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Solute and Contaminant Transport in Heterogeneous Soils

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Approximately 95% of the world's freshwater is stored in aquifers, and since more than 90% of the world's population relies on these reserves for drinking water supply and for irrigation, it is crucially important to protect these reserves from contamination by surface applied agrochemicals and pollutants. Agriculture is responsible for 70% of the World's water consumption and by the year 2025, water consumption is likely to increase by 40% if current demands for quality and quantity of food and water are maintained (IPCC, 2001). One-third of the World's population presently reside in countries that are water-stressed ie. use more than 20% of their renewable water supply. If projected forecasts in climate change are correct, then many other countries including Australia will experience severe water stress by the year 2025 (IPCC, 2001). Recycling of wastewater and sewage is therefore essential for economic and ecological survival. The use of manufactured inorganic fertilizers will not ensure projected future agricultural production levels, therefore, the nutrient content of municipal and industrial wastewater makes it very attractive for fertilizer. However, domestic sewage, even after treatment, contains significant concentrations of potentially toxic contaminants including heavy metals, pesticide residues, endocrine disrupting compounds, synthetic estrogens, and pathogenic microorganisms. Leaching of contaminants through the soil into groundwater aquifers is therefore a major hurdle to the safe disposal of treated sewage on land and to long-term sustainability of drinking water supplies. In order to better manage groundwater, one needs to carefully understand how surface-applied water and solutes are transported through the unsaturated zone to deeper groundwater.

We will discuss important factors controlling the mechanisms of how water and solutes are transported through soils. These factors are illustrated with examples from current research. New results on modeling preferential transport of nutrients and a new concept of spatiotemporal solute leaching are also presented.

After rain or irrigation, water and any solutes in the water infiltrates through the soil surface and percolates in the vadose or unsaturated zone by one of two mechanisms. The first mechanism is matrix flow. Matrix flow or Darcy flow is the flow of soil water that is proportional to the vertical hydraulic gradient and is described by Richard's equation and Darcy Law. The flow of solutes in the water is often described by the classical Advection-Dispersion with Reaction equation (ADRE). On the other hand, preferential flow is the fast, concentrated and far-reaching flow of water and solutes through a relatively small portion of the soil matrix. With preferential flow, water carrying solutes, nutrients, microbes and pollutants may by-pass the root zone entirely and be rapidly transported to the

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groundwater (Stagnitti, 1999). The rate of transport may be so fast that there is insufficient time for chemical or biological degradation, particularly if the contaminant is leached from the root zone. Once the contaminant has reached the oxygen-limited groundwater, chemical decomposition may take a very long time, even as much as hundreds of years, and the aquifer therefore may not be exploited for human or stock consumption. Remediation of the groundwater is also very costly. Mechanisms which cause water and solutes to follow a preferred path must be considered explicitly in order to reduce the risk of potential groundwater contamination and avoid costly remediation.

The extent and magnitude of preferential flow depends on the soil composition, soil structure and infiltration rate (Stagnitti and Elango, 2001). The major mechanisms responsible for preferential flow include (a) macropore or biopore flow, (b) soil water fingering caused by unstable wetting fronts, (c) flow over and through subsurface layers of differing soil textures and properties, and (d) flow in hydrophobic or water repellent soils. Macropore and biopore flow is commonly found in well structured, fine-grained soils. Macropores are formed by geological forces such as shrink-swell cracks as commonly found in clay soils, channels formed by depressions and soil erosion, and decayed root holes. Structural voids in the soil can also result from biological forces such as animal burrows and worm holes. These are called biopores. Experiments have found that macropores and biopores which often amount to less than 1 % of the pore space can account for the transport of as much as 90 % or more of the infiltrated water and solutes. For example, Smettem et al (1991) found that a single 0.3 mm diameter macropore can conduct more water than a 100 mm diameter homogeneous soil core. Jones (1971) found that as much as 50% to 90% of the stormflow in rivers in the United Kingdom is carried through macropore networks and that these networks can carry water and solutes through subsurface soils at rates as high as 9 km/d.

Preferential flow can also be caused by layering of subsurface soils. Layering affects vertical percolation and induces lateral flow along the layer and "funneling" between layers (Kung, 1993). The diversion of flow caused by layering is significant because even in areas where groundwater monitoring is conducted routinely; the pollution may be missed entirely if the observation well is placed in the wrong location.

Even in uniformly, unstructured, homogeneous soils, infiltration of water and solutes does not occur uniformly. The development of soil-water fingers can develop in the soil and persist with time, even after many cycles of wetting and drying. These fingers, once developed, tend to persist in the same location. The consequence of soil-water fingering is that certain regions in the soil may never receive adequate water or nutrients, and thus result in reduced agricultural or forestry production. Research has shown that fingering can be produced whenever the soil hydraulic conductivity increases with depth, or the conductivity of a top layer is smaller than that of a bottom layer, or when infiltration of non-ponding rainfall occurs, or in water repellent soils. The formation of soil water fingers in sandy soils and water repellent soils has been extensively studied (Parlange et al, 2002). It is not intuitive that the infiltrating water will develop into fingers. However, the mechanism producing soil-water fingers is analogous to rain drops on a window pane. The balance of gravity and surface tension determine the number of fingers produced, and their diameter, moisture content and velocity. These can be predicted by mathematical models (Parlange et al, 2002). Once the fingers are formed in relatively dry porous media, they do not change location even after several infiltration events. Only complete saturation and subsequent drainage alters the finger structure.

The fourth preferential flow mechanism is soil hydrophobicity. This is a property of soil that reduces infiltration capacity, promotes preferential flow, inhibits crop germination, reduces nutrient and chemical holding capacity and accelerates erosion. Water repellent soils are found in every continent in the world and in particular are located in regions with low rainfall and soils with poor condition eg. sandy soils with high humic and organic content (Doerr et al, 2000). Water repellent soils lead to inconsistent moisture distributions in the A horizon of the soil profile and severely limit the germination of crops and pastures. Clay spreading is a useful measure for ameliorating water repellency. It is a common practice in Australia. However, this is only an economically viable option if there are sufficient clay reserves located on the farm and not more than 500 to 800 m from the application area.

It is clear from the current volume of research that preferential flow generated by whatever mechanism can transport water and solutes well ahead of the main front and far beyond the depths predicted by simple models based on Darcy's Law. Therefore, if preferential flow is ignored serious underestimation of the risk of groundwater contamination may occur.

MATERIALS AND METHODS

Sampling the unsaturated zone in soils may serve as an early warning system for groundwater contamination (Stagnitti, et al. 1998). However, one of the greatest uncertainties in monitoring groundwater contamination is the possibility that solutes flowing in preferred paths bypass samplers. Thus scaling point-source measurements to field-scale estimates may be unreliable and misleading even in the case when geostatistical methods are employed (Stagnitti et al, 1999). Various methods for sampling unsaturated flow have been proposed. Methods for continuously sampling solutes in the unsaturated zone involve the collection of soil water drained by either the force of gravity (eg, gravity pan samplers, agricultural tile lines, and shallow wells) or by applying a "capillary" suction (eg, porous cup samplers, wick or suction lysimeters). Gravity pan samplers collect the percolate from a saturated portion of the soil immediately in contact with the sampler, and thus may lead to "bypassing" (ie. solutes and water flowing around the sampling device).

A modification of the gravity pan sampler is the Alundum tension plate sampler, in which the percolate is extracted from the unsaturated soil by suction applied across an alundum filter disc. Fiberglass wick lysimeters operate by the same principle (Boll and Selker, 1992). The wicks are self-priming and act as a hanging water column, providing a suction to the unsaturated soil. The wicks are also non-reactive and therefore can be used to sample solutes (Boll and Selker, 1992). Wick sampling units may consist of a single fiberglass wick spread over a fixed area or several wick lysimeters located on a square grid. The term multiple sample percolation system has been used to describe the latter sampling device (Stagnitti, Li et al, 1999).

Multiple sample percolation systems have been used by the authors for several years (eg. Stagnitti, Li et al, 1999). Typical sampling devices consist of twenty-five individual fiberglass wicks placed on a 5 x 5 cm grid on the basal surface area of the sampling unit. The base-plate is then firmly pressed against the base of the soil by springs. The length of the wick provides a capillary force that is approximately equivalent to that found in the soil and thus can be used to sample unsaturated flow. Being a porous medium, the wicks provide boundary conditions which mimic those found in the soil (Boll and Selker, 1992). The soil core is usually irrigated by a X-Y raster-scanning, drip-irrigation system connected to a peristaltic pump. The aerial coverage, speed and direction of irrigation are electronically controlled by two stepper motors with the result that the irrigation system delivers a constant and uniform application of water and soluble nutrients on the soil surface.

Using this apparatus, several experiments were recently conducted on a range of Australian soils (Stagnitti et al, 1998, 1999, 2001). Figure 1 illustrates an example of the typical spatial variation in flow patterns from one of these experiments. The experiment was conducted to evaluate the impacts of a commonly used herbicide Atrazine and fungicides (not reported here) on the production of wine and possible contamination of soils. The leachate was collected over 66 days. A constant and uniform application of water was applied to the soil surface. However, notice the considerable variation in soil water leached from the soil (Figure 1). Atrazine was applied as a single dose to the soil surface (Figure 2). Again notice the significant pattern of variation in leached Atrazine mass and how this pattern also differs considerably from the soil water leachate shown in Figure 1.

This study concluded that Atrazine was moderately persistent in ground water and soil water. While Atrazine in the soil profile largely disappears after one year, a by-product, hydroxyatrazine persists at measurable concentrations in soil for a much longer time. The threat to local aquifers from Atrazine use is uncertain because of a lack of metabolite toxicity data. Therefore in regions with shallow groundwater, Atrazine may pose a risk. These results dramatically demonstrate that preferential flow can not be ignored in modeling solute transport.

RESULTS AND DISCUSSION

All forms of preferential flow, whether macropore, biopore flow or soil water fingers resulting from unstable wetting fronts, increase the rate at which water and solutes travel through the vadose zone and therefore potentially increase the risk of groundwater contamination. The most challenging problem confronting mathematical modeling of solute transport in soils is how to characterize and quantify the geometric, hydraulic, and chemical properties of the porous media. To reduce the complexity involved in modeling the transport process, many models are based on assumptions of homogeneous soil structure and instantaneous sorption - sometimes referred to as the LEA (linear equilibrium adsorption) assumption. The general equation governing contaminant transport under saturated, steady flow conditions, and with chemical reaction, has the form of the classical advection-dispersion-reaction (ADRE) equation (Parker, and van Genuchten, 1984). The ADRE has a simple form because it describes an ideal process of equilibrium transport. However, the LEA assumption is seldom valid in field soils. Non-ideal transport (non-equilibrium transport), as observed in many experiments, is more the norm than the exception. The causes of non-equilibrium transport in soils are soil heterogeneity and non-equilibrium chemical sorption.

Considering the bicontinuum conceptualization, a two region solute transport model (TRM) was developed to describe non-equilibrium solute transport in aggregated soils (Brusseau and Rao, 1990). The bicontinuum concept physically represents the soil structure in aggregated soils. The region within the aggregates is the immobile region where water and nutrients are stagnant except for lateral diffusion. The region between the aggregates is the mobile region where water and nutrients move due to advection and dispersion. Although this model was originally developed for solute transport in aggregated soils, it is often used to model other non-equilibrium transport processes including preferential flow. The performance of these models was recently evaluated on experimental data by Stagnitti, Li et al (1999). They concluded that neither model adequately represents solute transport in variably saturated conditions.

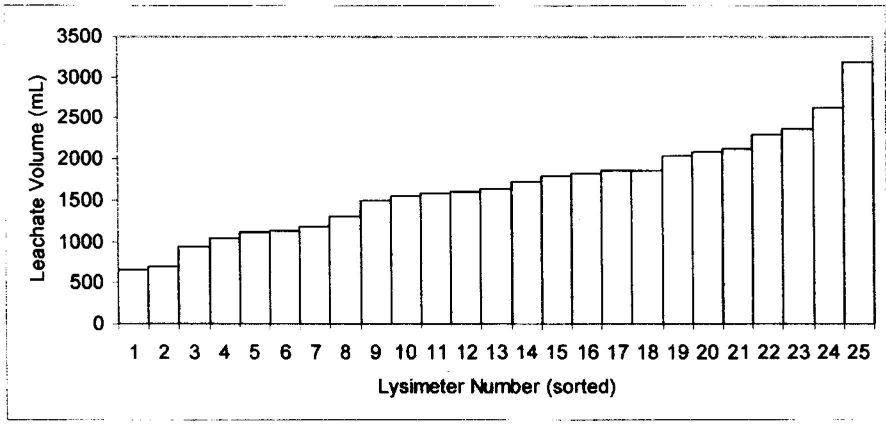

Figure 1. Leachate for a soil monolith collected over 66 days from a vineyard in the South Australian Riverland region, near Overland Corner, Australia.

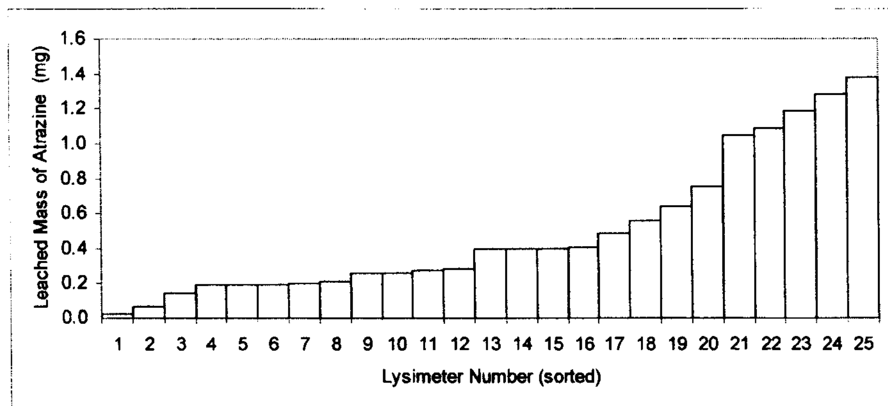

Figure 2. Leached mass of Atrazine. Notice the very large variability in leaching patterns over a small spatial scale.

What these results clearly demonstrate is that modeling solute transport in heterogeneous porous media under variable saturation is very problematic. Extending the bicontinuum approach to solute transport, we developed another solute transport model called the preferential solute transport model (PSTM) (eg. see Stagnitti, 1999 for more details). This model is a multi-region or multiple porosity solute transport model that is able to simulate single species solute transport in variably saturated porous media. In this model, the soil is conceptualized as a medium containing a number of discrete pore groups or capillary bundles in which water and any solutes in the water are vertically displaced with a characteristic velocity. One pore group or capillarity bundle represents the immobile region in the soil. Several other capillary bundles model matrix flow (or mobile water) and in addition, a number of additional capillary bundles are included to model macropore or preferential flow. In this respect the PSTM represents an extension to the two-region TRM model. Lateral diffusion is modeled by simple linear mixing coefficients. By adjusting these coefficients, any form of solute breakthrough curve ranging from stochastic-advective to diffusion dominated flow can be easily modeled.

The PSTM model was recently applied to study the transport of various nutrients (chloride, nitrate and phosphate) through a moderately preferential soil. The experimental data were described in Stagnitti et al, (1998). The results of the model investigations are presented in Figures 3 to 6. Figure 3 presents the actual and modeled leached soil water. Figures 4 to 6 present the predicted and actual leached chloride, nitrate and phosphate. All the chloride applied on the soil surface was leached from the experiment after 22 days. Just more than 70% of the applied nitrate leached from the soil core in the duration of the experiment, indicating nitrification and mineralization. Less than 1% of the applied phosphate leached during the experiment. Soil sectioning indicated that the phosphate was readily absorbed in the first 2 cm of the soil. Given that all the data was modeled with a common set of parameter values (eg. saturated hydraulic conductivity, etc), the agreement between predicted and actual soil water and solute breakthrough is remarkably good, even for phosphate which was very strongly bound to the soil.

A common problem encountered in all solute transport models including the PSTM is the difficulty of characterizing the subsurface preferential flow paths. A useful approach to this problem was the development of a single-value heterogeneity index of preferential flow, called the *HI* (Stagnitti et al, 1999).

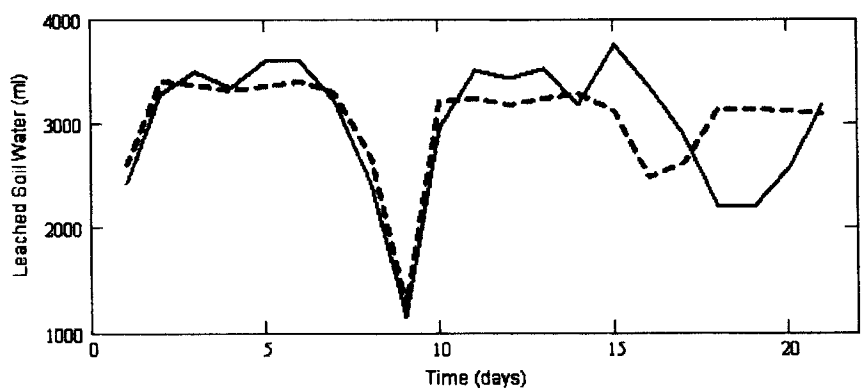

Figure 3. Application of the PSTM to experimental results for nutrient leaching in a moderately preferential soil. Experimental data is from Stagnitti et al, (1998). The leached soil water is plotted with time. The solid line is actual data and the dashed line is modeled leached soil water.

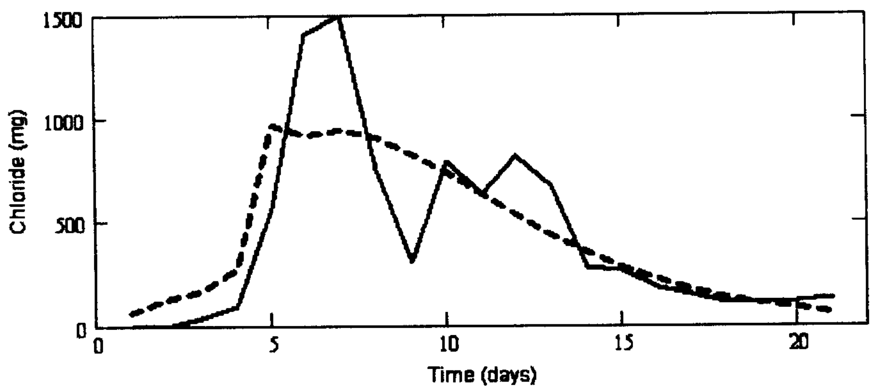

Figure 4. Application of the PSTM to leached chloride with time. The solid line is actual data and the dashed line is modeled leached mass.

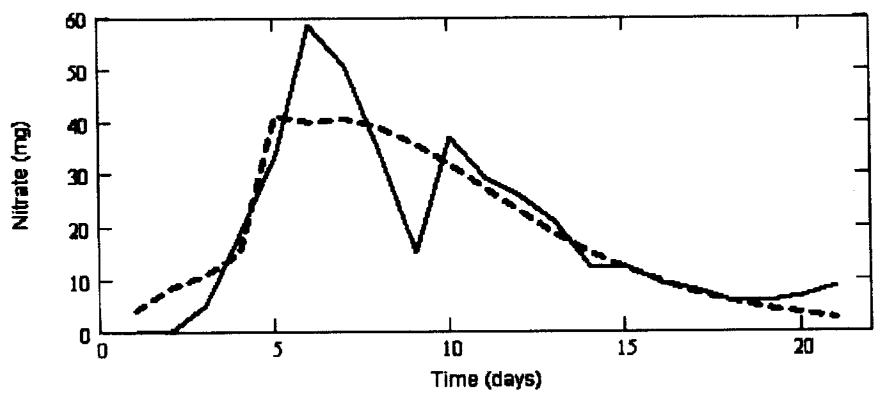

Figure 5. Application of the PSTM to leached nitrate with time. The solid line is actual data and the dashed line is modeled leached mass.

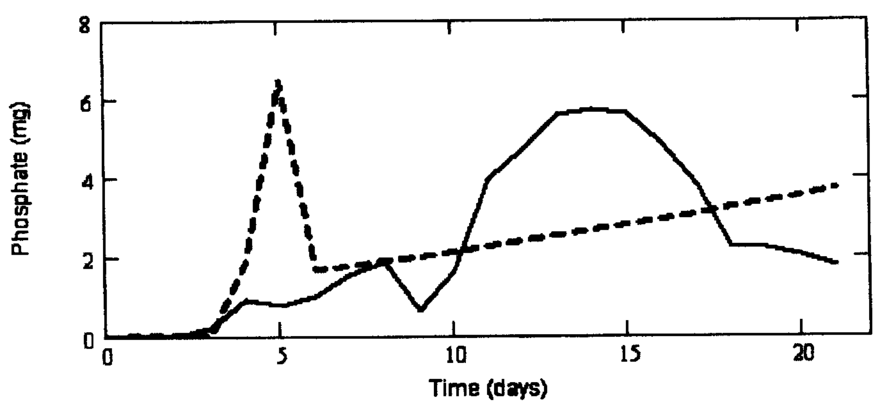

Figure 6. Application of the PSTM to leached phosphate with time. The solid line is actual data and the dashed line is modeled leached mass.

The *HI* is given by (Stagnitti, Li et al, 1999):

$$HI(\alpha,\zeta) = \sqrt{3}\frac{\sigma}{\mu} = \left[\frac{3\zeta}{\alpha(\alpha+\zeta+1)}\right]^{\frac{1}{2}} \tag{1}$$

where ζ and α are fitted parameters to the beta statistical distribution. It is easy to calculate index values using Equation (1) for multiple sample percolation experiments. When $HI = 1$, then uniform flow is exhibited, that is each region of the soil is contributing exactly the same amount of solute or water than any other region. When $HI > 1$, this indicates preferential flow. Examples of the application of this index have been discussed in Stagnitti, Li et al, (1999) and de Rooij and Stagnitti, (2000). The index has proven to be a very versatile tool in solute transport theory.

The concept of heterogeneous leaching modeled with a beta probability distribution, led de Rooij and Stagnitti (2000) to define the concept of a Spatial Solute Distribution Curve (SSDC). This curve predicts the amount of solute mass or volume of leachate from a certain proportion of the soil. Thus the SSDC is a complementary tool to the classical tool of solute transport theorists, the temporal solute breakthrough curve (BTC). More recently, de Rooij and Stagnitti (2002) proposed a unifying theory of spatiotemporal solute transport by combining both the classical concept of a BTC with the SSDC into a single description, a bivariate probability distribution. Using this approach, not only can the temporal breakthrough of a solute or contaminant with any depth in soil be predicted at any time but also what proportion of this concentration results from what proportion of the contributing spatial area. This indeed is a significant advance in solute transport theory.

In conclusion, preferential flow may be found in all types of soils and all types of landuse. It has the property of accelerating the passage of solutes, nutrients, contaminants and microbes through soils. Current predictive models of solute transport do not explicitly consider preferential flow but model solute transport with an "average" or bulk flow path. This may lead to significant underestimation of solute leaching and increased risk of groundwater contamination. New models that explicitly incorporate preferential flow greatly aid interpretation of solute transport studies and improve prediction of solute and water flux. Application of these models will lead to improved management practices resulting in less contamination and need for remediation.

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