Oxygenates

WanDer LUST

by Hal White

***This is the first in a series of articles by Hal White that explores "a dimension as vast as space and as timeless as infinity ... representing the middle ground between light and shadow, science and superstition ... between the pit of man's fears, and the summit of his knowledge" (to shamelessly paraphrase Rod Serling's* Twilight Zone).**

MTBE Taste and Odor Thresholds ... The Myth of Protectiveness

Two often-touted "beneficial" characteristics of MTBE are its low taste and odor thresholds, reputed to be significantly lower than levels to which exposure might produce toxic effects (if any) in humans. While taste and odor thresholds vary from person to person, several studies indicate that most people can detect MTBE in water by either taste or odor (or both) at concentrations in the range of 10 to 40 parts per billion.

Such a range must surely be low enough to provide a high degree of protectiveness from exposure to MTBE-contaminated drinking water, right? As a prelude to answering this question, consider the following scenario, which is based on two real-life cases (and embellished only slightly in order to meld them together):

> In Somewhere, U.S.A, a community where drinking water comes from domestic groundwater wells, some of the residents have noticed that unless they shower with their windows open, they experience dizziness, headache, and nausea. Beyond this inconvenience, however, no one has noticed anything out of the ordinary about his or her water. But, over a holiday weekend, one family is visited by in-laws from out-of-town. Upon their arrival, the guests are given refreshing glasses of ice water and immediately gag in response to the turpentine-like taste. As their visit progresses, they become dizzy and nauseous any time any tap in the house is turned on.
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> At the insistence of their guests, the homeowners contact the state health department, which promptly dispatches a crew to investigate. Water samples are collected and analyzed and found to contain several tens of milligrams per liter of MTBE—several hundred times higher than the supposed taste and odor threshold and high enough to account for the dizziness, nausea, and headaches experienced by many in the neighborhood. By the time the investigation is completed, many households in the neighborhood are found to have MTBE-contaminated water.

Many of you who work in state leaking underground storage tank programs can probably recall similar examples from your own experience. And many of you may have scratched your head and wondered: Considering the low taste and odor thresholds for MTBE, how is it possible that people living with MTBE-contaminated water can blithely drink water that must obviously have an offensive taste and smell?

The answer to this question is a function of dispersion and desensitization. In our scenario, MTBE concentrations in the domestic wells increased gradually over time so that the people in the neighborhood became desensitized to the foul smell and taste of their water. Even when showering, the neighborhood residents didn't notice a bad smell, although they did experience physical illness caused by exposure to high concentrations of MTBE, symptoms that were somewhat relieved by opening the bathroom windows. The out-of-town guests, who were not desensitized, were immediately able to recognize that the water smelled and tasted bad.

Transport of Dissolved Contaminants

Now, let's get a bit more technical. First, it is important to understand that dissolved contaminants migrating in the subsurface through porous media do not travel as a concentrated, discrete slug that ultimately enters a well and instantaneously raises the concentration of the extracted water to that of the slug. The leading edge of a contaminant plume is typically very dilute, with concentrations increasing upgradient back toward the source. As the plume continues to expand, concentrations gradually rise in the wells located downgradient from the source.

This basic behavior holds true even if the plume detaches from the source. A detached plume will migrate as a "pulse" or slug, but concentrations will still be lower around the periphery and higher in the core. If a detached plume continues to migrate past wells that intersect it, then at some point concentrations in these wells will decrease as the plume moves even further downgradient.

Transport of dilute dissolved contaminants is a function of advection, hydrodynamic dispersion, and other chemical, biological, and physical reactions. Advection refers to the movement of molecules (or particles) imparted by flowing groundwater. The advective rate of transport is generally defined (imprecisely, as will be shown later) as the *average* linear groundwater velocity.

Hydrodynamic dispersion occurs as a result of molecular diffusion and mechanical mixing and causes the dissolved contaminant plume to spread out with distance from the source. Molecular diffusion is generally only significant when groundwater movement is very slow. Mechanical mixing occurs as groundwater flows through the aquifer matrix, twisting around individual grains and passing through interconnected pore spaces at differing velocities.

The movement of some dissolved contaminants may also be affected by chemical, biological, and physical reactions, such as sorption and biodegradation, which act to decrease the transport velocity and reduce concentrations in the plume. MTBE is only minimally affected by sorption processes and degrades very slowly in many (but not all) subsurface environments—as such, in some environments its behavior is substantially similar to that of a nonreactive tracer.

Calculating Travel Time

Classical tracer studies devised to study advection-dispersion phenomena typically employ a cylindrical column that is filled with porous media. A continuous supply of tracer at a specified concentration is introduced at one end of the column under steady-flow conditions, and outflow concentrations are measured at various times after the tracer is injected.

A graph of the outflow concentration with time is known as a breakthrough curve (Figure 1). Initially concentration of the tracer in outflow samples is zero. Beginning with the time of first arrival of the contaminant front, tracer concentrations increase gradually at first then accelerate before reaching a steady-state equal to the concentration of the source. The inflection point of this curve (the vertical dotted line) represents the hypothetical arrival time of an undiluted slug of contaminant moving at the *average* linear groundwater velocity.

There are two problems with the comparison of true contaminant transport and an undiluted slug. First, due to the presence of the porous media, slug (or plug) flow is impossible. Even at a relatively small scale (i.e., these cylindrical columns) the "plume" of tracer would be dispersed with distance in the column due to molecular diffusion and mechanical dispersion.

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Second, some of the tracer molecules are moving faster than the *average* linear groundwater velocity, and some are moving slower. This is also true for the water molecules—it's just that we do not measure the velocity of individual water molecules. Hence, a common misconception is that due to dispersion, contaminants may move faster than groundwater. A more correct statement is that some contaminants may move faster than the *average* linear velocity of the groundwater.

This distinction concerning velocity is very important. It also leads us to another realization: if some contaminant molecules are traveling faster than the average linear groundwater velocity, then the *maximum* linear groundwater velocity rather than the *average* linear groundwater velocity should be used to calculate the time it will take contaminants to first reach a receptor. (How significant a difference this will actually make will be discussed in a later article written in collaboration with Jim Weaver of the EPA's Office of Research and Development.)

Take-Home Message

So, back to the original question of the protectiveness of taste and odor thresholds. The take-home message is that no matter how low the MTBE-contaminant thresholds, they cannot be relied on to provide any measure of protectiveness from exposure. Why?

- Contaminants initially arrive at receptors at low concentrations and increase gradually, and the rate of increase may be slow enough to allow those affected to become desensitized. Then, when the presence of contamination is finally realized, concentrations may be high enough to cause adverse health effects.
- Contaminants may be transported at rates that exceed the *average* linear groundwater velocity. In order to calculate contaminant travel time (i.e., the time required for contaminants to first reach a receptor), it is the *maximum* linear groundwater velocity that is relevant, not the *average* velocity. ■

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Figure 1

BREAKTHROUGH CURVE OF A NON-REACTIVE TRACER