USING NONLINEAR DYNAMICS FOR ENVIRONMENTAL MANAGEMENT OF THE VADOSE ZONE AND GROUNDWATER

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1. Introduction

It has been recognized in recent years that remediation of contaminated soils and groundwater at many sites has not been as successful as expected. Conventional soil vapor extraction and pump-and-treat methods in many cases have been unable to extract the anticipated mass of contaminants. Despite an initial removal of a high mass of contaminants, the concentration of removed contaminants slowly decreases with time [1, 2], and unremoved contaminants may remain in the subsurface for decades or longer. The reason for this is that the rate of removal diminishes over time, since removal is a diffusion-controlled process restricted to the slow transfer of immobile chemicals from the soil or rock matrix into the air/water conducting pathways. Vacuum extraction also becomes ineffective when the vacuum causes the atmospheric air to enter the subsurface. One of the potential approaches to improve remediation technologies could be based on using specially engineered pulsing methods based on the methods of nonlinear dynamics and chaos. The application of this approach is consistent with recent findings showing the effectiveness of applying nonlinear-dynamics and chaotic-behavior theory to flow and transport processes in both partially saturated and saturated subsurface media.

The goals of this paper are to: (1) present the results of laboratory and field investigations demonstrating that flow and transport processes in unsaturated soils and fractured rock can be investigated by applying the methods of nonlinear dynamics and deterministic chaos, and (2) discuss the use of these methods to improve remediation technologies for contaminated soils and groundwater. Such an improvement would be welcomed in the fields of environmental management, containment, and remediation of contaminated sites.

2. Background of Nonlinear Dynamics and Chaos

Until recently, flow and transport processes in heterogeneous soils and fractured rock were assumed to be random, and were analyzed using conventional stochastic and deterministic methods (e.g., [4]). This assumption was made without considering that deterministic-chaotic processes could cause apparent randomness of experimentally observed data. Some examples of dynamic systems that display nonlinear deterministic-chaotic behavior, with aperiodic and apparently random variability, include atmospheric, geologic, geochemical, and geophysical processes, and viscous fingering in porous media. It is noteworthy that experimental and theoretical investigations have shown very similar patterns for different physical, biological, mechanical, and chemical systems. For the past 20–25 years, *chaos* has been used in the scientific literature not to define randomness, but rather to define the characteristics of chaotic dynamics generated by predominately deterministic processes. The field of chaotic dynamics, known popularly as chaos, is among the most fascinating new fields in modern science, clarifying our perception of order and pattern in nature [5].

The term *deterministic chaos* is used to describe dynamic processes with random-looking, erratic data, in which random processes are not a dominant part of the system [6]. Such systems are dissipative, nonlinear, and sensitive to small variations in initial conditions and control parameters. In a deterministic-chaotic system, new emergent structures and properties may arise. Although chaotic fluctuations could theoretically be purely deterministic, with no random quantities, real physical processes usually contain a stochastic (or noise) component.

3. Results of Laboratory and Field Experiments

Laboratory and field infiltration tests have showed that a groundwater system in heterogeneous soils and fractured rocks exhibits the properties of a nonlinear dynamic system, generating a deterministic chaotic behavior with a random component as affected by superposition, feedback, and competition of two key elements [7]:

1. *Complex geometry of preferential flow paths* (as affected by rock discontinuity and heterogeneity on all scales—from a rough fracture surface to an irregular fracture network),

2. *Nonlinear dynamic processes* such as episodic and preferential flow, funneling and divergence of flow paths, transient flow behavior, nonlinearity, film flow along fracture surfaces, intrafracture water dripping, entrapped air, fracture-matrix interaction, and pore-throat effects.

Our analysis shows that vadose zone processes meet the criteria of a nonlinear dynamic system, because unsaturated flow processes are nonlinear, sensitive to initial conditions, dissipative, generated by intrinsic properties of the system (not random external factors), and are not governed by Darcy's law at a local scale during the periods of chaotic fluctuations. The fractured-rock flow system (as a dissipative system) contains elements that continuously fluctuate, which result in nonperiodic fluctuations of pressure, flow rate, and dripping observed in laboratory and field experiments.

For deterministic-chaotic, intrafracture flow processes, the models of chaos theory can be used for accurate short-term predictions of system behavior, whereas conventional stochastic models should be used for long-term predictions. Furthermore, deterministic chaos, in conjunction with system noise and errors of measurements, create a source of irreducible uncertainty for long-term predictions. Therefore, making more precise measurements of initial and boundary conditions and system parameters cannot significantly improve the predictability of a vadose zone system.

The positive feedback between fluid transport and mineral dissolution creates a complex reaction-front geometry such as fingers [8]. The deterministic-chaotic diffusion-reaction process (for assessing reaction rate in chemical systems) replaces the old stochastic transport models [9,10]. According to the deterministic-chaotic concept, macroscopic transport coefficients, such as diffusion coefficient and reaction rate, will exhibit irregular behavior as a function of the control-system parameter [11]. The nonequilibrium and nonlinear processes, typical for self-organizing and nonlinear phenomena, are known to exist at the reaction front, resulting in fingering and branching of the reacting zone [11]. These processes result in oscillations, chaos, and waves that have been found to appear at different scales: centimeter-scale redox-front zone in siltstones, meter-to-kilometer-scale zone of uranium deposits, submeter-scale weathering fronts in manganese-rich sedimentary rock, dissolution holes in karstified limestones, etc. [11].

4. Improvement of Remediation Technologies for Contaminated Soils and Groundwater

Recent theoretical, modeling, laboratory, and small-scale field investigations have demonstrated the potential for using pulsed soil air extraction, air sparging, and groundwater pumping [1,2,3, 12,13]. Pulsed remediation of contaminated sites can be enhanced using a chaotically induced regime of liquid flow and chemical transport in unsaturated-saturated media. This regime can be stimulated by (1) periodic pulsing using acoustic stimulation, or (2) mixing liquid flow and contaminant transport.

Pulsing can be performed in the subsurface using, for example, acoustic or seismic methods. Recent investigations have showed evidence that nonlinear dynamic processes in the subsurface are induced during low-frequency acoustic [14,15] and ultrasound [16,17] applications. For example, the stress-strain relationship of soils is nonlinear and hysteretic, especially in cohesionless soils [14, 15]. The application of periodic stimulation will enhance colloidal transport together with contaminant transport [16], increase hydraulic conductivity of both unsaturated [18] and saturated [19] media, and decrease capillary forces and adsorption [19]. A successful application of a dynamic stress for stimulating enhanced DNAPL transport has been demonstrated using bench-scale experiments [20-22].

Mixing is the physical process of solute spreading into a fluid, caused by the stretching and folding of material lines and surfaces in heterogeneous media [23]. In contrast to *dilution*, mixing takes place within much shorter time scales, increasing the plume boundary area and causing higher local concentration gradients, and thus promoting effective solute dilution. Weeks and Sposito [23] showed that the mixing of a solute plume by unsteady groundwater flow, in an aquifer with a pronounced hydraulic-conductivity variation, would be most effective if chaotic path lines were induced. They also showed that this process is driven by unsteady advection, which acts to stretch and fold fluid filaments in such a manner that plume boundaries become highly irregular. Even though mixing is ubiquitous in natural and technological processes, this phenomenon is not well understood. A number of research studies over the last 10–15 years showed that pulsing and chaotic mixing enhance the production of technological processes and extraction of chemicals [24-26]. Chaotic flows can provide for efficient fluid mixing, yielding dilution effects that are effective and predictable, using methods of nonlinear dynamics [27]. The effectiveness of mixing can be controlled by evaluating the diagnostic parameters of chaos, such as stretching and folding of flow and transport parameters in the phase space. Mixing is currently used in the oil industry, municipal wastewater treatment, remediation of contaminated tanks [28], and soil gas treatment [29].

5. Conclusions

The significance of using nonlinear dynamics in earth sciences disciplines is difficult to overestimate, because we now collect a tremendous amount of data characterizing a variety of temporal and spatial subsurface processes. Nonlinear dynamics is particularly useful in discovering the system dynamics from a time series of some easily measured parameters. These parameters can then be used to assess the spatial variation of flow processes in the subsurface, which are difficult, if not impossible, to measure directly.

Nonlinear dynamic models are an important step forward from the classical statistical approaches, but they are at an early stage of development. Challenging theoretical and practical problems remain to be studied. One of these problems involves using the theory of chaotic processes of chemical diffusion and mixing in designing remediation schemes for contaminated sites. Chaotic pulsing and mixing of polluted liquid and vapor can create an accelerated pace of remediation needed for cost-effective vadose zone and groundwater management methods. This approach will be particularly beneficial for low-permeability subsurface environments and the removal of spatially isolated pools and ganglia of NAPLs and other chemicals.

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