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Hopmans, J. W., and M. Th. van Genuchten. 2005. Vadose Zone: Hydrological Processes. In: D. Hillel (ed.), *Encyclopedia of Soils in the Environment*, pp. 209-216, Elsevier Ltd., Oxford, United Kingdom.

## VADOSE ZONE

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### Hydrologic Processes

**J W Hopmans**, University of California–Davis,  
Davis, CA, USA

**M Th van Genuchten**, US Salinity Laboratory,  
Riverside, CA, USA

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### Introduction

The distinction between groundwater and the unsaturated zone is usually made within a hydrologic context that views water as the agent of change of the subsurface and the main driver for transport of chemicals between the atmosphere and groundwater. This region between the soil surface and groundwater table known as the vadose zone, involves a complex array of time-dependent, nonlinear physical, chemical, and biological processes, including interactions with groundwater and the atmosphere. The soil is the uppermost part of the vadose zone, subject to fluctuations in water and chemical content by infiltration and leaching, water uptake by plant roots, and evaporation from the soil surface. It is the most dynamic part of the subsurface, as changes occur at increasingly smaller time and spatial scales when moving from the groundwater toward the soil surface. Soil depth is usually controlled by the maximum rooting depth of plants (generally within a few meters of the soil surface). By contrast, the vadose zone may extend much deeper than the surficial soil layer and includes unsaturated rock formations and alluvial materials to depths of 100 m or more.

In the last few decades of the twentieth century, research interests in the deeper vadose zone have increased dramatically, instigated by a need to sustain quality of groundwater and maintain adequate

resources for drinking water and ecologic purposes. Unquestionably, our society has negatively impacted the quantity and quality of its soil, water, and air resources. Chemical pollution generated by past agricultural, industrial, and municipal activities has contaminated soil and groundwater and surface-water systems worldwide. Unfortunately it continues to do so up to the present. Scientists and others are now increasingly aware that soil is a critically important component of the Earth's biosphere, not only because of its food-production function, but also as a safe-keeper of local, regional, and global environmental quality. For example, management strategies in the vadose zone will offer the best opportunities for preventing or limiting pollution, and for remediation of ongoing pollution problems. Because chemical residence times in groundwater aquifers can range from a few years to thousands of years, their pollution is often essentially irreversible. Prevention or remediation of soil and groundwater contamination starts, therefore, with proper management of the vadose zone. Understanding the intricate processes in the vadose zone is a challenge because of the many complex nonlinear physical, chemical, and biological interactions that simultaneously control the transfer of heat, mass, and momentum between the atmosphere and the groundwater table.

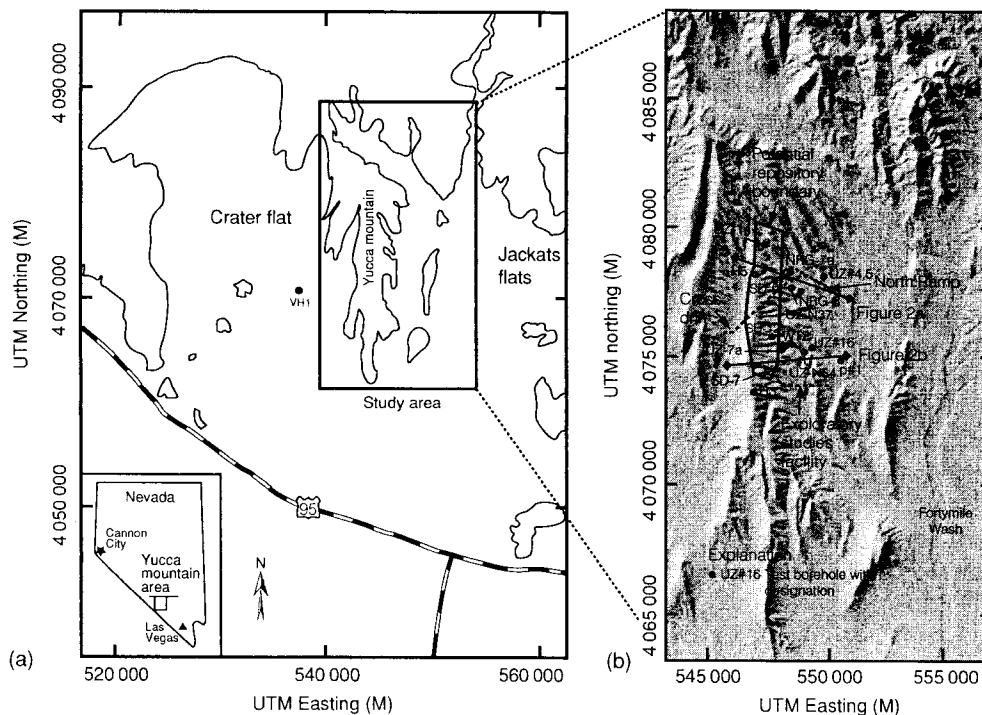
### Physical Processes

The physical characteristics of the vadose zone control such processes as natural or artificial recharge to deep groundwater and surface water-groundwater interactions. When considering the water budget of the vadose zone as a whole, many terms are similar and equally as important as those of a soil-water budget, with differences in measurement techniques mostly

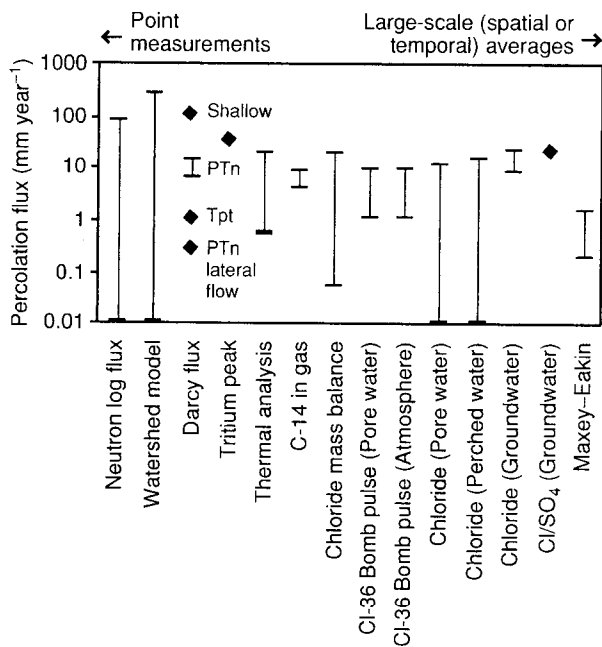
predicated by differences in the spatial scale. Whereas typical soil-infiltration measurements are conducted over areas smaller than  $1 \text{ m}^2$ , estimates of infiltration rates over much larger areas and depths are required in the vadose zone, for which the assumption of one-dimensional flow is generally inadequate. Whereas the soil-water budget requires quantification of drainage, i.e., flow of water beneath the rooting zone (See **Drainage, Surface and Subsurface**), the water budget of the vadose zone includes net infiltration (See **Infiltration**), percolation, and recharge rates at large depths. 'Net infiltration' is generally defined as the water flux below the root zone that is not further influenced by evaporation or plant transpiration. 'Percolation rate' is defined as the net infiltration rate at any depth within the vadose zone, whereas 'recharge rate' defines the water flux into the groundwater across the groundwater table. Depth variations in percolation rates are caused by lateral flow and temporal variations in precipitation and evapotranspiration (See **Evapotranspiration**), whereas estimated rates are affected by measurement type. Specific vadose zone methods to estimate percolation and recharge rates include physically based methods that assume darcian water flow (See **Darcy's Law**) throughout the vadose zone, and tracer methods. The darcian methods generally require dedicated and highly specialized instrumentation for large-depth

measurements, but neglect fractured flow. Environmental tracer methods estimate percolation rate or age of water at a given depth based on *in situ* concentrations of natural tracers such as tritium, chloride, chlorine-36, and nonradioactive isotopes such as deuterium and oxygen-18, assuming that these are mass-conservative.

Accurate estimation of vadose zone water and solute fluxes is especially challenging in arid climates, where they are orders-of-magnitude smaller than in humid agricultural settings. However, because of these small flow rates, the relevant time scales of recharge rate can be orders-of-magnitude larger. A variety of methods have been reviewed, including detailed numerical modeling, to estimate percolation and recharge rates at Yucca Mountain, Nevada. The different methods were compared to study the potential and performance of Yucca Mountain as a repository site for high-level radioactive waste over time scales of 1000 years and longer (Figure 1). The mean water table depth is approximately 500 m, whereas the potential repository location is at a mean depth of 300 m below the land surface, within a densely welded and fractured tuff horizon. In February 2002, President George W. Bush endorsed a formal recommendation by the Department of Energy (DOE) for the Yucca Mountain to accept a total of approximately 85 000 metric tons of radioactive wastes.



**Figure 1** Location of (a) the Yucca Mountain area, Nevada, and (b) the study area. (Reproduced with permission from Flint AL, Flint LE, Kwicklis EM, Faryka-Martin JT, and Bodvatsson GS (2002) Estimating recharge at Yucca Mountain, Nevada, USA: comparison of methods. *Hydrogeology Journal* 10: 180–204.)



**Figure 2** Comparison of percolation fluxes estimated by various methods. Bars represent ranges of estimates; points represent single estimates. PTn and Tpt indicate different hydrogeologic units of the Yucca Mountain site. (Reproduced with permission from Flint AL, Flint LE, Kwicklis EM, Faryka-Martin JT, and Bodvarsson GS (2002) Estimating recharge at Yucca Mountain, Nevada, USA: comparison of methods. *Hydrogeology Journal* 10: 180–204.)

Estimated percolation rates at Yucca Mountain vary between 0.5 and 20 mm year<sup>-1</sup> (Figure 2), with differences in magnitudes controlled by variable precipitation, topography, soil depth, and highly variable, physical vadose zone properties, including fractures and faults. The different methods each yield percolation values typical of their specific space and time scales, with results complementing and partially overlapping each other. For example, shallow methods are representative for relatively small time scales, whereas rates estimated from the deep vadose zone and recharge measurement techniques are an integration of spatial mixing over much longer time scales.

## Chemical Processes

The justification of vadose zone characterization and monitoring of contaminant transport arises from the simple observation that, for contaminants and microorganisms to reach the groundwater table, they must pass through the vadose zone first. Therefore, monitoring of the vadose zone and appropriate management practices using vadose zone concepts is a prerequisite for understanding and successfully preventing groundwater contamination. Much of the

*Handbook of Vadose Zone Characterization and Monitoring* is devoted to current and emerging techniques for vadose zone measurement and monitoring of chemical and microbial pollutants. The general theories and concepts of chemical fate and transport in the vadose zone are largely identical to those occurring in soils. Therefore, the focus here is on the added complexities to which constituents are subjected as they move through the vadose zone. Most additional complications in vadose zone transport arise because of the much wider range in relevant space and time scales and the presence of preferential flow mechanisms (fractures, sediment, and rock beddings) that make it difficult to delineate transport networks for the larger vadose zone. Moreover, the increasing physical heterogeneity (*See Spatial Variation, Soil Properties*) and associated spatially variable soil moisture conditions and preferential flow mechanisms of the vadose zone affect geochemical and microbial reactions, resulting in spatial and temporal variations of concentrations and transport of which the implications have yet to be fully understood.

As dissolved solutes move through the vadose zone, various physical, chemical, and biological properties control their fate. In addition to diffusion and dispersion, the fate and transport of chemicals in the subsurface are influenced by sorption on to the solid phase and biological transformations. Diffusion and dispersion of the transported chemical are a function of both pore size distribution and water content. Mechanical or hydrodynamic dispersion is the result of water mixing within and between pores as a result of variations in the pore-water velocity. Increasing dispersivity values causes greater spreading of chemicals, thereby often also decreasing their peak concentration. Sorbed chemicals move through the vadose zone slower than noninteracting chemicals, with the degree of sorption largely depending on mineral type, specific surface area of the solid phase, and organic matter fraction. In addition, biogeochemical processes and radioactive decay affect contaminant concentration, for example by cation exchange, mineral precipitation and dissolution (*See Precipitation–Dissolution Processes*), complexation, oxidation–reduction reactions (*See Oxidation–Reduction of Contaminants*), and microbial biodegradation and transformations. Moreover, all of these processes depend on such environmental conditions as temperature, pH, water saturation, and redox status (*See Redox Potential*), including, their spatial variations.

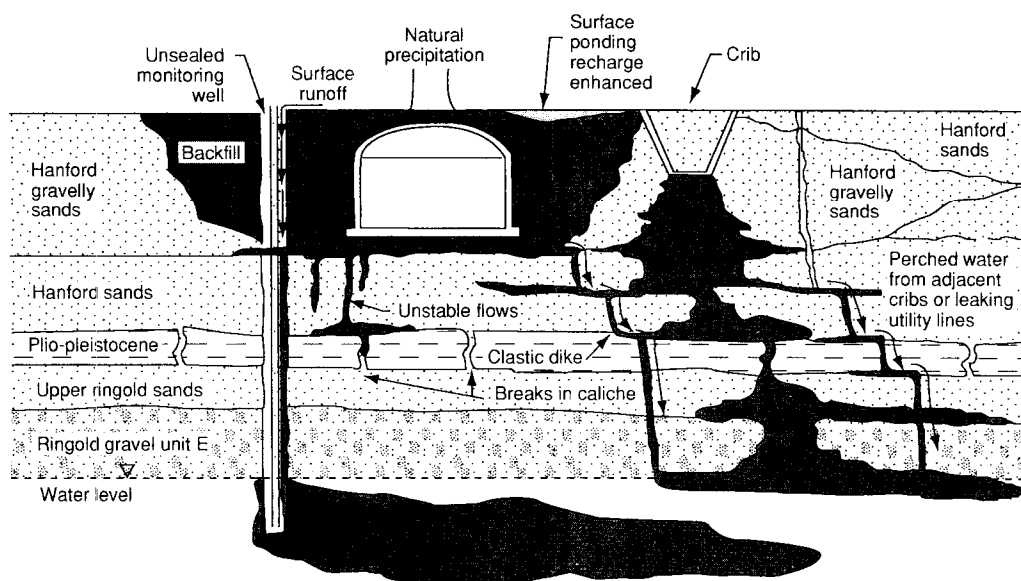
The fate and transport of microorganisms (including pathogenic bacteria, viruses, and protozoan parasites) follow many similar processes to chemical compounds. For example, many microbes exhibit

enhanced transport relative to the water solution as a result of electrostatic repulsion from negatively charged solid surfaces, as well as owing to size exclusion from smaller areas of the pore space. There is also evidence that biologically reactive solutes and bacteria preferentially adsorb to gas-liquid interfaces and may be subject to interfacial adsorption-desorption processes. In addition, transport of microorganisms is controlled by their retention (such as filtration) in the porous matrix, which is a function of the size of the specific microorganisms, the water-filled pore size distribution, and pore-water velocity as well as concentration and ionic composition of the aqueous phase. As such, microbial biomass accumulation may reduce the porosity and alter the hydraulic properties of vadose zone soils. Additionally, inorganic, organic, and microbiologically active colloids with diameters between 0.01 and 10  $\mu\text{m}$  can strongly adsorb otherwise immobile chemicals or microbes and thus facilitate their transport by acting as a mobile solid phase.

No better example of the complexities of vadose-zone transport can be illustrated than by highlighting progress made at the US DOE Hanford site in Washington State, toward measurement, characterization, modeling, and remediation of vadose zone contamination from leaking, high-level radioactive waste storage tanks. The subsurface fate of the nuclear waste is increasingly complex because of various potential preferential flow mechanisms occurring, such as fingered flow, tunnel flow, and flow associated with poorly sealed boreholes (Figure 3). Soon after World War II, the US Atomic Energy Commission built many 2.0- to 3.8-million-liter, carbon-steel

single-shell tanks at the Hanford Site to store high-level waste generated from production of plutonium and uranium. Inventory studies show that more than 4 million liters of waste leaked from these tank farms into the surrounding vadose zone. The vadose zone at Hanford consists of permeable and poorly consolidated sands and gravels that are bedded but highly discontinuous in the lateral direction. Also, the vadose zone includes many sharp contrasts in texture between layers. The regional groundwater table at depths of 60–90 m below the surface discharges to the Columbia River, which flows adjacent to the Hanford site. Gamma logging data from approximately 140 dry wells (boreholes) surrounding the tanks shows contamination to depths of at least 40 m, probably mostly caused by preferential flow. The different preferential flow processes have caused widespread contamination of  $^{137}\text{Cs}$  and other radionuclides, which otherwise would have been highly retarded. Fingered flow occurs because of density-driven flow, whereas tunnel flow is caused by zones of increased permeability around the tanks. The geologic complexities of the Hanford site, combined with man-made changes, have prevented adequate prediction of the transport of the various radioactive nuclides, even with the use of sophisticated multidimensional flow and transport models.

Whereas this example applies to point-source pollution, even more complications arise when responding to questions on nonpoint pollution of groundwater such as occurs through crop production by application of fertilizers (e.g., nitrates) and irrigation (e.g., salinity and toxic trace elements). Typically, using distributed modeling techniques, flow and transport



**Figure 3** Conceptual model of fluid blow beneath single-shell tanks at the US Department of Energy's Hanford site.

are simulated for major characteristic units within a watershed or landscape (e.g., using soil map units, vegetation type, and slope). However, the connection and integration of the resulting simulation units within the watershed beg many questions of scale and associated nonlinearity effects. These nonlinear effects may be exacerbated when including chemical processes that are highly variable in space and time because of local soil variations in soil chemical composition, saturation, aeration, pH, redox status, and other factors. There is a need for interdisciplinary and multifaceted research approaches to improve the understanding of biological effects on soil chemical reactions and processes.

### Biological Processes

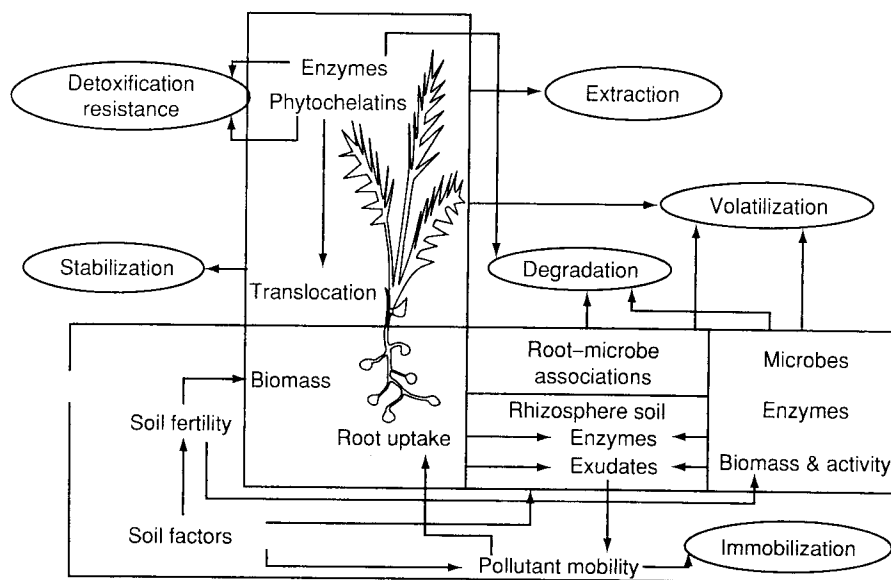
In the soil environment, bioremediation and phytoremediation can be used to reduce vadose zone and groundwater contamination, by means of biological processes sustained by selected plants or microbes. Favorable environmental conditions of plant and microbial growth in soils and the vadose zone allow for bioremediation of contamination by inorganic and organic chemicals. Microbial processes mainly transform the parent chemical, thereby reducing its concentration, and by the formation of less-toxic metabolites, whereas plants can accumulate specific chemical species, e.g., through bioaccumulation of heavy metals in plant tissues. In addition, root water uptake by plants and trees can reduce leaching (*See Leaching Processes*) of water and salts below the rooting zone, thereby controlling percolation rates and contaminant transport through the vadose zone.

Differences between the microbiology of the vadose zone and the saturated zone are mostly caused by differences in water saturation, which affects the prevailing fluid fluxes and the availability of oxygen and other nutrients. With oxygen being the oxidizing agent for aerobic microorganisms, its supply may be limited in the deep vadose zones and/or in locally saturated (parched) areas. For most other nutrients, fluxes are controlled by the degree of water saturation and associated percolation rates and by organic matter supply rates. Consequently, nutrient availability is relatively abundant in the root zone and in humid climates, while their fluxes generally are limited in the vadose zones of arid climates. Although the vadose zone is generally unsaturated, local water-saturated inclusions may occur, promoting anaerobic microbiological processes, using electron acceptors other than oxygen, such as nitrate,  $Mn^{4+}$ ,  $Fe^{3+}$ , or sulfate, depending on the redox status of the system. Irrespective of climate, the local nutrient supply in the vadose zone is at times predominantly controlled by

diffusion to or from regions where transport is mainly by preferential flow through macropores (*See Macropores and Macropore Flow, Kinematic Wave Approach*) and cracks. Whereas, in general, microbial population density and activities are low in the vadose zone below the soil-rooting zone, their densities and activities can be orders-of-magnitudes higher at contaminated sites that facilitate microbial colonization. Microbes are generally located at air-water and water-solid interfaces; however, microbial heterogeneity is generally unpredictable, as it is conditioned by local variations in nutrient availability.

Enhanced microbial degradation (*See Pollutants: Biodegradation*) is generally achieved by gaseous nutrient deliveries of electron donors and acceptors to the contaminated sites, e.g., by bioventing through injection of air to simulate aerobic biodegradation of petroleum hydrocarbons (*See Hydrocarbons*). Microbial degradation of recalcitrant organic contaminants may require a secondary carbon supply, whereas other nutrients such as N and P are sometimes required. Inorganic contaminant concentrations of heavy metals or radionuclides can be reduced by microbes through their transformation (*See Metals and Metalloids, Transformation by Microorganisms*) to less-toxic states or by changing their mobility by using them as electron acceptors. A specific form of bioremediation is phytoremediation (defined as remediation through plants), which is mostly effective in near-surface soils. Many processes may contribute to phytoremediation (**Figure 4**), including specific root uptake followed by bioaccumulation and/or volatilization, and biodegradation in the rhizosphere (*See Rhizosphere*) sustained by root exudates and organic matter of decaying roots.

Certain plants have been adapted genetically to grow in soils containing toxic levels of metals. A classic example of this is the use of specific plants for the bioaccumulation of selenium, for example crop and grassland species. Research in selenium remediation methods accelerated in the 1980s after the discovery of high concentrations of Se in agricultural drainage water, followed by high mortality rates of grazing waterfowl at Kesterson Reservoir in Merced County, California. The specific advantage of crop or grassland plant species to remediate Se-laden soils is that these can be harvested and subsequently used as a Se supplement for Se-deficient rangelands. Studies have demonstrated that grasses such as tall fescue can effectively take up Se if soils are supplemented with organic matter. Other successful examples include bioaccumulation of lead and other toxic metals, and radionuclides such as Cs, U, Cd, and Cr.



**Figure 4** Simplified overview of soil-plant-microbe processes and interactions involved in phytoremediation. (Reproduced from Wenzel WW, Adriano DC, Salt DI, and Smith R (1999) *Phytoremediation: a plant-microbe-based remediation system*. In: Adriano DC, Bollag J-M, Frankenberger WT Jr, and Sims RC (eds) *Bioremediation of Contaminated Soils*, pp. 457-508. Agronomy Series No. 37. Madison, WI: American Society of Agronomy, Inc.)

There are many questions that need to be resolved before bioremediation techniques can be applied universally to a wide range of contaminant classes. Major issues revolve around the complex interactions between microbiological, geochemical, and hydrogeologic processes, the unpredictable local distribution of microsites, and the difficulty in supplying nutrients to these spatially distributed, contaminant-transforming microorganisms (*See Spatial Patterns*). In addition, successful bioremediation is controlled by the physical (e.g., soil moisture, temperature, oxygen diffusion) and chemical (e.g., organic matter type and content, soil adsorptive properties, availability of micronutrients) soil environment.

An additional example of mostly unknown territory occurs in the mixing zone between surface and subsurface water underneath streams, known as the hyporheic zone (HZ). This region of increased biochemical activity within the upper few centimeters of stream sediment affects the type and rate of material transformation as water moves downstream, thereby significantly changing stream-water composition and the stream ecosystem, as well as groundwater chemistry. Specific examples include the influence of oxygen supply to fish eggs buried in the HZ, the influence of particulate and dissolved organic matter on microbial activity and resulting stream-water chemistry, and the function of the HZ to denitrify, thereby ameliorating high-N stream load. There is a definite need to understand better the hydrology of the HZ and the coupling of

hydrologic with biogeochemical processes, through dedicated interdisciplinary experiments and numerical modeling.

### Scale Issues

For the past few decades, soil scientists have applied soil physical data to characterize flow and transport processes in large-scale, heterogeneous vadose zones, using measurement scales that are typically much smaller. For example, prediction of soil-water dynamics at the field scale is usually derived from the measurement of soil hydraulic properties from laboratory cores, collected from a limited number of sampling sites across large spatial extents. Soil parameters obtained from these small-scale measurements are included in numerical models with a grid or element size that is many times larger, with the numerical results extrapolated to predict large-scale flow and transport behavior. Because of the typical nonlinearity of physical properties, their use across spatial scales is inherently problematic. Specifically, the averaging of processes determined from discrete, small-scale samples may not describe the true soil behavior involving larger spatial structures. Moreover, the dominant physical flow processes may vary between spatial scales. Considering that soil physical, chemical, and biological measurements are typically conducted for small measurement volumes and that the natural variability of soils is enormous, the main question asked is how

small-scale measurements can provide information about large-scale flow and transport behavior. Answers to this question may require the estimation of appropriate, effective soil parameters for use in describing the behavior of pollutant plumes at the field or landscape scales.

A conceptual solution to the problem of scale issues of vadose-zone modeling might lie in considering the controlling effect of small-scale processes on larger-scale flow behavior. Hence, vadose zone properties are nonunique and scale-dependent, resulting in effective properties that vary across spatial scales and merely serve as calibration parameters in simulation models. Therefore, their accurate prediction in heterogeneous materials can only be accomplished using scale-appropriate measurements, including those that measure at the landscape scale.

### Opportunities and Challenges

There are a number of opportunities that have come about in the past decade through experimental innovations and increasing environmental awareness. These opportunities include improved physical characterization of the vadose zone at larger spatial scales, which needs to be extended to chemical and biological measurements also.

First, it is becoming increasingly clear that there is a pressing need for subsurface observations and property-measurement techniques at spatial scales much larger than the usual laboratory or field-plot scale. The scale problem is extremely complex because of the general presence of large spatial and temporal variabilities of the soil physical, chemical, and biological properties in question. For example, at the heart of many hydrologic projects lies the need to understand better the flow and transport of water and associated chemical constituents into and through the vadose zone above an aquifer, and within a watershed. Hence, developmental work is needed on fundamental concepts and measurement technologies to establish appropriate soil parameters for use in theories or models describing the behavior of vadose zone water flow and pollutant plumes across spatial scales. In addition, appropriate measurement techniques and field experiments are needed to characterize effective field-scale and landscape-scale soil properties. In particular, we note the potential of using inverse methodologies perhaps in combination with rapidly improving invasive and noninvasive geophysical techniques, to infer *in situ* dynamic soil physical characteristics and the development of instruments that combine multiple measurements within a single device, thereby minimizing soil heterogeneity effects.

Second, although it is evident that large-scale characterization is needed, there is also increasing awareness within the scientific community that the physical, chemical, and biological processes in the vadose zone are controlled by mechanisms operating at the pore-size scale. Improved predictions of subsurface flow and transport will probably be a function of the development and application of innovative pore-scale modeling approaches (e.g., Lattice-Boltzmann, percolation, and related methods), and associated measurement techniques that operate at the microscopic level. Examples of the latter are nuclear magnetic resonance (NMR), computed tomography (CT), and spectromicroscopy.

Third, improved characterization and interpretation of subsurface processes will require increasing efforts toward an interdisciplinary partnership, integrating physical with chemical and biological processes. The soil physicist and/or vadose zone hydrologist must seek collaborations in other disciplines to ensure that different measurement types are collected and integrated to study more effectively and determine relationships between flow and transport processes at the microscale and in the laboratory, with ultimate application to the watershed scale. To achieve this goal, soil physics must be taught within the broader context of hydrology and the environmental sciences.

**See also: Darcy's Law; Drainage, Surface and Subsurface; Evapotranspiration; Hydrocarbons; Infiltration; Leaching Processes; Macropores and Macropore Flow, Kinematic Wave Approach; Metals and Metalloids, Transformation by Microorganisms; Oxidation-Reduction of Contaminants; Pollutants; Biodegradation; Precipitation-Dissolution Processes; Redox Potential; Rhizosphere; Spatial Patterns; Spatial Variation, Soil Properties**

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## Microbial Ecology

P A Holden and N Fierer, University of California–Santa Barbara, Santa Barbara, CA, USA

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### Introduction

The vadose zone consists of unsaturated porous media and rock extending from the surface soil to the groundwater table. This zone is characterized by a lack of water relative to other major Earth compartments such as the ocean, fresh water, aquatic sediments, and groundwater. Low nutrient availability, low water content, and low potential energy per unit volume of water, termed ‘water potential,’ constrain life in the deeper vadose-zone relative to the surface. However, the vadose zone harbors numerous and diverse microbes, including bacteria, fungi, protozoa, and viruses. Vadose-zone microbial ecology refers to the study of interactions between vadose-zone microbes and their environment. Generally, microbial population density, diversity, and total activity, as well as available nutrients, and moisture and temperature fluctuations, decline sharply with depth below surface soil. For example, relative to surface soil, culturable heterotrophic bacteria in the unsaturated subsurface are only one-tenth as numerous. Regardless, the integral mass of microbes along the depth profile is large, which accounts for the overall importance of vadose-zone microbes as catalysts in terrestrial nutrient-cycling, including pollutant biodegradation.

### Definition of the Vadose Zone

The vadose zone is the Earth’s terrestrial subsurface that extends from the surface to the regional groundwater table. As shown in **Figure 1**, the vadose zone includes surface soil, unsaturated subsurface materials, and a transiently inundated capillary fringe. The subsurface materials include partially weathered soils and unweathered parent material. The vadose zone may be very shallow (less than 1 m) or very deep (extending hundreds of meters or more), depending on the depth to the water table.

The vadose zone has low water content relative to the saturated zone below the water table and is therefore commonly referred to as the unsaturated zone. Above the capillary fringe, vadose-zone pore spaces are generally air-filled, with thin water films coating solid particles. Pore spaces become water-filled when rainfall percolates, followed by drainage and gradual drying. It is the relative lack of water and its