TRILLIUM'S Two Scents

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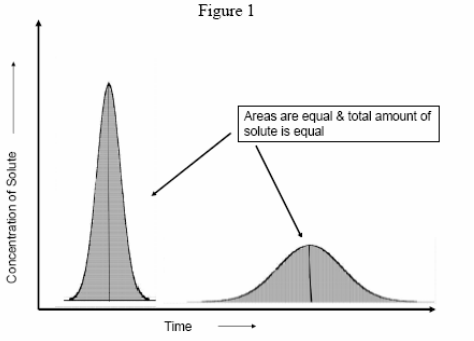
President's Corner

James S. Smith, Ph.D., CPC, President/Chemist

Column chromatography is 100 years old. In 1906, Michael Tswett, a Russian botanist working in Poland, published the first paper describing his process for separating leaf pigments in a German journal. Chromatography is a physical method of chemical separation that uses a fluid phase passing through a stationary phase of large surface area. Chromatography is based on the principle of selective retardation: some sample components stay in the stationary phase longer than others as the fluid phase passes through.

This principle is also the basis for transport of water-soluble components through an aquifer system, where the groundwater is the fluid phase and the aquifer material is the stationary phase. Thus, the basic principles of chromatography apply to the transport of chemicals in groundwater:

Figure 1



- During transport through the stationary phase, the band of the chemical increases with increasing distance traveled, a process called "band broadening" (Figure 1), which can result from several processes including dispersion, molecular diffusion, and mass transfer between the mobile and stationary phases.

- The nature of the stationary phase depends primarily on the total organic carbon (TOC) content of the aquifer material. The effective TOC determines the number of theoretical plates, or separation ability under equilibrium conditions, for the soluble compounds in the groundwater.

- The linear velocity of a dissolved chemical band (i.e., the median or average value associated with the band - Figure 1) divided by the linear velocity of the fluid gives that chemical's retardation factor.

- Sample size or concentration does not affect chromatographic separation unless it overloads the system. When that happens, the necessary equilibrium conditions cannot be established and separation does not occur. Overloading causes broad, distorted bands (peaks) and poor resolution.

- Analytical chromatography assumes that the chemicals to be separated are initially dissolved in the fluid phase. This is rarely the case for chemicals released to the environment, where the rate of dissolution (e.g., of an LNAPL) can effect an apparent separation entirely unrelated to chromatographic principles.

- Great care is taken in analytical chromatography to ensure a homogeneous stationary phase to minimize band broadening and maximize resolution. Aquifer materials, by contrast, are inherently heterogeneous stationary phases that do just the opposite.

With these principles in mind, I invite you to explore further the forensic capabilities for dating groundwater releases, starting with the Guest Column by Charles McLane and Robin Magelky in this issue.

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Presented by:
James Smith, Ph.D.
Charles McLane, Ph.D.

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Trillium grandiflorum (Jason Pruitt)

Guest Column

Charles F. McLane and Robin D. Magelky, McLane Environmental LLC

Estimating Contaminant Plume Travel Times: Moving Beyond Darcy's Law

Often, an environmental consultant (hydrogeologist, chemist, or engineer) is called upon to estimate how long it took, or might take, for a dissolved chemical plume to migrate from a source area to a certain receptor location. Or, sometimes the historical time of release from a known or suspected source is estimated by back-calculating from the measured length of the plume today. One of the ways this is commonly done is to assume that the plume velocity can be estimated by calculating the average groundwater velocity based on Darcy's law. In other words, Darcy's law is used to estimate the average groundwater velocity, and that velocity is used to either (1) project the plume forward in time to see when it will reach the receptor, or (2) calculate the length of time it would take for groundwater to traverse the length of the plume, and then to subtract that time from today's date to estimate when the release occurred. This method is wrong and will not lead to accurate and reliable results. The fact that it is wrong has been known for quite some time in the field of quantitative hydrogeology and contaminant transport, but in many instances it seems to be either forgotten or ignored.

The reason that a simple Darcy's law calculation cannot be used to estimate the travel time of a plume is that, while it accounts for the average rate of groundwater flow (advection), it does not account for the fact that flow through the aquifer causes a spreading of the chemical "front" (dispersion). The effects of dispersion on plume movement are clearly laid out in almost every introductory textbook on hydrogeology and porous media transport. Articles published over 20 years ago recognized that "Dispersion is of interest because it causes contaminants to arrive at a discharge point … prior to the arrival time calculated from the average groundwater velocity." (Mary Anderson, 1984, "Movement of contaminants in groundwater: Groundwater transport—advection and dispersion." In *Groundwater Contamination*, The National Academy of Sciences, pp 37-45).

More recently, Ernesto Baca ("On the Misuse of the Simplest Transport Model," *Ground Water Journal*, 1999, Vol. 37, No. 4, p 483) very clearly describes the error that can arise when dispersion is neglected in plume transport travel time calculations. His simple example shows that, whereas a Darcy's law velocity calculation would tell you it took 25 years for a contaminant to move from a source area to the property boundary of a site, a more appropriate plume transport model calculation demonstrates that the tip of the plume would cross the property boundary in nine years. That's an error of 16 years, or roughly 180 percent!

*(See **Guest** on page 4)*

Watch out for Morlocks!

Wouldn't it be great if we could time travel? What a perfect solution for the problem of too many samples and too little time. What if we could slip back a few days and get everything done? No, time travel is not a reality yet, but some laboratories have found a way to pretend that it is.

Many bench records in the laboratory are handwritten documents, and it would be rare to find someone who hasn't put the wrong date on something important at one time or another. Most software systems for analytical instruments have a clock that can be set by the operator. Now and then this clock may need to be reset because of things like software glitches, power failures, and daylight savings time. The eccentricities of a laboratory information management system (LIMS) may result in an incorrect analysis date listed on a report. Most of these are just honest mistakes.

The correct remedy for all of these errors is to draw a single line through the incorrect date and add the correct date along with the initials of the analyst and the date of the edit.

But there have been occasions when analysts have reset the clock in the software, or recorded the wrong date on laboratory documents, for less-than-honest reasons. That is called "time traveling." Maybe there are too many samples, not enough time, and the holding time clock is ticking. Maybe calibration just cannot be verified, and there isn't enough time to start over before the clock runs out.

The big problem for the data user is that time-traveling is not easy to detect. Falsification of dates on handwritten bench sheets is probably impossible to detect, unless the sample appears to have been extracted or analyzed before it was received by the laboratory or there is a discrepancy between dates in the sample tracking system and the bench logs.

Likewise, unless you happen to get data for more than one analysis run on the same instrument during the same time, you may never have a clue that the laboratory has been making temporal excursions. But, be aware that there are also occasions when you can legitimately have more than one analysis performed at the same time on the same instrument. One of these involves splitting a single injection onto more than one column or making simultaneous injections into multiple columns in a gas chromatograph. In both of these cases you will have data for more than one analysis initiated at exactly the same time. But if there is only one detector and you have data for overlapping runs, chances are good that something is bad.

What is the effect on the results? Time traveling allows an analyst to run anything anytime. Samples may have been extracted or analyzed outside of holding time, outside of the method-specified calibration period, or even without a valid calibration in place. That means compounds may be reported as not detected when they are really present or compounds may be mis-identified. Holding times are specified to minimize the alteration of the sample contents between collection and analysis. Compounds that volatilize or change over time may be diminished, or even gone, by the time the analysis is performed, if the holding time has been exceeded. Chromatographic retention times can shift over time, with the result that the software may not find an analyte even though it is present or may misidentify one or more similar compounds.

"Everything that we have, our whole existence, is chemical."
Whitson Sadler

Detector response will change over time. That's why a calibration curve must be established and verified before sample analysis. If you run outside of, or without, a valid calibration, there is no assurance that a reported concentration is correct.

Until someone has perfected a real time machine, it is better to use a laboratory you trust. Discuss with your laboratory representative how the laboratory responds to overloads before you send your samples. Understand that unpredictable things can happen, and it is always best to keep the lines of communication open from both ends.

Denise Shepperd

Guest *(continued from page 2)*

In a paper we prepared for the National Ground Water Association Environmental Law Conference in July of this year, we build on this theme by presenting the results of simple calculations performed for a variety of plume transport scenarios using a number of readily available plume transport models. When we compared our plume model arrival time results with those of a corresponding simple Darcy's law calculation, we found the Darcy's law calculations were in error by 100 percent or more in many instances.

Numerous investigators and "experts" continue (explicitly or implicitly) to tout the utility of the Darcy's law approach based on statements to the effect that "the dissolved chemical is transported at the same velocity as the ground water," or "the center of mass of the plume moves at the average rate of ground water flow." When calculating plume travel times or arrival times, these statements are incorrect or meaningless and incorrect estimates will surely result.

Darcy's law was intended to estimate groundwater velocity only, and to apply it to estimate the dispersive transport of a dissolved plume front is clearly a misuse. It is time we moved beyond Darcy's law when it comes to estimating plume transport and arrival times.

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