

Investigation and Remediation

Some Enlightenment on Density

by Blayne Hartman

Editor's Note: This is the fourth in a series of articles reviewing some of the physical/chemical properties that are commonly used in environmental assessment and remediation. This article will focus on the property of density.

Okay, the quiz for today is:

A DNAPL is:

- (a) A liquid more dense than water.
- (b) A new oxygenate to replace MTBE.
- (c) A new EPA office: Department of Natural Attenuation Policy and Logistics.
- (d) A competitor of Snapple.

Bet you got this one, didn't you? For those who did not, the correct answer is (a). Translated into everyday English, a DNAPL (dense nonaqueous phase liquid) is a liquid that does not mix with water and is heavier (more dense—that is, a sinker). An LNAPL (light nonaqueous phase liquid), on the other hand, is a liquid that is lighter than water (less dense—that is, a floater). Oil floating on vinegar salad dressing, for example, is an LNAPL. (I was enlightened by one student, who said you can observe the same effect when making margaritas from scratch in a blender.)

Okay, let's name some DNAPLs. How about:
trichloroethane (TCA), trichloroethylene (TCE),
perchloroethylene (PCE), dibromoethane (EDB)

And some LNAPLs:
gasoline, diesel, motor oil, cooking oil

See Any Trends Here?

To understand what's going on, we need to review a few basic concepts relating to the relative weight of a liquid versus water. To do this, we need to start with the elements that make up these materials.

Notice that all of the LNAPLs listed above are common fuel products or oils—hydrocarbons. Hydrocarbons are compounds that consist primarily of two elements: hydrogen and carbon. Put the names together and you get “hydrocarbon.”

Water is also composed of two elements: hydrogen and oxygen. (Do you ever wonder why we don't call water hydro-oxygen? I do.) Notice that hydrogen is common to both hydrocarbons and water—in both cases, there are about two atoms of hydrogen for each carbon or oxygen atom. So, in essence, the difference between hydrocarbons and water is that the former contains carbon and the latter oxygen. Carbon has an atomic weight of 12. Oxygen has an atomic weight of 16. So, as a first approximation, it is reasonable to expect hydrocarbons to weigh less than water.



Now let's look at DNAPLs. Most chlorinated and brominated solvents are simply hydrocarbon molecules (e.g., ethane, ethylene) that contain one or more chlorine or bromine atoms. The atomic weight of chlorine is 35.5. The atomic weight of bromine is 80. Both of these atoms are very much heavier than the oxygen in water, so we can reasonably expect materials with these elements in them to weigh more than water.

Are you starting to get the picture? In the discussion so far, I have made one tacit assumption: that the space that each compound takes up (i.e., its molar volume) is the same. In other words, a hydrocarbon, solvent molecule, and water molecule take up the same space. In actuality, this is not the case. So when determining whether a compound will or won't float in water, it is important to compare not just the weight of a material, but the weight for the same volume occupied.

This ratio of a compound's weight to volume is known as its density. Commonly, the density of a liquid is compared to that of water. The ratio of a compound's density to the density of water is known as the specific gravity. Specific gravity is a convenient reference point, because liquids with specific gravities greater than 1 are sinkers and those with specific gravities less than 1 are floaters.

So What?

Assuming you haven't memorized the specific gravity of many compounds, you can estimate whether a liquid is a LNAPL or DNAPL by comparing the atomic weight of the element in addition to hydrogen with the atomic weight of oxygen. For petroleum hydrocarbons, carbon is the primary element besides hydrogen, carbon weighs less than

oxygen, and therefore liquid hydrocarbons are likely to float on water (and they do). For a compound containing chlorine or bromine, both of these elements are much heavier than oxygen, and it is likely that compounds with these elements will sink (and they do). Remember, this is an estimation only, because density is not dependent on atomic weight alone.

Wondering about MTBE? The above technique applies only to liquids (not gases or solids) that do not mix with water. MTBE mixes with water well enough that it does not form a separate fluid layer; hence it does not form a NAPL (non-aqueous-phase liquid).

Vapor Density

Now that you've got the concept of liquid density down, try this quiz:

You conduct a soil-gas survey at a facility containing aboveground tanks inside a building and find large concentrations of MTBE and TPH in the soil gas. You take soil samples to define the contamination and the soil analyses all are below detection. What's the explanation?

- (a) VOC analyses in the soil are not always reliable due to volatile loss.
- (b) The volatility of MTBE and TPH is high, so the soil contamination must have volatilized (evaporated) into the soil vapor.
- (c) The contamination started as a vapor.
- (d) Get a new lab.

Those of you who have managed to get through some of my previous articles (see "The Downward Migration of Vapors," LUSTLine #28) should know the answer to this quiz. For those of you who didn't (or those of you who have forgotten), the answer to this question requires us to consider the concept of vapor density.

The vapor density of a compound relative to air is approximately equal to the molecular weight of the compound divided by the molecular weight of air, or

$$D_v = MW_i / MW_{air}$$

Since the molecular weight of air is equal to 29 g/mole,

$$D_v = MW_i / 29$$

A familiar example is helium. With a molecular weight of 4 g/mole, it has a vapor density only 1/7 that of air, so of course, balloons filled with helium rise. Now, let's try a few of our favorite petroleum compounds:

Benzene:	Molecular weight: 78	Vapor density: $78/29 = 2.5$
MTBE:	Molecular weight: 88	Vapor density: $88/29 = 3.0$
Gasoline:	Molecular weight: ~100	Vapor density: $100/29 = 3.3$

Because many of the compounds associated with petroleum hydrocarbons have vapor densities significantly larger than air (two to four times), vapor density can play an important role in situations where petroleum hydrocarbons, such as fuels, are used or stored in an indoor, confined space. In these situations, the vapors emanating from a container or from liquid leaks can sink to the floor because of their high vapor density. Gas and electric companies are well aware of this behavior, which is why they require hot water heaters in garages to be a minimum distance off the floor to prevent the ignition of dense gasoline vapors "flowing" along the floor.

If air flow is restricted, such as in a closed room, the dense vapors can penetrate the concrete floor and enter the upper vadose zone. Such bulk dense vapor movement can continue to drive the vapor downward through the vadose zone until it is diluted to concentrations low enough (<1%) that density is no longer an important factor in the vapor transport process.

Vapor clouds reaching tens of feet into the uppermost vadose zone have been attributed, at least in part, to density-driven flow. Businesses and commercial operations that deal with chlorinated solvents (e.g., dry cleaners, vapor degreasers, spray facilities) are the most susceptible to this situation. Vapor clouds are a common occurrence beneath dry cleaners. The situation is not as common for petroleum hydrocarbons, because they rarely are stored indoors in confined spaces (due to their flammability). However, as far as USTs are concerned, leaks of "dense vapor" are possible from vent pipes, pipe joints, and tank bungs.

So, the answer to the quiz? Although there is currently much debate over the optimum way to measure VOCs in soils, it is likely that some would have been identified if the contamination was in the soil. Also, it is extremely unlikely that all of the soil contamination would have been lost to the vapor phase, especially if any moisture or carbon were present in the soil. Since you have no reason to doubt your lab, the remaining choice is (c). The measured contamination may have started as a vapor, penetrated into the vadose zone, and has yet to "equilibrate" with the surrounding soils, so it is detected in the soil vapor, but not in the soils themselves.

Two quizzes this time. I hope you enjoyed them. ■

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