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The guest editors introduce the papers in this issue's special section on contaminants in the vadose zone. The 12 papers provide examples of novel approaches to the challenges and advances in the prediction, characterization, monitoring, and remediation of contaminants in deep vadose zone environments.

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Contaminants in Vadose Zone Environments

Contaminants in vadose zone environments pose a long-term source and threat to groundwater resources, human health, and the environment. A number of technical, regulatory, and policy challenges and opportunities are associated with contamination in vadose zone environments, particularly in remediation. In this special section, 12 papers present novel approaches to characterize, monitor, remediate, and predict the transport and fate of contaminants in vadose zone environments.

Abbreviations: LNAPL, light nonaqueous phase liquid.

Vadose zone contamination is a significant global issue for protection of groundwater resources. While much of the focus is generally on arid and semiarid regions, vadose zone contamination serves as a continued “source” of contamination for groundwater and associated receptors at nearly all environmentally contaminated sites. However, deep vadose zone contamination, is a particularly difficult challenge because it is below the zone of practicable excavation and removal (generally 12–18 m), but above the water table. Implicit in this definition is an assumption that contamination in deep vadose zone environments is isolated from direct exposure. Rather, the pathway for exposure is associated with continued downward transport of contamination to groundwater resources where it becomes accessible for exposure and risk to receptors. Therefore, while the deep vadose zone is not necessarily considered a resource requiring restoration, limiting flux from contaminated vadose zone environments is key for protection of water resources and down-gradient receptors (Dresel et al., 2011).

Limiting contaminant flux to groundwater can occur through natural and engineered remediation processes (Brusseau et al., 2010; Carroll et al., 2012). Significant natural attenuation of contamination can occur in vadose zone environments and decrease the flux to groundwater. Application of active remediation approaches (Ginn and Boulding, 2003) may be necessary to further mitigate contaminant flux to groundwater and meet groundwater remediation goals. If mass flux to groundwater is sufficiently limited to remain protective of groundwater resources and potential receptors, monitored natural attenuation (USEPA, 1999) provides a regulatory basis for leaving contamination in place. The challenge is to define acceptable risk informed end states that are protective of human health and the environment and to apply remediation strategies that account for natural attenuation and control flux to groundwater. This construct provides the opportunity to target remediation strategies for the vadose zone that mitigate persistent sources of contamination and reduce transport through the vadose zone to receptors, in contrast to meeting regulatory concentration limits at specific point locations within the vadose zone.

Flux-based remediation approaches can be broadly categorized into three methods: (i) contaminant mass reduction, (ii) biogeochemical stabilization to retard contaminant mobility, and (iii) physical stabilization to slow the movement of contaminated pore water. Although the approaches for reducing the flux of contaminants within the deep vadose zone are functionally the same as those applicable to shallow vadose zone or groundwater remediation, the complexities of access and flow dynamics present significant challenges for deep vadose zone remediation. Flux reduction methods thus require development of technologies, approaches, and strategies to demonstrate that groundwater will remain uncontaminated or that contamination will remain below levels of concern in the future. Moreover, monitoring methods for complex subsurface environments, such as deep vadose zones, are currently not well developed and are a critical component of remediation strategies, including those for flux-based methods (Bunn et al., 2012). Demonstrating compliance

with groundwater concentration limits is straightforward, but it is difficult to monitor the vadose zone and demonstrate that the flux of contaminants will decline or remain sufficiently low, such that groundwater resources are protected over the long term.

Overview of Contributions

The 12 studies in this special edition of the *Vadose Zone Journal* evolved from a topical session “Understanding Behavior and Fate of Contaminants in Vadose Zone Environments,” at the American Chemical Society Fall Meeting, 28 August to 1 September 2011 in Denver, CO. The studies present novel approaches to characterizing and monitoring, remediating, and predicting contaminant transport and fate within deep vadose zone environments.

Several of the studies (Sihota and Mayer, 2012; Zhong and Oostrom, 2012) evaluated the issue of organic contaminants in the vadose zone. Sihota and Mayer (2012) used carbon dioxide flux measurements at the land surface to delineate source zones containing petroleum hydrocarbons and estimate degradation rates. Sihota and Mayer (2012) concluded that source-zone natural attenuation through biodegradation of hydrocarbon compounds may offer a sustainable remediation approach at contaminated sites. Their approach combined measurement of CO₂ flux with isotope measurements and reactive transport modeling at a field site in Minnesota. Reactive transport modeling, constrained by field measurements, was shown to be a powerful tool to integrate information and captured the processes of degradation at the field site. In the study of Zhong and Oostrom (2012), unsaturated column experiments were used to evaluate light nonaqueous phase liquid (LNAPL) removal during infiltration of a surfactant solution. LNAPLs are commonly encountered at organic-contaminated sites. A variety of remediation technologies have been developed for NAPL contamination in the vadose zone, including surfactant-enhanced removal. Zhong and Oostrom (2012) infiltrated low-concentration surfactant in step-wise flushes, enhancing reduction of LNAPL mass and the overall duration of remediation.

Soil desiccation implemented by injection of dry nitrogen gas is being evaluated as a potentially robust vadose zone remediation process to limit contaminant transport through the vadose zone. Companion manuscripts by Oostrom et al. (2012a) and Truex et al. (2012) describe testing of this vadose zone remediation strategy at the laboratory and field scales. Oostrom et al. (2012a) evaluated the effects of porous medium heterogeneity using intermediate-scale laboratory experiments coupled with simulation. The laboratory experiments evaluated the effectiveness of soil desiccation in dual permeability systems with permeability ratios to two orders of magnitude. The laboratory experiments evaluated the effectiveness of soil desiccation in dual permeability systems with permeability ratios of two orders of magnitude and showed rapid initial drying of the high permeability zones. The simulations reproduced experimental results using an extension of

two-phase characteristic curves developed by Webb (2000). Truex et al. (2012) documented the results of a field test at a 100-m-deep vadose zone test site contaminated with technetium-99 and nitrate. The field test confirmed the results of laboratory experimentation and simulations. The lateral and vertical distribution of drying near the injection well was influenced by subsurface heterogeneity; initial rapid drying occurred in higher permeability zones and delayed drying of initially wetter, lower permeability zones.

A challenge associated with in situ remediation of vadose zone contamination is delivery of reagents to the subsurface in a manner that does not induce downward contamination mobility and distribution. Foam is one delivery method that is being investigated and several aspects are described in this issue. Zhang et al. (2012) summarized the results of experimental and modeling investigation of foam delivery of amendments to the deep vadose zone for contaminant remediation. The effective foam viscosity was determined in a set of laboratory experiments, and a mathematical expression was developed to describe the viscosity. The modified effective foam viscosity model was used to simulate the experiments and reproduced the results reasonably well. Foam viscosity was shown to be significantly higher than the viscosity of gas and water and increased with the liquid fraction in the foam, the injection rate, and sediment permeability. Results from Zhang et al. (2012) suggest that foam is capable of distributing amendments for vadose zone remediation in heterogeneous sediments.

Wu et al. (2012) addressed the challenge of monitoring the delivery of amendments into the vadose zone. Wu et al. (2012) used laboratory studies to demonstrate the ability of complex resistivity and time domain reflectometry to track foam transport and evolution and identified the potential of complex resistivity method for quantifying associated remediation-induced (bio) geochemical reactions.

In a study involving placement of materials in vadose zone wells, Oostrom et al. (2012b) presented super absorbent polymers (SAP) as a remediation technology to remove pore water and associated contaminants. A series of column and flow-cell tests, conducted in both laboratory and natural sands, were used to test the technology. The sorbent was able to continuously extract water from the porous media, with the rate decreasing over time. The study demonstrated the potential of using SAP for vadose zone remediation.

In a study related to delivery of amendments to the vadose zone, Szecsody et al. (2012) investigated an approach using ammonia gas. Szecsody et al. (2012) conducted laboratory-scale experiments to evaluate the ability to treat uranium contamination in low water content vadose zone sediments with ammonia gas. Injection of ammonia gas increased pore water pH and dissolved aluminosilicate minerals, resulting in an increase in pore water cations and anions, which then decreased over time. The ammonia gas treatment significantly decreased the amount of labile uranium

in field-contaminated sediments by incorporation into precipitates and altered the long-term mobility through formation of mineral coatings. Study results indicate that ammonia gas partitions strongly into pore water with high retardation and a sharp reaction front, and that field-scale injection would likely be well controlled and effective at decreasing downward migration of uranium contamination. Szecsody et al. (2012) also determined that the gas injection and reaction front could be monitored using electrical methods.

Three studies in this issue investigated the vadose zone as a medium for transport and as a source zone. Stauffer and Lu (2012), Lu and Kwicklis (2012), and Robinson et al. (2012a,b) investigated larger-scale radionuclide transport in the unsaturated zone associated with high-level nuclear waste disposal. Stauffer and Lu (2012) developed a new method for quantifying uncertainty in contaminant transport. The method involves Monte Carlo sampling of retention curves for unsaturated porous media characterized by van Genuchten–Mualem constitutive relationships. The method was applied to three-dimensional simulations of contaminant transport at a field site and reduced the number of simulations over traditional Latin Hypercube Sampling Monte Carlo simulations. Lu and Kwicklis (2012) applied the method to investigate high-level waste disposal in the vadose zone. Robinson et al. (2012b) summarized large-scale field tests and modeling investigation of the unsaturated zone as a barrier to radionuclide transport from a proposed high-level nuclear waste repository. Robinson et al. (2012a) demonstrated that the processes of recharge and deep percolation, water flow partitioning between fractures and rock matrix, diffusion into the matrix, sorption, and colloid filtration all affect radionuclide transport.

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