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ing methods that rely upon knowledge of the internal structure of the software. Such testing is inappropriate for compilers since compiler writers usually wish to keep the internal details of their programs secret for commercial reasons.

Conventional testing exercises a program to demonstrate satisfactory behavior, and is first done by the programmer as a check on the coding. Unfortunately, such a method relies upon the ability of the programmer and the depth of understanding of the specification, and hence is rarely adequate in itself.

Current research in this area is along two lines: the construction of sophisticated tools to analyze software to locate defects; and the production of proof systems to enable the construction of mathematically based proofs of correctness. The analysis tool method has the advantage of being able to take existing program text for analysis, and it can often reveal defects without additional cost to the developer (apart from removing the defects). Unfortunately, substantial defects can remain in software which no tool can detect, such as a misunderstanding of the specification. Hence, while analysis tools are important, they have too many limitations to be the sole method of program validation.

Program proof systems have been available to the research community for several years, but few have been used to a significant extent in the industry. These systems are hard to use, most are only capable of handling unrealistically simple programs, and only a few are of the quality needed for commercial exploitation. There is also a fundamental limitation. For sound practical reasons, proof systems use the high-level language program for analysis, implying that the actual program depends upon the compiler (and linker, and so forth) to function correctly. It follows that exercising the final program is an essential part of validation, because limitations in compiler validation services and proof systems make it inappropriate to rely upon them for critical software validation. This requirement is disappointing in that program correctness is a static property which tools should be able to determine. Although there are limitations arising from the theory of computable functions on determining correctness, few of these limitations apply to the programs that are of major industrial concern.

Formalized testing services. An international scheme exists for the accreditation of test laboratories for objective testing. For instance, during major construction works involving concrete, test cubes are made and sent to accredited laboratories to ensure that the concrete is of the correct strength. In the United Kingdom, this scheme is run by the National Physical Laboratory and seems an ideal mechanism for giving a formal status to testing. The COBOL compiler validation service of the National Computing Centre is the only software service that has been accredited so far. While there is little doubt that other compiler validation services are suitable for accreditation, the question arises as to whether further testing services could be formalized and hence be suitable for recognition. The problem is that the software industry is relatively young, and hence formalized methods have not yet been developed. A possible scheme for testing could be unit testing. For instance, if unit testing could demonstrate that all the statements in a program had been executed with apparently acceptable results, then this method could be developed as a formal testing service. Work along these lines is continuing but has not yet been successful in terms of industrial acceptance.

For background information SEE DIGITAL COMPUTER PROGRAMMING; PROGRAMMING LANGUAGES; SOFTWARE ENGINEERING in the McGraw-Hill Encyclopedia of Science and Technology.

B. A. Wichmann

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Soil

Recent research in soil science has resulted in improved models for understanding soil water movement on the field scale and solute transport in soil and aquifer systems.

Water movement. Much effort is presently being spent in refining mathematical tools to describe water movement in soils. While it is recognized that soil column experiments are invaluable for understanding single processes, eventually it becomes necessary to study soil water movement at the field scale. In this type of research, complicating factors such as soil variability must be taken into account.

Fingering and border irrigation represent subjects in which significant progress has been achieved in elucidating the movement of water in soils. This type of research requires studies both in the laboratory and on the field scale. Mathematics, particularly the use of numerical techniques, plays an important role.

Fingering. In a soil that is saturated with water, a few macropores can carry water and solutes rapidly into the soil. A homogeneous soil may also develop preferred paths, or fingers, as illustrated in Fig. 1, which shows the first experimental evidence of such paths. Two fingers appear in a coarse sand layer below a fine sand layer. The movement in the coarse layer is much faster than in the fine, thus providing a mechanism for the rapid pollution of deep aquifers.

A useful stratagem for understanding why fingers form is to imagine a sponge saturated with water having a few drops hanging underneath it. If the sponge is situated just above a layer of coarse sand, the drops will be absorbed by the sand; since water is being replenished from above, fingers are formed. The phenomenon seems deceptively simple; however, several attempts at numerical simulation have failed, even though the phenomenon has been confirmed in both the laboratory and the field. Recently, critical experiments have clarified the picture.

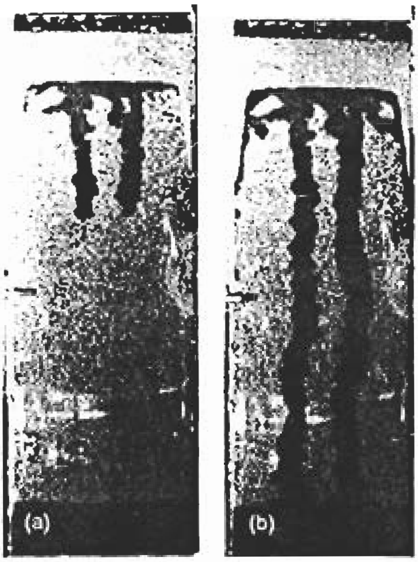

Fig. 1. Experimental evidence of fingering. (a) After 10 min, two fingers have started below the fine layer. (b) Fingers have reached bottom after 20 min. (*From P. E. Hill and J.-Y. Parlange, Water front instability in layered soils, Soil Sci. Soc. Amer. Proc., 36:697–702, 1972*)

It has been determined that if the coarse sand is uniformly prewetted, fingers tend to disappear; however, the succession of wetting and drying cycles as they occur in the field preserves fingering. If the fingers have existed for several days, lateral diffusion of water causes their widening until the column appears uniformly wet. However, adding dye to the incoming water shows that water movement downward is still confined to the original narrow fingers. If the column is left to drain for 24 h, rewetting from the top reproduces the same fingers. Thus, appearance of uniform wetness does not preclude the existence of fingers. This paradox is resolved by noting that lateral diffusion drains water from the fingers and wets the sand around until the water pressure is uniform. However, drainage and wetting occur along different paths in the pore space. This hysteresis leads to nonuniform water distributions which maintain preferential paths for water. This process is one that may affect water movement in the field. Others being studied include air effect, soil swelling, macropores, soil sealing due to raindrop impact, and erosion.

Developing a model that will incorporate all processes and describe surface and subsurface flow in a watershed, its interaction with groundwater, and the final outflow is a formidable task. Thus, hydrologists often resort to empirical models.

Border irrigation. Consideration of a field-scale irrigation problem illuminates the role of mathematics in developing a hydrographic model. In one such problem, water enters a field along a border at a given rate Q (Fig. 2). A water layer of depth y spreads on the surface and reaches a distance s at time t. Water also seeps into the soil, and I is the amount infiltrated at position x and time t. C_0 is the average water layer thickness.

To describe the flow, three nonlinear coupled partial differential equations must be solved: two (Saint-Venant's) equations express conservation of mass and momentum above the soil, and one (Richards') equation expresses conservation of mass below the surface. Accurate numerical solutions became available only in 1987. In this type of study, the accuracy of each element in the numerical procedure must be checked carefully. Thus, it is necessary to assume certain particular properties and conditions such that a simple solution of known accuracy also exists. Then by comparison with the results of the general numerical procedure for this particular case, the solution can be assessed.

These simple solutions are often called analytic, to distinguish them from numerical solutions. Such distinctions can be artificial; that is, all numerical solutions require some analysis, and most analytical solutions require some numerical input. Thus, the terms numerical and analytical are actually only relative. When two solutions to the same problem exist, one could be called numerical and the other analytical, if the first requires more numerical calculations than the second, because the problem was simplified by analysis in the second case. In addition, many new analytical techniques have been introduced and are being investigated, including similarity variables, first integrals, transformations, double integration, and linearization.

Once the complex numerical procedure for border irrigation has been validated, its very complexity will prevent its application for management purposes. It then becomes imperative to seek approximations to reduce the numerical calculations to a practical level. The numerical solution then becomes a crucial tool in assessing the accuracy and validity of the approximations.

The most promising approximation replacing the Saint-Venant's equation is the Lewis and Milne equation, which generally states that the amount of water entering the field is equal to the amount of water stored above and below the surface (Fig. 2). The amount of water stored above the soil surface is calculated by assuming that the water layer has a constant thickness C_0 (Fig. 2). The amount of water stored below the surface (I; Fig. 2) must still be obtained by numerical integration of Richards' equation. By comparison with the full numerical solution, it is

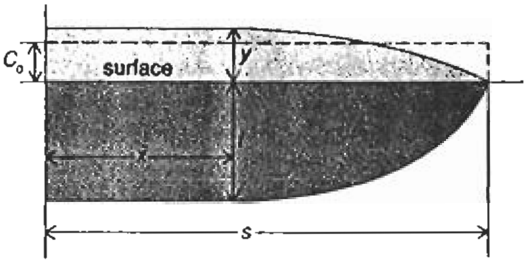

Fig. 2. Distribution of water that has entered a field. The water enters at the left, which is the left border of the field, and spreads to the right to a distance s on the soil surface while seeping down below the surface. The shaded area represents the area over which the water has spread.

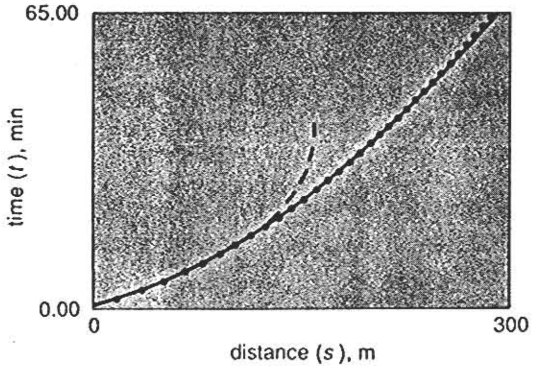

Fig. 3. Distance traveled on the soil surface by water as a function of time. The solid line represents the full numerical solution; the broken line is the series solution; and the data points show the improvement attained for the time series solution when Pade approximants are used.

found that this approximation can be used with confidence for all practical conditions encountered in the field.

The numerical calculations can be reduced even further, for example, to predict the distance as a function of time by using Pade approximants (a mathematical time series procedure designed to help convergence) in a method that consists of solving both the Lewis and Milne equation and the Richards' equation by time series. The series is then summed again by using Pade approximants to improve the convergence of the series. Comparison with the full numerical solution shows that this last approximation is valid with some limitations. In particular, it breaks down if irrigation lasts many hours. **Figure 3** illustrates the results for conditions obtained at an experimental farm. The full numerical solution shows that the time series solution breaks down after 20 min, whereas Pade approximants extend its validity for more than 1 h.

The simpler a result, the more readily it can be used to measure soil properties. For instance, measuring the distance s as a function of time t yields the conductivity (permeability) readily when Pade approximants are valid. One advantage of the method is that conductivity is obtained as an average over the whole field, essentially bypassing the complications of soil variability.

J.-Y. Parlange; R. Glass

Solute transport. The transport of surface-applied or soil-incorporated chemicals in soil and aquifer systems has been of interest to soil scientists and hydrologists for many years. Modern agriculture now uses large quantities of fertilizers and pesticides which are beneficial only in the upper part of the soil profile. Translocation of these chemicals from the root zone to deeper layers not only makes them unavailable for plant growth but also poses a threat to the quality of groundwater. The intentional or accidental release of organic and inorganic chemicals from municipal and industrial waste disposal sites and their subsequent movement into and through the vadose (water-unsaturated) zone presents similar hazards to the environment.

The need to understand and manage the behavior of chemicals in soils has stimulated the development of various models of solute transport. Unfortunately, chemical transport in the vadose zone is complicated by a vast array of space- and time-dependent physical, chemical, and biological processes. They include convective mass transport, diffusion, dispersion, sorption or exchange onto the solid phase, solute precipitation–dissolution, nuclear or microbial decay, volatilization, and multiphase flow. Because of the complexities involved, most or all solute transport models must be considered simplifications of actual processes. Still, these models are extremely valuable tools in both research and management. Most transport models currently used for predicting solute transport in soils are expressed mathematically in terms of convection and dispersion processes.

Convection and dispersion. Solute transport in soils occurs by convective mass transport, diffusion, and dispersion. Convection (or advection) refers to the passive movement of a dissolved tracer with flowing soil water. In the absence of diffusion and dispersion, water and the tracer move at the same average velocity. The convective solute mass flux J_m per unit cross-sectional area perpendicular to the transport direction is given by Eq. (1), where c is the solute concentration

$$J_m = qc = \theta v c \qquad (1)$$

and q is the fluid flux density given by Darcy's law. Because transport occurs only in the liquid phase, the average pore-water velocity v of a solute in soil is higher than q by a factor equal to the inverse of the volumetric water content θ, that is, $v = q/\theta$. Solute transport also occurs by diffusion and dispersion. Diffusion is a spontaneous process that results from the natural thermal motion of dissolved ions and molecules. Diffusive transport in soils tends to decrease existing concentration gradients and is described by Fick's first law. Solute dispersion during transport results from the fact that local fluid velocities inside individual soil pores and between pores of different shapes, sizes, and directions deviate from the average pore-water velocity. These variations lead to a mixing process that is macroscopically similar to mixing caused by diffusion. Because of this similarity, diffusion and mechanical dispersion are generally considered additive and characterized by one overall macroscopic dispersion coefficient D.

The effects of convection and dispersion are best illustrated by means of a hypothetical laboratory experiment in which water and a dissolved tracer are applied to an initially tracer-free, uniformly packed soil column of length L (**Fig. 4**). The column is subjected to steady-state water flow under either water-saturated or unsaturated conditions by properly regulating soil water pressures at the column inlet (influent) and exit (effluent) locations. As more of the tracer solution is added, the initially very sharp concentration front near the soil surface becomes more and more spread out (Fig. 4*b*) because of the combined effects of con-

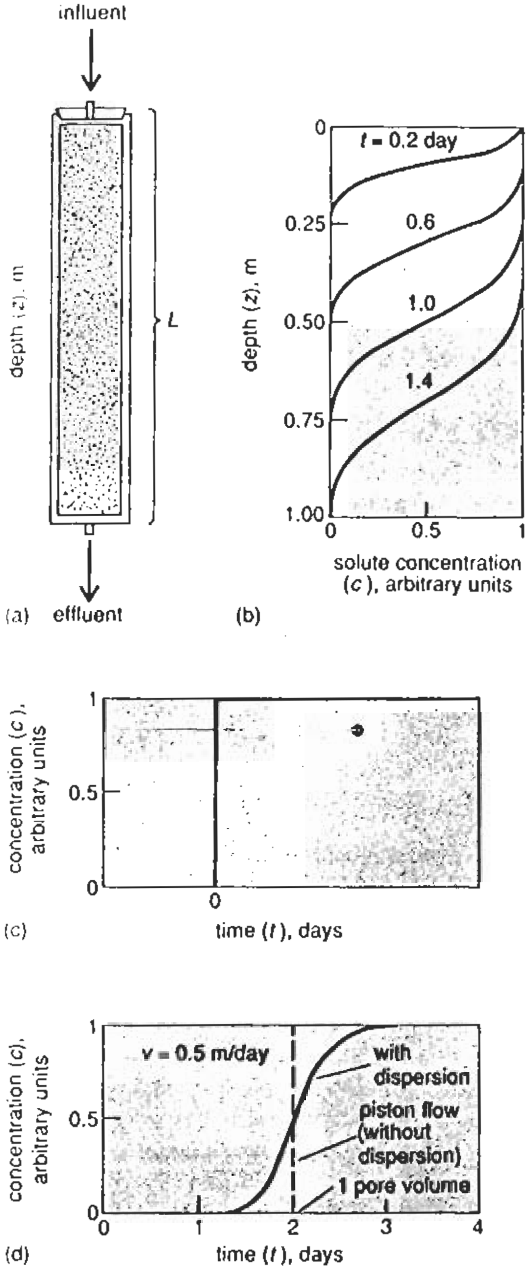

Fig. 4. Hypothetical laboratory tracer experiment. (a) Column of soil. (b) Concentration distributions inside the column. (c) Influent curve. (d) Column breakthrough curves with and without dispersion.

vection and dispersion. Eventually a smooth sigmoidal effluent curve is measured at the column exit as shown in Fig. 4*d*. In the absence of dispersion and assuming a perfectly inert tracer (no interactions with the solid phase), the solute front will travel as a square wave through the column (often termed piston flow) to reach the bottom of the column at time t as shown in Eq. (2). This occurs after exactly one pore

$$t = L/v \tag{2}$$

volume of tracer solution has been collected at the column exit. Pore volume refers to the amount of water leached through a column divided by the amount of water stored in that column. In reality, the arriving front will never be of the square type, but will be smeared out as a function of diffusion and dispersion (Fig. 4*d*).

Sorption. Solute transport is also affected by possible interactions of a chemical with the solid phase of the soil. Most chemicals interact with the solid phase through a variety of sorption or ion-exchange processes, so that the chemical moves slower than water and appears later in the effluent than is the case with an inert tracer. One major challenge for accurately predicting solute transport is the quantification of sorption as a function of the concentration. At very low concentrations, sorption s onto the solid phase by many organic and inorganic chemicals is directly proportional to the solution concentration c as shown in Eq. (3), where K_d is an empirical distribution coeffi-

$$s = K_d c \tag{3}$$

cient. In some cases, K_d may become negative, indicating that only a fraction of the liquid phase participates in the transport process. This occurs when the chemical is subject to anion exclusion. Anion exclusion results from the repulsion of anions from negatively charged surfaces of clays and ionizable organic matter. It causes anions to stay away from particle surfaces and to concentrate in the center of a pore (**Fig. 5**). Because local water-flow velocities are zero at pore walls and maximum in the center of pores, anions such as chloride on the average travel faster than water. For the same reasons, cations concentrate on or close to negatively charged soil particle surfaces, resulting in positive K_d values and lower effective transport rates in soils.

Nonequilibrium transport. Predictive models of solute transport often assume that the sorbed concentration is

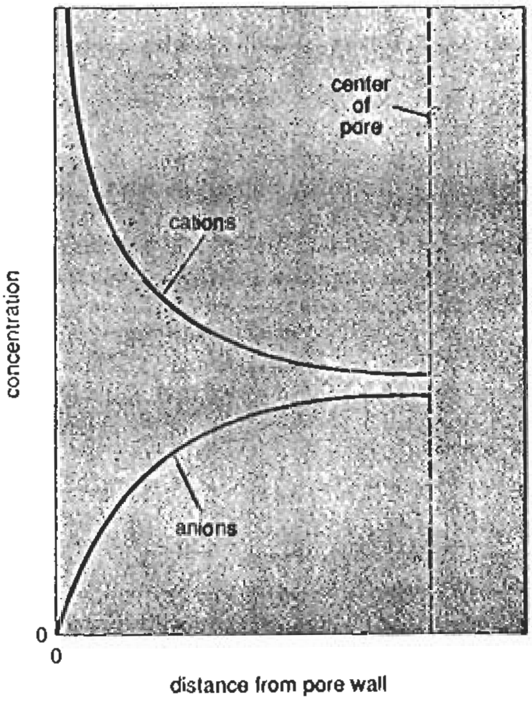

Fig. 5. Anion and cation distributions in a soil pore with negatively charged pore walls.

always in equilibrium with the solution concentration. This approximation is not always true for the high water-flow rates that normally occur in soils. A variety of chemical-kinetic and diffusion-controlled rate laws have been proposed to describe nonequilibrium processes in soils. The most popular and simplest nonequilibrium model assumes first-order linear kinetics. Although this and related rate models have led to some improvements in predictive capability, success has generally been limited to relatively low flow velocities. A more refined chemical nonequilibrium model that did lead to improved predictions is the two-site model where sorption is thought to consist of two components, one governed by equilibrium sorption and one by first-order kinetics. Two-site nonequilibrium sorption is frequently observed during transport of various organics and trace elements in soils.

Apparent nonequilibrium may also occur when the sorption rate is limited by the rate at which solutes diffuse to reaction sites. This diffusion-controlled concept has resulted in so-called physical nonequilibrium models that partition soil water in mobile (flowing) and immobile (stagnant or nonmoving) phases. The approach assumes that the pore-water velocity is bimodal: convective and dispersive transport is confined to only a fraction of the liquid-filled pores, while the remainder of the pores have stagnant water. This stagnant water has been visualized as thin liquid films around soil particles, dead-end pore water, nonmoving water inside aggregates, or relatively inaccessible regions associated with unsaturated flow.

Physical nonequilibrium is especially prevalent in structured soils and fractured aquifer systems. Water and dissolved tracers in structured soils may move rapidly through the larger (interaggregate) macropores between aggregates or peds, while the transfer of solutes inside smaller (intraaggregate) micropores is largely dominated by the much slower process of diffusion (**Fig. 6**). Such conditions can lead to preferential flow of surface-applied chemicals through a soil profile; that is, chemicals bypass much of the soil matrix and thus reach the groundwater table much earlier than is predicted with equilibrium models. Cracked clay and peat soils are especially vulnerable to preferential flow, particularly during, but not limited to, water-saturated conditions; decayed root channels and earthworm holes also contribute to this accelerated transport. Preferential flow also affects the efficiency of reclaiming salt-affected or otherwise contaminated soils by leaching with rain or irrigation water.

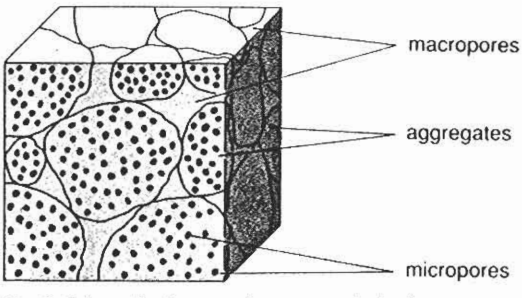

Fig. 6. Schematic diagram of an aggregated soil.

Field-scale transport. In addition to heterogeneities associated with soil structure and aggregation, field-scale chemical transport is also complicated by heterogeneities resulting from the natural spatial and temporal variability of processes and properties in undisturbed soil profiles. Soils usually exhibit a complex array of heterogeneities, ranging from relatively well-defined macroscopic soil horizons to numerous unconsolidated microscopic soil lenses having essentially unknown geometry and revealing highly variable chemical and physical properties. Because of this variability, recent research has focused on field-scale transport as a stochastic rather than a deterministic process. For example, field experiments suggest that flux-related parameters, such as pore-water velocity, usually have a lognormal distribution over a field, while capacity-type variables, such as water content, are often normally distributed. These observations have resulted in a variety of stochastic or geostatistical descriptions of field-scale solute transport.

For background information *see* *Diffusion in gases and liquids*; *Numerical analysis*; *Soil*; *Transport processes* in the McGraw-Hill Encyclopedia of Science and Technology.

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Soil chemistry

Recent advances in soil chemistry have cast a new light on the kinetics and mechanisms of soil chemical processes and have expanded understanding of the patterns of mineral crystal growth in soils.

Kinetics and mechanisms. The study of the kinetics of soil chemical processes is one of the most important research areas in soil chemistry. It is also one of the most difficult because of the complex heterogeneity of soils. However, ongoing research in kinetics will prove valuable in ascertaining mechanisms and in modeling soil chemical reactions.

Much of the soil chemistry research over the past 155 years, since the elegant work of J. Thomas Way, considered the founder of the science of soil chemistry, has dealt with equilibrium processes. While this research has proved enlightening, it has not increased understanding of rate phenomena in soils. In addition,