

ECG Environmental Briefs

ECGEB No 15

Non-aqueous phase liquids: properties, risk reduction and remediation

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The term non-Aqueous Phase Liquids (NAPLs) describes a class of organic liquids that are immiscible with water. NAPLs are among the most common organic contaminants in the sub-surface environment as a result of their ubiquitous use, accidental release during handling or transport, leakage from storage tanks, and poor disposal practices.

The key defining properties of NAPLs are their chemical composition, density, wettability and interfacial tension, viscosity, solubility, and vapour pressure. Density is particularly important, as NAPLs are usually further categorised as Light NAPLs (LNAPLs), which are less dense than water, and dense NAPLs (DNAPLs), which are denser than water. The most common LNAPLs are fuels and oils, such as petrol (gasoline), diesel, heating oils and jet fuel (kerosene). Typical DNAPLs include chlorinated solvents, coal tars and polychlorinated biphenyl oils.

Environmental Behaviour

When an NAPL is introduced into the soil environment it normally migrates downward. The path taken can, however, be quite complex and depends on the pore or fracture size of the soil and the concomitant capillary forces generated when the NAPL comes into contact with water in the soil's unsaturated zone and at the water table. LNAPLs normally cannot penetrate below the water table because of buoyancy forces, although a sufficiently large LNAPL mass will depress the water table. DNAPLs, on the other hand, can and very often do penetrate the water table.

At the trailing edge of the NAPL body, NAPL droplets (termed residuals and encountered as blobs or ganglia stretching through several pore spaces) become detached and are normally held in these pore spaces by capillary forces. This happens both in the unsaturated and saturated zones of the sub-surface environment. In

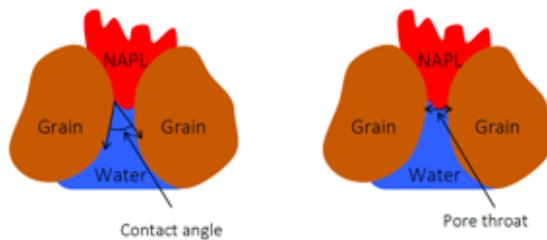


Figure 1. The contact angle and pore throat size play key roles in the dynamics of NAPLs through soils.

the unsaturated zone, vaporisation of NAPL components produces a mobile contaminant plume in the vapour phase. Residuals in the unsaturated zone may also dissolve in infiltrating rainwater, which eventually provides a source of groundwater contamination. In the saturated zone, NAPL residuals slowly dissolve in flowing groundwater to create a contaminant plume.

Capillary Forces

The entry of a NAPL into an air- or water-filled pore or fracture is determined by two important pressure terms. The first is the capillary pressure, P_c , which is defined by the following equation:

$$P_c = P_{nw} - P_w \quad (1)$$

where P represents pressure and the subscripts c , nw , and w refer to capillary, non-wetting, and wetting, respectively. A wetting fluid is one that spreads over a surface in competition with another fluid. In soils and rocks, water is usually the wetting fluid when in competition with a NAPL. However, when in contact with air, NAPLs are the wetting fluids.

Wetting behaviour is characterised by the contact angle (**Figure 1**). The contact angle is the angle made by a tangent to the non-wetting fluid and the solid surface proceeding from the point where the three phases come

into contact. This contact point is in reality a contact line when viewed in three-dimensional space.

The second pressure term is the entry (or displacement) pressure, P_e , and is given by the Laplace equation:

$$P_e = 2\sigma \cos(\theta)/r \quad (2)$$

Here σ is the interfacial tension between water and the NAPL, θ is the contact angle, and r is the pore throat radius. The contact angle term appears as a cosine term. If θ is 0° then the cosine term is 1. On the other hand, a contact angle of 90° gives a cosine of zero, implying that a positive entry pressure only arises at a curved interface. For the NAPL to displace water from a pore, the following inequality must hold true:

$$P_{nw} > P_w + 2\sigma \cos(\theta)/r \quad (3)$$

Thus, in soil media with large grain size, the entry pressure is small and NAPLs—especially DNAPLs—tend to displace water from pores. On the other hand, in locations with small grain sizes NAPLs find it far more difficult to displace water. Thus, if a highly permeable layer (such as sand) overlays a less permeable layer (such as silt or clay), NAPLs will migrate vertically downward in the top layer but then migrate horizontally when encountering the bottom layer. Identifying the migration pathway of a NAPL therefore requires a good understanding of sub-surface lithology.

Solubilisation and vaporisation

Key concerns after a NAPL spill are its impacts on the environment and the resulting liabilities of site owners where the release has occurred. Density and viscosity control the length of time during which a NAPL body will remain mobile. Chlorinated solvents have high densities and low viscosities therefore do not remain mobile for long. In contrast, creosotes and coal tars have densities only slightly greater than that of water and large viscosities and can therefore continue to migrate for considerable periods of time.

The partial pressure of NAPL components in the vapour phase of the unsaturated zone is an important risk driver for contaminant migration to off-site targets. In the absence of a complete understanding of the physical chemistry of a NAPL mixture, it is generally assumed that Raoult's Law gives the partial pressure, p_i , of a component in the vapour phase:

$$p_i = x_i p_i^{\text{sat}} \quad (4)$$

Here, x_i is the mole fraction of component i and p_i^{sat} is the saturated vapour pressure of component i . Clearly, low

molecular mass components with low boiling points are particularly mobile in the vapour phase.

Raoult's Law is also used to estimate component solubilities, using an analogous equation to equation 4 where s refers to the solubility:

$$s_i = x_i s_i^{\text{sat}} \quad (5)$$

The reader should begin to understand from the forgoing discussion that although NAPL releases result in the creation of a contaminant source zone, it is the appearance of NAPL components either in the vapour or aqueous phase that is usually first detected and that provides the background to environmental risk assessments.

Risk Reduction and Remediation

Removal of the source or breaking the pathway can be used to reduce chemical hazard exposure to acceptable limits. For LNAPLs like petroleum, vapour phase extraction is very often effective for source removal. For example, vacuum enhanced recovery techniques rely on the vaporisation of volatile LNAPL components from the organic liquid phase and volatilisation of components from the water phase. Additionally, application of a high vacuum to the sub-surface induces air to enter, which provides fresh supplies of oxygen and thereby aids the biodegradation of the hydrocarbon components present in the source zone. For chlorinated hydrocarbon solvents (DNAPLs), some success has been achieved with the joint application of an electron donor system (emulsified soya oil, methanol and lactate) and a halo-respiring bacterium. Other approaches have been used depending on the location and type of NAPL spill (1, 2).

References

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