colloids is very limited.

Generally, the topsoil is potentially more influenced by higher rates of hydrophobic organic matter input (Fishkis et al., 2015; Fröberg et al., 2003; Goebel et al., 2005, 2011). One of our hypotheses is therefore that the colloids released from a repellent topsoil are in average more hydrophobic than those detached from the underlying wettable subsoil. We further suppose that the relative amount of the hydrophilic colloids will increase with leaching duration because colloids are easier detached as the functional group arrangements associated with wettable surfaces changed during leaching, i.e. due to swelling (Diehl, 2013; Urbanek et al., 2007).

Summarizing, at present information regarding the hydrophobicity/hydrophilicity status of the suspended colloids in leachates drained to the subsurface media is scarce. Therefore, following the findings and conclusions published by Fishkis et al. (2015) and Dymov et al. (2015, 2017), we have the following hypothesis: i) the total amount of colloids that can be released from the soil matrix depends on soil wettability (either hydrophobic or hydrophilic), ii) colloids released from a repellent topsoil are more hydrophobic than those detached from the respective underlying wettable subsoil, because, topsoil is more influenced by higher rate of hydrophobic organic matters (Bachmann et al., 2016; Fishkis et al., 2015; Fröberg et al., 2003; Goebel et al., 2005, 2011), iii) the relative amount of the hydrophobic colloids is increased by time and depended on soil carbon stock and wettability, and iv) the leached colloids may contribute differently to changes of subsoil wettability by time due to the specific hydrophilic or hydrophobic character of the colloids which is determined by the emitting soil horizon. The objectives of this study are correspondingly focused on the wetting properties of the soil and leachates:

- i) Comparison of the hydrophobicity status of the suspended colloids in leachates from a repellent topsoil and the respective underlying wettable subsoil under saturated conditions,
- ii) Evaluation of the relative amount of hydrophobic colloids from the wettable and repellent soils with leaching time, and,
- iii) Investigation of soil water repellency persistency in term of repellency index ( $R_I$ ) and contact angle (CA) changes before and after leaching.

## MATERIAL AND METHODS

### Soil sampling and soil properties

The studied spruce forest soils are classified as Stagnic Podzol ( $O_e-O_e-O_a-AE_h-B_s-B_w-B_{gd}$ ) ( $50^\circ 7' 39.64''$  N;  $11^\circ 51' 18.51''$  E) and located in the Fichtel Mountains in southeast Germany.

**Table 1.** Physical and chemical properties of the studied soils.

Property soil	Depth (cm)	Texture <sup>a</sup>	pH <sub>H2O</sub>	pH <sub>CaCl2</sub>	C <sub>org</sub> (%)	DOC (mg L <sup>-1</sup> )
Repellent	0–4	Sandy loam	4.30	3.40	11.00	20.00
Wettable	26–55	Sandy loam	4.60	3.60	1.30	2.40

<sup>a</sup> Estimated in the field by hand texture according to Fishkis et al (2015). C<sub>org</sub>: organic carbon, DOC: Dissolved organic carbon.

This site was already studied by Fishkis et al. (2015). Bulk soil from the top (0–4 cm) and from subsoil horizons (26–55 cm) were gathered as repellent and wettable soil, respectively. Prior studies using contact angle measurement showed that surface horizons ( $O_e-O_a-AE_h$ ) of this location were hydrophobic, while, the deeper subsoil horizons ( $B_w-B_{gd}$ ) were hydrophilic (Fishkis et al., 2015). Three undisturbed soil cores (5 cm diameter, 5 cm height) were taken from the mentioned depths to determine field bulk density of the soil layers. The samples were gently passed through a 3.60 mm sieve with minimum disturbance to prevent destruction of hydrophobic particle surfaces by abrasion. Sieved samples were then air-dried in the lab.

Organic carbon (C<sub>org</sub>), dissolved organic carbon (DOC), pH, and soil texture were analyzed according to Fishkis et al (2015) (Table 1). The C<sub>org</sub> and DOC content were measured by dynamic flash combustion (Thermo Quest, Flash EA, Wigan, United Kingdom) and by high temperature analyzer (Elementar, high-TOC, Germany), respectively. Porosity ( $P=1-BD/PD$ , BD and PD are bulk and particle densities, respectively) was calculated and pore volume (PV) was considered as saturated water filled pore volume (Klute and Dirksen, 1986; Kirkham, 2005) established during the column experiments. The  $K_s$ , saturated hydraulic conductivity, was measured by the constant-head procedure through an infiltration experiment and calculated by Darcy's equation (Klute and Dirksen, 1986).

### Column preparation and leaching set-up

Six PVC columns (7 cm diameter, 17 cm height) were packed for each soil sample to field bulk density. A rigid coarse plastic membrane (i.e. 0.5 mm in diameter) was also used to stabilize the soil materials. The soil columns were saturated via capillary rise by submerging the wettable and repellent soil columns into tap water for 24 and 48 h, respectively. Water ponding was subsequently observed on the top of the columns. Because the studied soils were not aggregated the presence of larger amounts of poorly accessible soil volume inside aggregates (immobile water volume fraction) could be excluded. Accordingly, it was assumed that the columns were saturated under these initial conditions and during the following percolation experiment. The upper and the lower boundary condition of the columns were constant pressure head and seepage face, respectively. Chloride ( $\text{Cl}^-$ ) was used as the conservative chemical tracer. A volume of 10 mM NaCl solution (equal to 0.1 PV of the hydrophobic soil) was poured on top of the soil columns while they were saturated. Then a saturated flow condition (zero pressure at the contact plane of soil and infiltrometer) was applied at the top of the soil columns using a disc infiltrometer. Effluent was sampled at periodic intervals (i.e. in steps of 0.1 PV before 0.5 PV, and in steps of 0.25 PV leachate for the rest of the experiment) from the bottom outlet of the columns. Soil columns were leached based on  $K_s$  and pore volume PV. The duration of leaching experiments (i.e. 2 and 2.5 h for repellent and wettable soil, respectively) was considered as time equivalent to account for eight PVs. Totally, 35 samples were taken for each column run to analyze the hydrophobicity of the colloidal suspensions.

### Measurement of soil and suspension hydrophobicity

The status of water repellency of both soils was tested before and after the leaching experiments applying the sessile drop method (Bachmann et al., 2000) and the soil water repellency index,  $RI$ , method (Tillman et al., 1989). Soil samples were oven-dried at 40°C before the measurements.

To evaluate  $RI$ , the cumulative liquid infiltration rate  $I$  of water and ethanol were measured for the time interval  $< 180$  s with a microinfiltrometer (Sepehrnia et al., 2016, 2017). The infiltrometer was placed on top of the samples and the results were plotted against  $t^{0.5}$ . Three replicate soil cores (5 cm height, 5 cm diameter) were prepared for each soil with the same bulk density which was used for the column experiments. The infiltration process were conducted with a negative pressure equivalent of  $h_0 = -2$  cm water column. The sorptivity for water ( $S_w$ ) and ethanol ( $S_e$ ) infiltration were calculated using the equation  $S(h_0) = I / t^{0.5}$  (Philip, 1957).  $RI$  as a measure of the extent of soil water repellency (Tillman et al., 1989) was calculated from equation (1):

$$RI = 1.95 S_e(-2 \text{ cm}) / S_w(-2 \text{ cm}) \quad (1)$$

A soil is classified as being water repellent if  $RI > 1.95$ .

The sessile drop method was performed using a CCD-equipped contact angle microscope (OCA 15, Data Physics, Filderstadt, Germany). The initial contact angle was evaluated by placing a water drop of 1  $\mu\text{L}$  on the soil cores used later for  $RI$  measurements (Fishkis et al., 2015). After termination of mechanical perturbations of the droplet ( $t > 30$  ms after contact with sample surface), the CA was measured at both intersections of the drop contour line with the horizontal solid surface baseline by automated drop shape analysis using the software SCA15 (DataPhysics, Filderstadt, Germany) (Bachmann et al., 2000). Three drops were measured for one soil core. A soil was classified as water repellent if  $CA > 90^\circ$ , subcritical-repellent if  $0^\circ < CA < 90^\circ$ , and water wettable if  $CA = 0$  (Bachmann et al., 2007).

Hydrophobicity of the effluent was assessed using the C18-method proposed by Klitzke and Lang (2007). In this separation method, a defined hydrophobic solid surface (Octadecyl: micro-particles; 40  $\mu\text{m}$  diameter) is used instead of a non-polar organic solvent to attach hydrophobic colloids to the granular particles which removes them from the effluent liquid. The suspensions were filtered immediately after sampling over a 15  $\mu\text{m}$  Nylon mesh (VWR International, GmbH, Germany) prior to turbidity measurements ( $T_1$ ) using a spectrophotometer (LAMBDA 1050 UV/Vis/NIR, Perkin Elmer). The emission

wavelength of 420 nm was chosen to maximize the average of turbidity. The detector was centered at  $90^\circ$  to the incident light path (Brown and Peake, 2003; EPA, 1993). Thirty milligrams of C18 microparticles (VWR International, GmbH, Germany) and 10 mL of suspension were mixed in a glass tube allowing for hydrophobic colloids to sorb onto the hydrophobic surface of the microparticles. The tube was attached to a horizontal shaker for 2 h at 100 rpm. After the shaking period, C18 particles were separated using the 15  $\mu\text{m}$  nylon mesh and the turbidity of the filtered suspensions was determined ( $T_2$ ). The suspension hydrophobicity index ( $HI$ ) for all particles  $< 15 \mu\text{m}$  is then calculated according to the equation 2.

$$HI = \frac{T_1 - T_2}{T_1} \quad (2)$$

### Statistical analysis

The experiment was performed using a complete randomized design with three replications for contact angle (CA) and repellency index ( $RI$ ) as dependent and the studied soils (repellent and wettable) as independent variables. A further similar complete randomized test was done for effluent concentrations  $C/C_0$  to compare the first seven effluent samples (pore volumes 0.1 PV to 1.0 PV) for differences between the wettable and the water repellent soil in the initial phase of the experiment. Statistical analyses were done using SAS (Statistical Analysis System) and the mean comparisons were performed by the LSD test (SAS Institute, 2004).

## RESULTS AND DISCUSSION

Basic soil properties are given in Table 1. Basic parameters of the columns are presented in Table 2. Repellent soil had significantly higher total and dissolved organic carbon content ( $C_{\text{org}}$  and DOC), saturated water content ( $\theta_s$ ), porosity ( $P$ ), and saturated hydraulic conductivity ( $K_s$ ) compared to wettable soil.

Contact angle (CA) and repellency index ( $RI$ ) data before and after the percolation experiment of the wettable and repellent soil are summarized in Table 3. CA and  $RI$  of the repellent soil material were strongly affected ( $p < 0.001$ ) by the percolation experiment, i.e. CA dropped from  $107^\circ$  to  $71^\circ$ , while the CA of the wettable soil was stable with  $0^\circ$  before and after leaching. Similarly,  $RI$  of the water repellent soil decreased significantly ( $p < 0.05$ ) after leaching from  $140 (\pm 13)$  to  $57 (\pm 11)$  and, in agreement to CA results,  $RI$  of the wettable soil was  $< 1.95$  and remained unchanged (Table 3). For the repellent soil the comparison of CA and  $RI$  values before and

**Table 2.** Physical properties of the soil columns during leaching under saturated flow condition.

Property soil	$\theta_s$	BD	PD	$P$	$V_t$	PV	$K_s$
	( $\text{cm}^3 \text{cm}^{-3}$ )						
Repellent	0.72	0.51	2.20	77.00	654	471	0.90
Wettable	0.51	1.25	2.65	53.00	654	334	0.50

**Table 3.** Mean and standard error of contact angle (CA) and repellency index ( $RI$ ) of the studied soils before and after leaching ( $n = 6$ )<sup>a</sup>.

Property soil	CA		$RI$	
	before	after	before	after
Repellent	107 ( $\pm 13$ ) <sup>***</sup>	71 ( $\pm 18$ ) <sup>***</sup>	140 ( $\pm 13$ ) <sup>***</sup>	57 ( $\pm 11$ ) <sup>***</sup>
Wettable	0.00 <sup>***</sup>	0.00 <sup>***</sup>	1.84 ( $\pm 0.20$ ) <sup>***</sup>	1.67 ( $\pm 0.26$ ) <sup>***</sup>

<sup>a</sup> denotes the number of replicates for the columns of each soil in the leaching experiment. CA: Contact angle,  $RI$ : repellency index. <sup>\*\*\*</sup> denotes the properties which are significantly different between soils on significance level 0.001.

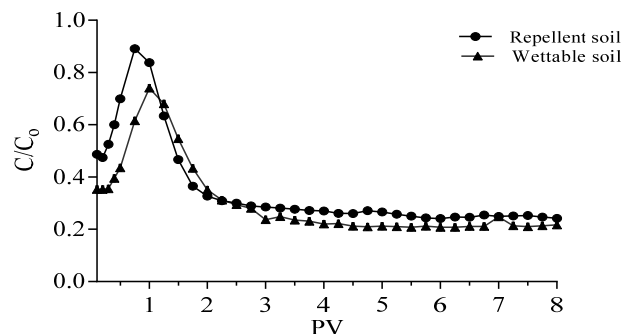
after leaching suggested on one hand that measurable portions of hydrophobic material could have been removed and transported with the percolation solution (Ritsema and Dekker, 1998). On the other hand, non-polar functional groups that are responsible for measured repellency on the particle surfaces may have been oriented away due to conformational changes of the functional groups, i.e. from the solid surface into deeper layers of the interphase after contact with water (Diehl, 2013). The latter effect was similarly observed for technical polymers (Ferguson and Whiteside, 1992) as well as for column capillary rise experiments made with a water repellent sandy soil (Reszkowska et al., 2014). Fishkis et al. (2015) also found the negative relations between the soil water repellency level (as quantified by CA) as function of water content (ranged from  $pF = -\infty$  to  $pF = 4.2$ ). They found that the CA was affected significantly by saturation history (wetting and drying cycles); so that at a given water content, the CA was significantly larger during drying than during rewetting. These observations are in line with the changes in persistency of water repellency as found in this study by CA and *RI* before and after leaching.

### Cl<sup>-</sup> tracer breakthrough curve characteristics

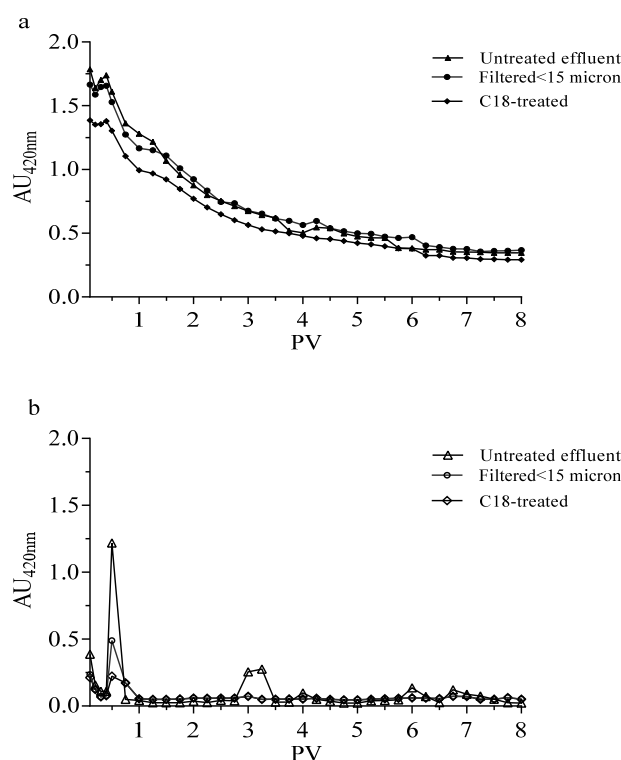
To compare the water flow characteristics in both soils, mean breakthrough curves (BTCs) of Cl<sup>-</sup> are presented in Fig. 1. The BTC for the wettable soil was characterized by a concentration peak in  $C/C_0$  at 1 PV which is typical for homogeneous media and suggests that preferential flow did not occur in the packed columns (Guo and Chorover, 2003). The repellent soil BTC showed a tendentially earlier peak maximum with higher Cl<sup>-</sup> concentrations in the 0.1 PV to 0.75 PVs ( $p < 0.05$ ) interval. Faster movement of Cl<sup>-</sup> could principally occur due to higher local pore water velocities (i.e. preferential flow on the pore scale, Jarvis et al. (2008)). It could also be supported by a lower retention capacity of the repellent soil to hold Cl<sup>-</sup> ions due to a lower specific surface charge, which is indirectly indicated by the higher CA (Bachmann et al., 2007; Deurer and Bachmann, 2007; Raats, 1973; Ritsema and Dekker, 1994, 1998). The decreasing slopes after the maximum concentration of the BTCs of both soils were approximately similar in shape and overlapping regarding the respective values of the standard deviation. This trend continued for the rest of the experiment.

### Leaching and hydrophobic character of the organic colloids

Effluent turbidity of unfiltered, filtered, and C18-treated effluent samples as a function of the out-flux water volume is presented in Fig. 2. For the entire leaching experiment, significantly higher turbidity was observed in the unfiltered samples of the repellent soil (Fig. 2a) compared with the effluent of the wettable soil (Fig. 2b). These data suggest that the repellent soil, higher in SOC content, released a higher total amount of mobilized colloids during the leaching process. The peak at 0.5 PV in the effluent turbidity of the wettable soil has a height of 1.2 AU (absorbance units). It shows a much stronger pronounced characteristic corresponding to a short-time event compared with the more or less monotonically decreasing turbidity with time observed for water repellent soil. In average, as mentioned, the turbidity of the repellent soil was on a much higher level, indicated by the maximum absorbance of 1.75 at 0.5 PV. The turbidity of the wettable soil effluent sharply decreased after 0.5 PV and, on average, the values remained below 0.25 AU for the rest of the experiment. However, in addition to the first turbidity peak, the unfiltered effluent of the



**Fig. 1.** Breakthrough curves of the inert tracer chloride (Cl<sup>-</sup>) passing through the repellent and wettable soils. Depicted are mean values of six replicate soil columns with a mean standard error of  $\pm 0.18$  (wettable) and  $\pm 0.13$  (repellent columns).



**Fig. 2.** Variations of turbidity as absorbance with water as reference (baseline set to zero for water) for the effluents of repellent (a) and wettable (b) soils. Depicted are mean values of six replicate soil columns with a mean standard errors of  $\pm 0.50$ ,  $\pm 0.40$  and  $\pm 0.37$  in Fig. 2a, and  $\pm 0.2$ ,  $\pm 0.1$  and  $\pm 0.04$  in Fig 2b for untreated, filtered (<15micron), and C18 effluents, respectively.

wettable soil columns showed some fluctuations in turbidity when approaching the end of sampling with increased values at 3 PV, 4 PV, 6 PV, and 6.75 PV (Fig. 2b). This could indicate sudden events of separation and removal of dispersible colloids i.e. caused by spontaneous destruction of soil bulk aggregates or smaller components detached from particle coatings as reported by Laegdsmand et al. (2005). The effluent turbidity of the repellent soil decreased much slower than for the wettable soil and reached a stable plateau of 0.5 AU after 7 to 8 PV (Fig. 2a).

The differences between the leachates for the wettable and repellent soils (Fig. 2a) may be caused by larger source of readily available organic colloids on the particle surfaces of the

repellent soil particles. A second mechanism could also be a higher release rate of recaptured colloids on the repellent soil surfaces along the columns due to lower adsorption energies. However, if the leachate data (Fig. 2) are compared with the studies of Deb and Shukla (2011), Flury and Qiu (2008), Laegdsmand et al. (2005) it is confirmed that higher total DOM leaching resulted from a larger source of available colloids due to the higher total OM content in the repellent soil (Table 1). Further, Laegdsmand et al. (2005) investigated the leaching of dispersible colloids and DOM from columns (4 cm diameter and 6 cm height) packed with natural soil aggregates (2–4 mm) and observed that colloid leaching increased also for aggregated systems with increasing organic matter content.

More specifically, analyzing the contribution of colloids to turbidity, the plots related to the filtered effluents (excluding particles larger than 15  $\mu\text{m}$ ) also showed higher mobilization of colloids from the repellent soil compared to the wettable soil. Generally, differences between the turbidities of untreated effluents and filtered effluents of the repellent and wettable soils were almost negligible which suggest that the transported particles were predominantly colloids < 15  $\mu\text{m}$  in size (Fig. 2b), supporting the assumption of predominantly colloidal transport. The filtered effluents showed somewhat higher values in some points of the repellent soils compared to the unfiltered effluents which might fell into the experimental error ( $\pm 0.06$ ) during absorbance measurements.

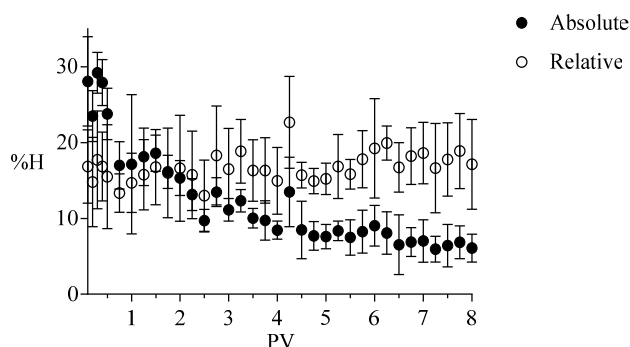
Generally, the high turbidity values are probably caused by colloidal species including a mixture of hydrophobic, hydrophilic, and amphiphilic components as stated by Mainwaring et al. (2013) or Tschapek and Wasowki (1976). The presence of hydrophobic colloids in the effluent of wettable soil suspensions was detected only at 0.1 PV and 0.5 PV with a hydrophobicity index (H) of 9.5% ( $\pm 9.9$ ) and 54% ( $\pm 19$ ), respectively. Thus, a large part of the increased turbidity found at 0.5 PV (Fig. 2b) is apparently related to the temporary mobilization of hydrophobic organic colloids leached from the bulk soil. Such a high value (54%) for the wettable soil was never reached for the repellent soil. This suggests the preferential release of hydrophobic components, probably occluded in organic matter before the release, from particle surfaces, which are in average characterized as hydrophilic by the CA and RI values. Total turbidity of the suspensions was significantly increased at these selected sampling points. Dymov et al. (2015) also found that the hydrophobic property (in term of CA) for the upper mineral horizons of four studied soils were largely determined by the contents of free and occluded organic matter fractions. On the other hand, the data of 3, 4, 6 and 6.75 PVs for wettable soil (Fig. 2b) do not indicate an increased H because no differences were observed for the turbidities at these PVs. This shows that probably no relevant amounts of hydrophobic colloids were mobilized after 1 PV and that an increase of total turbidity is not necessarily an evidence for a higher amount of hydrophobicity of the suspension components for the wettable soil. Dymov et al. (2017) investigated the polycyclic aromatic hydrocarbons concentrations (PAHs) and water repellency (in term of CA) in burnt and unburnt soil horizons ( $O_1$ - $O_{ea}$ -E-Bs) of lichen pine forests. They attributed the increase of soil water repellency (i.e., CA) to the high amount of PAHs accumulated in fractions of free and occluded organic matter. Dymov et al. (2017) also observed a gradual increase of the CA values in E and B horizons. They suggested that this could be associated partly with the composition of the horizon-specific SOM composition, but also partly due to the migration of hydrophobic components from upper soil layers with soil water transport. If the results including the CA (Table 1) and the amount of hydrophobic

colloids for the wettable soil are compared with Dymov et al. (2015, 2017) and Laegdsmand et al. (2005), it might be assumed that the hydrophobic components in the leachate samples at 0.1 PV and 0.5 PV are likely originated from the release of larger occluded colloidal organic matter particles which were originally covered with a hydrophilic coating before the detachment from the solid interface. Experimental evidence also suggests that hydrophilic and hydrophobic components are packed side-by-side on the particle surface forming a chemically composite surface on the molecular scale (Tschapek, 1976). Woche et al. (2017) showed by X-ray photoelectron spectroscopy (XPS) that always polar and non-polar functional groups are present on solid surfaces of soil organic matter, no matter if the soil is water repellent or exhibit complete wettability. Only the ratio of non-polar to polar functional groups in the interface increased with increasing water repellency level of the samples, which is not reflected by conventional bulk analysis of the respective soils. Therefore, depending on the respective binding strength of the organic matter subunits, components usually in the size of colloids, with a net dominance of either hydrophilic or hydrophobic character can potentially be released from both types of soils as confirmed by this study.

The absolute hydrophobicity on the leachate components showed a continuous release of hydrophobic colloids for the repellent soil with a maximum value of 30% at 0.2 PV (Fig. 3). Absolute reduction with a significant negative slope ( $R^2 = 0.77^{***}$ ) was greater than the relative hydrophobicity reduction with a positive and gentle slope ( $R^2 = 0.18^*$ , Fig. 3). Data of Fig. 3 were also separated into two parts to find any trend in time for H characteristics during leaching. These data, however, demonstrated that the gradient was not significantly different for the 5 PVs to 8 PVs intervals ( $R^2 = 0.13^{ns}$ ) compared to the 0.1 PV to 5 PVs ( $R^2 = 0.05^{ns}$ ). In conclusion, the absolute and relative changes of the suspension hydrophobicity demonstrated that during the entire process the suspended colloids leached from the repellent soil were mostly hydrophilic.

Many studies focused on the wettability of leachates through chemical fractionation of DOM (Crow et al., 2009; Dilling and Kaiser, 2002; Fröberg et al., 2003; Lindroos et al., 2002). Wandruszka et al. (1997) have shown that aqueous solutions of soil humic acids respond also to the addition of cations by forming intramolecular and intermolecular microaggregates or compact structures with relatively hydrophobic interiors and hydrophilic surfaces. Lindroos et al. (2002) found that the groundwater mainly consisted of hydrophilic neutral compounds. Crow et al. (2009) investigated chemical structures of the leached materials, but did not investigated the hydrophobicity status of the colloids itself. They reported that the respective soil horizon determines in the predominant molecular components of the leachates, i.e. hydrophobic and hydrophilic acid groups dominated in leachates from Oe-horizons compared to the Oi- or Oa-horizons.

The relation between colloid release, DOC, and SOC content was thus assessed for both soils of this study. The absolute amount of SOM and DOC were higher in the repellent soil compared to the wettable soil (Table 1). The DOC/SOM ratio for the wettable and repellent soils, however, was quite close on the same level; i.e., 2.70 and 2.60, respectively. This indicates that the release of colloids is proportional to the existing carbon stock in the soil and could be independent from soil wettability. Laegdsmand et al. (2005) also found a significant greater DOM leaching from the soil with 3.5% OM compared to one with 2.5%, while the DOM/SOM ratio was also similar for the two soils.



**Fig. 3.** Absolute hydrophobicity in the effluent during leaching for the repellent soil (i.e.  $T_1-T_2$  in equation 2, data points are represented by filled circles). Linear regression:  $HI (\%) = -2.41PV + 22$ ,  $R^2 = 0.77^{***}$ , (line not shown). Corresponding relative hydrophobicity index ( $HI$ ) values ( $(T_1-T_2)/T_1$  of suspended particles are represented by open circles ( $HI (\%) = 0.31PV + 15.5$ ,  $R^2 = 0.18^*$ ). Error bars are standard deviation of six replications in column experiments (\* and \*\*\* denote the significant status of the hydrophobicity as function of PV on significance level 0.05 and 0.001, respectively).

The leachate hydrophobicity (Fig. 3) and the persistency of matrix water repellency (i.e.,  $CA = 71^\circ$ ) showed that the repellent soil did not quickly rendered wettable (Table 3). This suggests, in line with the predominant release of hydrophilic colloids, that much of the hydrophobic components remained at the interfaces of the solid particles. Urbanek et al. (2007) found also varying ratios of hydrophilic (C = O) and hydrophobic functional group (C–H) components at the solid particle interface as well as in the interior of aggregates which was affected by the respective land-uses system. In a recent paper, Woche et al. (2017) suggested the elemental surface O/C ratio as a general parameter linking surface wettability (in term of CA) and surface elemental composition of soil particle interfaces. This analytical approach might, on one hand, close the gap between the specific surface chemistry of the solid particles and its wetting properties in a dynamic context. On the other hand, corresponding analytical tools may help to unravel the relation between chemically altered surfaces, i.e. after detachment of organic components, and the amount and nature of released DOM components as has been done in this study.

## CONCLUSION

This study showed that natural hydrophobic colloids could be mobilized from bulk soil and transported through the wettable and the repellent soils. The major fraction of the leached colloids was hydrophilic and independently from the respective wettability status of the soils. The total amount of the leached colloids were higher for the repellent soil due to the higher SOC content, whereas the normalized values (ratio between DOC/SOC) were quite similar compared with the wettable soil. Leaching of the smaller fraction of hydrophobic colloids was continuously observed in the effluent samples of the repellent soil. For the wettable soil the hydrophobic colloid contribution was not assessable except for two samples, whereby one of these effluent samples showed the highest fraction of hydrophobic components.

The  $RI$  and  $CA$  values did not change after leaching for the wettable soil while a significant reduction was found for the repellent soil. We conclude that these results have some out-

comes: A certain amount of natural hydrophobic colloids will, on one hand, potentially be released from wettable soil horizons and are mobile in the soil matrix. On the other hand, hydrophobic soil horizons release always predominantly hydrophilic colloids. This supports the assumption, that pollutants, i.e. preferentially bound either to hydrophilic or hydrophobic organic compounds, can principally be released and transported over longer distances, no matter what the wettability state of the respective soil horizons is. Regarding the impact of the released colloids on deeper layers, the mostly wettable subsoils will continuously receive also a smaller fraction of hydrophobic colloids. As observed for many subsoils (Woche et al., 2005), the wettability of the majority of subsoil horizons may not be necessarily influenced intensively by this DOM influx, i.e. originated from an overlaying repellent soil horizon, due to the majority of hydrophilic colloids. However, regarding the wide spectrum of soils and soil forming processes much more research is needed to obtain a comprehensive view regarding the relation between DOM release, transport, hydrophobic character of colloids and the specific interaction regarding soil wettability. So far, some hypotheses can be suggested: 1) Hydrophilic colloids are predominantly released from the repellent soil because of their higher affinity to water, 2) Hydrophobic soil horizons may also release a certain amount of hydrophobic colloids, 3) Hydrophilic colloids (probably organic matter-associated) dominate composition in the leachates because during the wetting process hydrophobic leached materials may also become hydrophilic as stressed by Deb and Shukla (2016) for the hydrophobic contaminants, 4) Therefore, detachment and release of natural hydrophilic compounds might be rated as more effective for the co-transport of contaminants in environments for most soils which are considered as non-hydrophobic, 5) Hydrophobic soils, however, will need definitely more attention in further investigations.

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