"Unraveling the Mysteries of Chemical Movement Through Soil"
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Faculty Research Lecturer
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I am very honored to be asked to address you today as the 51st Faculty Research Lecturer at UCR. I have spent my entire professional career here after a brief postdoctoral appointment at Wisconsin, and have been privileged to work with a number of talented students and other professionals over the years. What I would like to do today is tell you the chronological story of one of my long-term research studies, the movement of pesticides and fertilizer chemicals through soil that is in its natural state.

## Historical Background

The reason that we study chemical movement in soil is largely because many chemicals end up contaminating our water supplies. To understand how the environment came to be so polluted with agricultural chemicals, it helps to know a little bit about the history of food production. In the 1950's, when the population of the world was less than half what it is today, poor areas of the world frequently experienced famine. Population forecasts of continued growth were accompanied by predictions of mass starvation caused by inadequate food supply. Then along came the Green Revolution, in which modern farming methods were adopted to vastly increase land productivity. Food production jumped ahead of population growth, and has stayed there ever since. A big part of this success story has been due to agricultural fertilizers and pesticides.

When my career started in the early 1970's almost all of the world's agricultural research was associated with increasing crop production. US farmers put massive amounts of nitrogen-based fertilizer on a variety of crops, and controlled weed and insect pests exclusively through the use of pesticides. Regulation of agricultural chemicals was nonexistent, partly because of the high priority placed on production, and partly because of a mistaken belief that soil could retain and neutralize any chemicals placed it. This myth was effectively dispelled when groundwater sampling and analysis began in earnest in the late 1970's. During a five-year sampling period in California for example, 57 different pesticides were detected in over 4500 wells, and the chemical dibromochloropropane (DBCP) alone was detected in over 2500 locations. Obviously, the soil was not as perfect a filter as had been believed.

Scientists had done a bit of study of chemical movement in soil, but almost exclusively in the laboratory in carefully packed columns containing soil that had been sieved and broken up into individual particles. Some elegant mathematical models had been developed to simulate this movement, and they worked quite well. Unfortunately, these models couldn't explain the widespread dissemination of chemicals that had been observed in groundwater, particularly of the pesticides which often were quite immobile in laboratory experiments due to their attraction to solid phase surfaces of clay or organic matter. So something about soil in the field environment was different than in the laboratory. Part of the difference could be attributed to structure: cracks, holes, etc. in natural soil that allow water to move more rapidly than in the adjacent intact soil matrix. But there were many types of soil, those with a lot of sand in them, that didn't have much structure, and a lot of pollution had been detected in groundwater underneath them. So it was something of a mystery as to why chemicals moved so fast through these types of soils, and a good portion of my professional career has been spent trying to figure out why.

## My Early Days

I got my first introduction to the complexity of transport through sandy soil as a postdoc at Wisconsin in 1973, working on a project designed to convince the local potato farmers to add fertilizer in the irrigation water rather than spread it on the soil. The field soil, called Plainfield sand, was highly uniform without any apparent structure, and seemed to us to be the closest thing to a packed lab column imaginable. The farmers customarily grew potatoes on little hills constructed on the field, and buried a band of nitrogen fertilizer under the side of the hill about a

foot from the tuber. We thought this fertilizer would get largely wasted because it would dissolve and wash down into the soil as the irrigation water was added.

At the end of the season, we got a shock--the control plots mimicking the farmer's management practice actually lost less nitrogen below the crop than our carefully managed system that slowly provided dissolved nitrogen to the plant with the water that we added. Eventually we figured out why by adding some dye to the soil and digging it up. The water we added was streaming down the plant stem and also running off the shoulder, producing a very spatially non-uniform drainage pattern under the crop (Figure 1). The farmers were placing their fertilizer band right where the X is on the figure, and because not much water was going there, it slowly released to the plant roots and didn't move much. In contrast, a lot of our nitrogen was streaming down the channels under the plant and furrow, and wasn't being taken up by the crop. We blamed it on the surface contour, and on high stem flow down the plant, which was probably only part of the explanation.
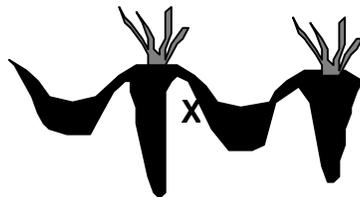


**Figure 1. Dye trace pattern of water movement under the potato crop. The X indicates the location of the fertilizer band placement by local farmers.**

## UCR Field Experiments

It wasn't until 1980 that I got the money and the nerve to do a large-scale field experiment studying chemical movement. By this time I was expecting the soil to have a lot of variability, so I wanted to take enough samples to have good statistics. We added an application of the pesticide napropamide together with a pulse of chloride to trace the water movement to a 0.64 ha field that was being sprinkler irrigated every day. After we had added 25 cm of water over the next two weeks we came in with a hydraulic coring rig and took 36 soil cores to a depth of 3m across the field, and sub-sampled at 10 cm intervals within each core. Because the pesticide was strongly attracted to the soil and organic surfaces in the solid phase, conventional theory predicted that it would all be found within the top 20 cm. What we found instead is shown in Figure 2.
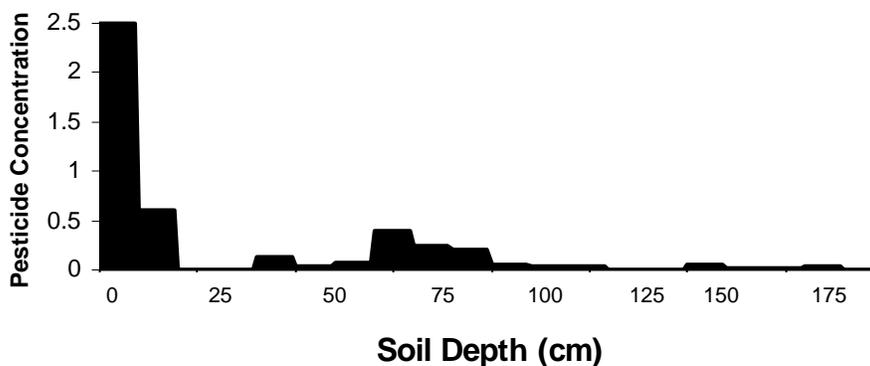


**Figure 2. Field-averaged napropamide recovery in the first field experiment. Maximum predicted depth according to conventional theory is 20 cm.**

Although about 75% of what we recovered was near the surface, the remainder went significantly deeper, and we even found traces at 1.8 m. Extreme movement like this had not been reported before, but that turned out to be because no one had sampled that much deeper than they expected to find the chemical in past field studies. In fact, if we had sampled to only 30 cm, our findings would have looked quite typical, because we would have missed the deeper movement completely.

Our second major field experiment was conducted on the same site several years later. This time we wanted to study in detail the movement of the water, so we added a concentrated pulse containing bromide, which moves as a water tracer. We installed 105 solution extraction samplers at 16 sites around the field, at depths ranging from 30 to 450 cm. We watered our field every other day for over a year, until all trace of the chemical had moved past our deepest monitoring depth of 450 cm. The next year we returned to the site and took six deep cores to 25m. We encountered a great deal of spatial variability in the downward movement of the pulse, as shown in Figure 3. Even though we had a highly uniform sprinkler system, the pulse moved at different speeds in different locations, and showed substantial evidence of tortuous movement. As a result, little useful information could be gained by looking at one site.
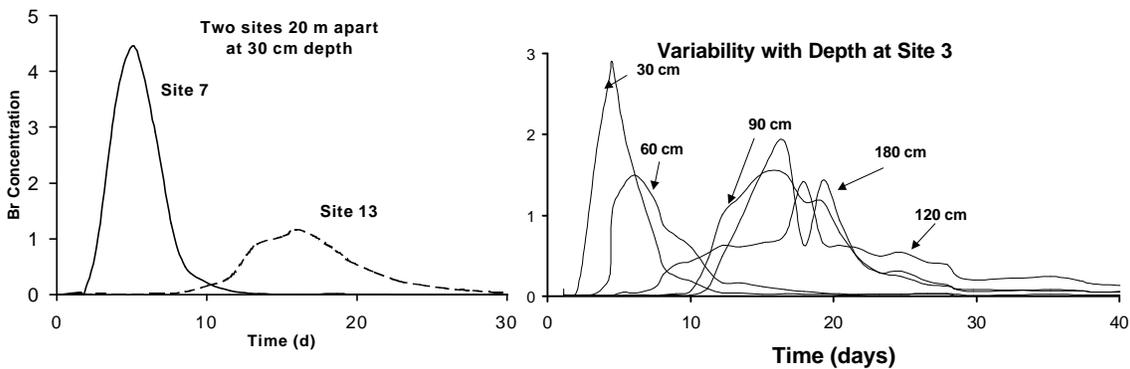


**Figure 3. Solution sampler Br concentrations measured at two locations 20-m apart (left) and at multiple depths at the same site (right)**

The next thing we tried was area-averaging all 16 replicate solution sampler concentrations at each depth, to produce a field-scale downward pulse. That smoothed out the variability considerably, as shown in Figure 4.
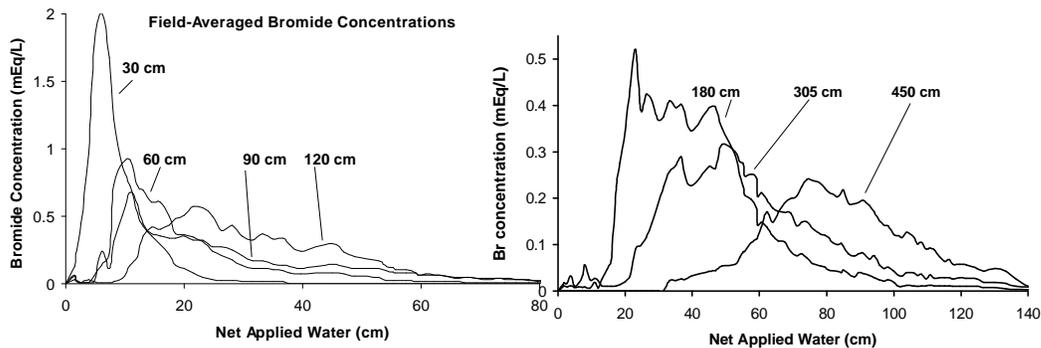


**Figure 4. Field-scale Br concentrations averaged over the 16 sites at each depth.**

This area-average profile provided a useful data set for testing models of chemical movement at the field scale. These models were generally one-dimensional because of data limitations, and were starting to be used to predict the impact of agricultural fields on ground water quality. But the main model, called the convection-dispersion equation (CDE), had never been tested at this scale before. This model assumes that the chemical moves downward at the average speed of the water, and that it spreads randomly within this uniform motion. We developed a test where we calibrated the model's parameters at the shallowest (30-cm) depth and subsequently predicted the concentration at greater depths. The result of this test using the CDE is shown in Fig 5.
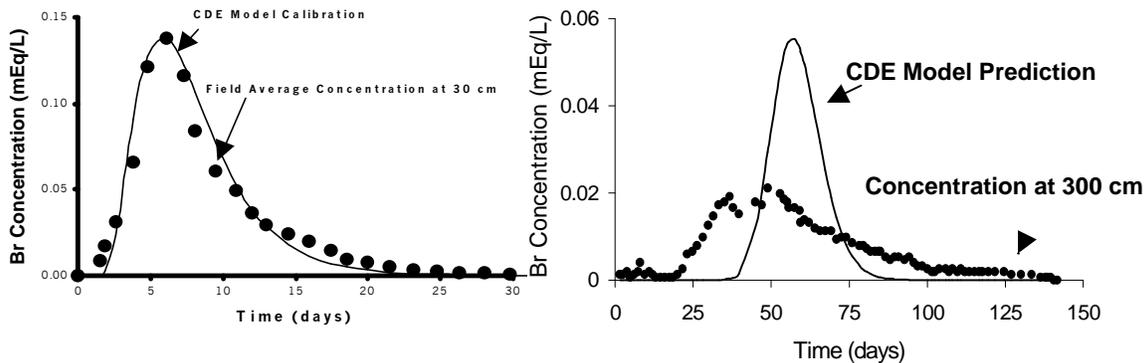
**Figure 5. Test at 300 cm of the CDE model calibrated at 30 cm.**

Obviously, the model seriously underestimates the spreading of the pulse at this scale. If used to predict chemical movement to ground water, it would fail drastically to estimate the first arrival time, or any of the early or late contamination characteristics. Clearly, a different model was needed for the field.

## A New Perspective: Travel Time

The field regime was always going to limit what we could do to describe chemical movement. Water flow was highly variable, and defied our attempts to measure the soil properties responsible for the variability at a small enough scale of resolution to be able to predict it. I finally decided to take a radically different approach to the problem of measurement and let the chemical movement itself tell me what the water was doing, by revealing how long the molecules take to move a given distance. This required recasting the problem stochastically, and basing the transport on the travel time probability distribution. Conceptually, we imagine adding a large number of molecules of a water tracer to the soil surface at t=0, and recording the arrival of the molecules as a function of time at some depth L of interest. For example, between time $t_1$ and $t_2$ we measure a total of n molecules arriving. Statistically, this means that the probability of the chemical tracer having a travel time $t_1 < t < t_2$ is n/N. We keep recording the arrival of the molecules over small time intervals until they have all crossed the exit plane at $z = L$. Then we construct the probability diagram as shown in Fig. 6.
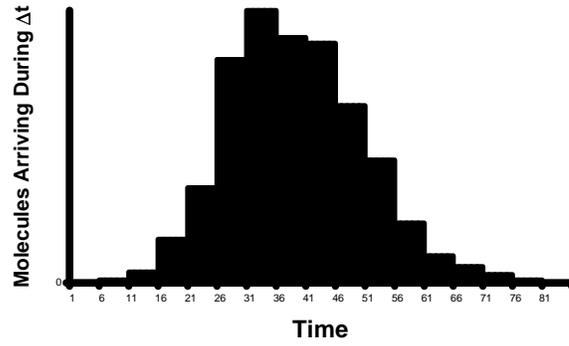
**Figure 6. Frequency histogram showing molecules arriving at z = L as a function of time**

If we normalize this curve to have unit area, it may be interpreted as the probability density function (pdf) f(t) of the solute travel time. Thus, the probability $P(\tau)$ that a tracer added to the surface at t=0 will reach the outflow end at z = L in a time $t \leq \tau$ is

$$P(\boldsymbol{t}) = \int_0^t f(t')dt' \tag{1}$$

So how do we count molecules? We measure the chemical concentration, which is the density of the chemical in the solution phase. Thus, we may measure f(t) experimentally by adding a narrow pulse of chemical to the surface and measuring the concentration C(t) as a function of time as it arrives at the outflow end. Then we need only normalize the concentration-time function so that it has unit area. Thus,

$$f(t) = \frac{C(t)}{\int_0^\infty C(t')dt'} \tag{2}$$

The next step is to use this function to predict solute concentrations arriving at z = L for arbitrary input concentrations $C_{in}(t)$. If we assume that the molecule's travel time is not affected by the presence of other molecules, and that the travel time pdf does not change over time, then the output concentration is given by

$$C_{out}(t) = \int_0^t C_{in}(t-t')f(t')dt' \tag{3}$$

This representation has a major advantage in that it doesn't require us to make internal measurements of the properties of the soil between the surface and z = L; we just measure the outflow. The problem with Eq. 3 is that it isn't very useful. The pdf f(t) will obviously change whenever the rate of water flow in the soil changes, and this happens continuously in the field. Rainfall and irrigation are sporadic, and water evaporates at different rates during the day and time of year. In its present form, this theory has nothing to offer to the practical problem of predicting chemical movement in the field. So we made an "engineering assumption" that we knew wasn't exactly true, but that might be reasonably accurate. We assumed the pdf describing movement from the surface to depth L would be a unique function of the cumulative net applied water I(t), regardless of the rate at which we applied the water. Our new theory became

$$C_{out}(I) = \int_0^I C_{in}(I-I')f(I')dI'; \quad I(t) = \int_0^t i(t')dt' \tag{4}$$

where i is the water flux rate at the surface. Equation 4, which is sometimes called a transfer function, turned out to be a very good approximate model in many soils.

A major advantage of representing solute transport as a transfer function, is that all linear models of chemical movement (e.g. the CDE) can be expressed in this form, and that new models can be developed without having to express them as differential equations.

## A New Model: the Stochastic-Convective Transfer Function

It was obvious to us that our field-averaged data (Figure 4) was showing strong evidence of water flowing at a variety of speeds in different parts of the field. Therefore, it might be useful to test a model that assumed that these regions of water flow at different velocities did not mix their contents with adjacent regions as they moved. It is very easy to make this statement in terms of probability; it is simply

$$P(I; z) = P(\frac{IL}{z}; L) \Rightarrow f(I; z) = \frac{L}{z} f(\frac{IL}{z}; L) \tag{5}$$

In words, Eq. 5 is saying that the probability of reaching depth z before an amount of water I has been added is equal to the probability of reaching depth L before an amount of water IL/z has been added. Now this allows us to do a single experiment measuring P or f at one depth L, and we can use it to predict chemical movement past any depth z. We tested this model on our field data the same way we tested the CDE in Figure 5; calibrate it at z=30 cm and predict movement past other depths. Figure 7 shows the result in comparison with the CDE prediction.
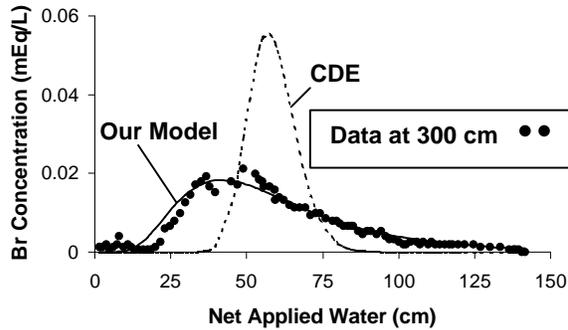


**Figure 7. Test of model Eq. 6 and the CDE on field data at 300 cm following calibration at 30 cm.**

The probability model fits the data very well, which told us some valuable things about field-scale transport. There were a host of applications for transfer function modeling, and a number of applications where it had distinct advantages over the conventional approaches. For example, we could now isolate the effects of chemical sorption to soil from the transport process, allowing us to test models of sorption with much more accuracy. This was particularly important in the field.

## Field-Scale Pesticide Transport Modeling

In Figure 2 I showed our pesticide field experiment results, showing that the strongly adsorbed pesticide had migrated much deeper than it was supposed to based on conventional wisdom. Since we had also added a water tracer (chloride) to this field at the same time as the pesticide, we could use transfer function modeling to ask an important question not easily addressed with other models. Could the deep movement be explained by water flow variability and equilibrium or rate-limited adsorption? The answer turned out to be no, as shown by Figure 8. We could not simultaneously fit both the shallow and deep parts of the pesticide curve using the water variability that was revealed by the chloride. We suspected that the reason was that there was an extremely rapid water movement going on through part of the profile, and that it had carried the chloride below the depth of monitoring. But we couldn't prove it, and I left this problem partially solved for many years.
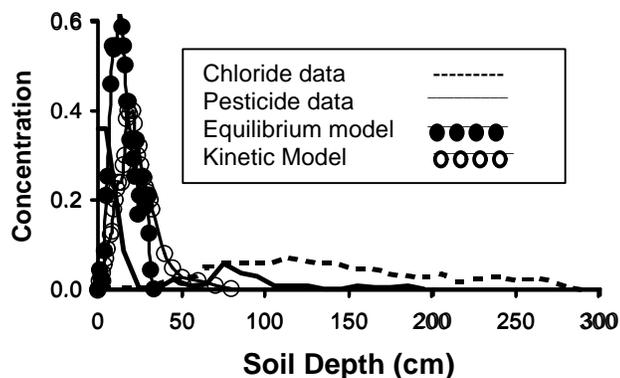


**Figure 8. Pesticide data predicted using measured chloride data and two hypotheses about the nature of sorption to soil.**

## My Current Research

After nearly 15 years, we have finally developed a hypothesis to explain what we saw in the field experiments. We now believe that the water flow becomes unstable when the application is stopped and the water starts draining. The reason this happens is a bit subtle to discuss here in detail but is mainly due to a reversal of the water pressure gradient behind the wetting front. We built a sand tank to conduct lab experiments on this hypothesis and have seen some encouraging results. Figure 9 shows the water profile moving uniformly downward through the tank as long as water is being applied, but shifting to unstable flow with fingering as soon as water application is stopped. We also conducted a field experiment on this and showed that the same thing is happening. It's more important in certain soils than in others, but all soils exhibit the behavior to varying degrees.

This discovery really opens up a Pandora's box, since our current theory of water flow in soil says that what we are seeing isn't possible. I suspect that this research will keep me busy and entertained for the rest of my career.
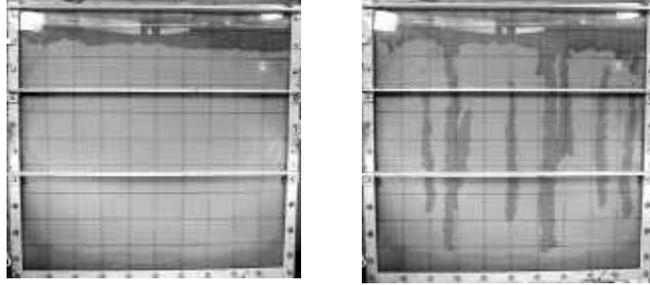
**Figure 9 Sand tank experiments showing water entering a soil during the water application phase (left side) and after the water application stops (right side), when the wetting front breaks up into unstable fingers.**

## Conclusions and Acknowledgments

I've been very happy here at UCR, and have been blessed with a number of outstanding students and postdocs who have labored alongside me on the problems I've discussed today and many others I haven't referred to. I've always found that the key to creativity and productivity is to have fun, and I've certainly enjoyed myself as I attempted to unravel the mysteries of chemical movement through soil. Thank you for your attention.