



Wettability hysteresis and its implications for DNAPL source zone distribution

Jodi L. Ryder*, Avery H. Demond

Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI, 48109-2125, United States

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ABSTRACT

Subsurface heterogeneity at sites contaminated with nonaqueous phase liquids (NAPLs) reduces the effectiveness of traditional remediation measures. One cause may be the increased proportion of NAPL that is hydraulically isolated due to capillary trapping in heterogeneously-wetted materials. This study examines the wettability of ten materials, ranging from minerals, such as calcite and dolomite, to carbonaceous materials, such shale and coal, in air and water, NAPL and air, and NAPL and water systems. The wettability differed depending on which phase the solid material was initially immersed in: the less crystalline solids, if initially contacted by water were water-wet, but if initially contacted by NAPL were NAPL-wet. This difference, termed here wettability hysteresis, was observed for a suite of halogenated NAPLs and was independent of equilibration time. The degree of wettability hysteresis was greatest in the NAPL and water systems, with the magnitude of the difference increasing with the carbonaceous materials. Since the degree of capillary trapping in subsurface materials is related to wettability, the phenomenon of wettability hysteresis suggests that system history is a factor that may increase the heterogeneity of NAPL source zones.

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1. Introduction

Pump and treat remediation methods for the removal of nonaqueous phase liquids (NAPLs) from the subsurface have been shown to be largely ineffective (Hunt et al., 1988; Wilson et al., 1990; Commission on Geosciences, Environment and Resources, 1994), achieving satisfactory results at only the most homogenous of sites (Commission on Geosciences, Environment and Resources, 1994). The natural heterogeneity of the subsurface in soil particle shape, size, and material influences the distribution of NAPLs, making it harder to mobilize the NAPL and thus prolonging its dissolution timescale (Bradford et al., 1999).

It is frequently assumed that the mineral phase of aquifers is composed of only silica (Anderson, 1986) which, in its pure state, is water-wet at pH values greater than 2 (Parks and de Bruyn, 1962). But, it has also been acknowledged that some minerals such as calcite, talc, and pyrite may display a less water-wet condition even in the absence of sorbed hydro-

phobic components (Anderson, 1986). Field observations at 43 Army sites with suspected denser-than-water NAPL (DNAPL) contamination revealed that 16% contained alluvial outwash or interbedding, hydrologic settings that are likely to contain carbon soil solids such as humic acid-coated sands, shales, or coals that may have a different wettability than silica (Committee on Source Removal of Contaminants in the Subsurface, 2004). Combes et al. (1998) used environmental scanning electron microscopy to show that wettability heterogeneity does occur at the pore-scale and even if a soil contains only 3.1% hydrophobic grains, 37% of the pore space will have at least one hydrophobic pore wall (Bauters et al., 2000). This heterogeneity in wettability could increase the quantity of source zone NAPL, as O'Carroll et al. (2004) showed that capillary property contrasts, including wettability differences, could lead to greater retention of NAPL. After studying capillary desaturation in five real NAPL-soil systems, Dwarakanath et al. (2002) concluded that more attention needed to be given to wettability and its effects on flow and transport.

Wettability is a three-phase property describing the tendency of one fluid to preferentially spread over a solid surface immersed in a second fluid. The term water-wetting

* Corresponding author. Tel.: +1 734 276 2061; fax: +1 734 763 2275.
E-mail addresses: ryderj@umich.edu (J.L. Ryder), averyd@umich.edu (A.H. Demond).

indicates that water will spread over a surface giving a contact angle less than 90° measured through the aqueous phase whereas, in non water-wetting systems, the contact angle will be greater than 90°. Strongly water-wetting indicates contact angles through the aqueous phase less than 20°. Moderately water-wetting indicates contact angles between 20° and 60°. Weakly water-wet indicates contact angles between 60° and 90° while contact angles between 90° and 120° are weakly NAPL-wet. Moderately NAPL-wetting describes contact angles between 120° and 150° and strongly NAPL-wetting contact angles are greater than 150° (Morrow et al., 1988).

Wettability may vary due to both liquid and solid surface composition. Young's equation specifies that the contact angle, θ , perhaps the most definitive measure of wettability (Melrose and Brandner, 1974), is a function of three interfacial tensions, γ_{SI} between the solid and the immersion phase, γ_{SD} , between the solid and the drop phase, and γ_{ID} between the two fluid phases (Hiemenz and Rajagopalan, 1997):

$$\gamma_{SI} - \gamma_{SD} = \gamma_{ID} \cos \theta \quad (1)$$

Sorption can occur at all three interfaces of the system. In order for wettability to reverse itself, that is to say, in order for a material to go from water-wet to organic-wet, $\cos \theta$ must reverse its sign. For this to occur, γ_{SI} must decrease or γ_{SD} increase, so that $\gamma_{SD} > \gamma_{SI}$. A number of studies to date have looked at the alteration of wettability due to the sorption of surface-active components from the organic liquid phase onto the aquifer solids. For example, Harrold et al. (2001) showed that exposure of quartz plates and sandstone cores to TCE could cause the solids to become hydrophobic. Although they could not discern which compounds were causing the wettability change in the case of the waste TCE, their laboratory grade TCE contained a stabilizer, triethylamine that could be surface-active. Zheng and Powers (1999) showed that changes in wettability could be linked to organic bases, while others have linked wettability changes to the sorption of carboxylic and phenolic acids (Standal et al., 1999) or petroleum or waste components over time (Denekas et al., 1959; Treiber et al., 1972; Powers and Tamplin 1995; Buckley et al., 1998; Hsu and Demond, 2007).

Far less consideration has been paid to the potential for wettability variation in the absence of surface-active solutes, based on the composition of the aquifer solid material itself. Most contact angle studies have focused on pure mineral phases such as quartz or calcite (McCaffery and Mungan, 1970; Schultz et al., 1977; Ethington, 1990; Giese et al., 1991; Jouany, 1991; Wu, 2001), but air–water contact angles from the literature suggest that many solids may be less water-wet than quartz (29°, Ethington, 1990), including: calcite (40°, Ethington, 1990), coal and shale (61° to 75°, and 31° respectively, Miyamoto et al., 1977), organic rich soil (62°, Kotlyar et al., 1999), and talc (80.4°, Giese et al., 1991). Schultz et al. (1977) reported contact angles for water drops on mica immersed in benzene, carbon tetrachloride, chloroform, and 1,2 dichloroethane of 25°, 25°, 30°, 35°, and 29° respectively. Organic carbon-containing soil materials are often cited as water repellent, NAPL-wet, or hydrophobic (Tschapek and Wasowski, 1976; Ma'Shum and Farmer, 1985; Anderson, 1986; Capriel et al., 1995). The term water repellency is commonly used in reference to near surface air–water systems, such as the plant root zone, and indicates a soil that is not easily

wetted or resists the imbibition of water (DeBano, 2000), but specific contact angles are rarely given. Such a soil may also be described as hydrophobic. Yet the term does not seem to necessarily indicate a contact angle greater than 90°, or that a NAPL will preferentially spread. Several investigations have cited specific surface chemical components believed to influence wettability including extracellular materials from soil organisms and fungi (Savage et al., 1969), polymethylene chains and fatty acids (Ma'Shum and Farmer, 1985), waxes under arid conditions (Wallis et al., 1993), polar waxes (Franco et al., 2000), alkyl carbons (Tampy et al., 1988; Capriel et al., 1995). These materials, derived from shorter term biological processes, may occur as coatings on mineral grains. In addition, materials formed over geologic time such as shales and coals may be present. The wettability of shales has not been reported, but coals are considered hydrophobic compared to quartz (Fuerstenau et al., 1983; Guy et al., 1996; Somasundaran et al., 2000). Because of the lack of definitive information on the wettability of aquifer solids, the purpose of this study is to examine the wettability of air and water, NAPL and air and NAPL and water systems to determine the potential for wettability variation due to heterogeneous solid composition in the subsurface. Since the subsurface is dynamic, with the three liquid phases varying in degrees of saturation over time, the wettability for these systems was examined as a function of initial fluid contact.

Although the contact angle is the least ambiguous measure of wettability (Melrose and Brandner, 1974), there are limitations to using a direct measurement of contact angle as the measure of wettability. For consistent, repeatable measurements, the solid surface should be molecularly smooth (Adamson and Gast, 1997). This requirement can be difficult to achieve with natural materials. Macroscopically measured contact angles may differ from the intrinsic contact angle due to contact angle hysteresis, defined as the difference between the advancing and receding contact angles. One explanation for this phenomenon is that when a droplet is increased in size, the advancing edge gives the contact angle against the low energy areas of the surface. However, when the droplet is decreased in size, the receding edge gives the contact angle of the high energy areas (Hiemenz and Rajagopalan, 1997). Capillary tests, such as the Amott–Harvey method (Amott, 1959), can also be used to infer wettability but require long experimental periods. Some capillary methods yield a contact angle, but these methods require a reference contact angle from a soil or core with a comparable pore size distribution. Although non-quantitative, the bottle test method (Dubey and Doe, 1993; Anckner and Powers, 1996) allows the rapid determination of the wetting fluid in porous media.

2. Materials

Ten solids were selected for the measurements of wettability, including common soil minerals, materials previously cited as hydrophobic, and carbon-containing rocks (Table 1). Quartz, the most common component of the subsurface, was used in two forms: microscope slides (Quartz Scientific, Fairport Harbor, OH) for contact angle measurements and foundry silica sand for the bottle tests. Calcite and dolomite are mineralized carbonates and common in both bedrock

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