Organic Gas Injection Delivery Behavior for Vadose Zone Remediation – 22415

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ABSTRACT

A good understanding of gas flow behavior in the unsaturated subsurface above a groundwater aquifer (i.e., vadose zone) is important for both assessing potential remediation technologies and implementation design. Vadose zone technologies that inject gas phase amendments can be useful for organic, inorganic, metal, and radionuclide contaminants, as demonstrated in applications of bioremediation, manipulation of the chemical environment, and stabilization remedies. However, generic and broadly applicable information regarding the delivery and distribution of gas amendments in the vadose zone has not been brought together in a way that would allow assessment of remedial alternatives or design of a remediation system based on amendment and porous media properties. One relevant technology is the injection of organic gas into the vadose zone for the purpose of stimulating microbial activity to degrade a contaminant and/or to change the subsurface to reducing conditions that promote contaminant precipitation or sequestration. This work used the HYDROBIOGEOCHEM code to investigate numerical scoping simulations for eight organic gases with a range of properties (Henry's law constant, solubility, density). These scoping simulations indicate that selection of a suitable organic gas is not a simple matter because the distribution and mass availability for microbial reduction is complicated by different physio-chemical properties of the potential amendments. It is the combination of partitioning, solubility, gas density, and subsurface properties that results in the mass distribution in the pore water. Additional work is needed to evaluate factors such as the impact of gas density on vertical amendment mass distribution, variations in porous media properties, and variations in the injection operational strategy. A better understanding of gas amendment delivery to the subsurface will facilitate feasibility study technology evaluations and system design for implementation to achieve successful remediation by providing broad insight on the combined effects of amendment and subsurface properties. This work may be applicable to waste sites at the U.S. Department of Energy (DOE) Hanford Site in southeast Washington state and other DOE sites, where past practices resulted in vadose zone contaminants such as uranium, nitrate, technetium-99, and hexavalent chromium.

INTRODUCTION

Vadose zone contamination (i.e., in the unsaturated subsurface above a groundwater aquifer) is important to many waste site remediation efforts because the vadose zone is often the site of the initial pollutant release via a surface spill, tank leak, or routine historical disposal practices. The vadose zone is also key to contaminant migration in the subsurface, with the potential to impact exposure at the ground surface (vapor intrusion) and to sustain groundwater contaminant plumes. Contaminant migration depends on the controlling physical, chemical, and biological processes, which are themselves dependent on contaminant and porous media properties. Understanding the governing processes in the context of site-specific conditions allows development and implementation of strategies and technologies for controlling vadose zone contamination.

The importance of understanding vadose zone contamination has been recognized in DOE collaborative efforts. Work was previously completed to summarize the state-of-science and to establish a roadmap for vadose zone science, with a focus on reducing uncertainty in support of sound decision-making [1, 2]. Recent strategic planning work has identified five vital scientific and technical objectives for controlling contaminants in the vadose zone: (1) predicting how contaminants are held up and released over time in the vadose zone, (2) understanding vadose zone soil moisture, (3) adequately representing boundary conditions, (4) *accounting for vadose zone gas behavior/movement for gas-phase treatment technologies*, and (5) encouraging field-scale testbeds for integrated studies.

A good understanding of gas flow behavior in the vadose zone is important for assessing potential remediation technologies, implementation design, and monitoring approaches. Vadose zone technologies that inject gas phase amendments can be useful for a variety of organic, inorganic, metal, and radionuclide contaminants through bioremediation, manipulation of the chemical environment, and stabilization remedies [3, 4]. However, generic and broadly applicable information regarding the delivery and distribution of gas amendments in the vadose zone has not been brought together in a way that would allow assessment of remedial alternatives or design of a remediation system based on amendment and porous media properties.

In situ bioremediation is being investigated for treatment of contamination in the vadose zone at the U.S. Department of Energy (DOE) Hanford Site in southeastern Washington State. The intent is to inject an organic gas (for example, pentane or propane) into the subsurface to stimulate microbial activity and produce a bioreduced zone for remediation of nitrate, cyanide, and chromate. Knowledge about microbial growth, nutrient requirements, and processes that create a reducing environment to indirectly reduce contaminants is key to the design and implementation of such a remedy. However, a challenge for field-scale implementation is delivery of sufficient mass of the gas amendment to achieve good treatment effectiveness. Because the biological reduction activity occurs in the soil moisture, the delivery approach requires adequate partitioning into the aqueous phase. Another challenge is monitoring the distribution of the organic gas and development of the reducing environment that drives the remedy approach.

This work describes a set of numerical scoping simulations to investigate delivery of organic gases to the vadose zone for bioreductive remediation.

OBJECTIVES AND APPROACH

The objective of this work was to conduct numerical simulations of organic gas injections and vapor transport in the vadose zone as a scoping investigation for understanding the effects of physio-chemical properties on the distribution of amendment mass. The intent was to improve understanding of organic gas delivery in the subsurface, to better implement the technology at the field scale.

The remediation technology concept of interest in this work involves (1) injection of an organic compound (amendment) in the gaseous phase into the vadose zone; (2) subsequent partitioning of the organic compound into soil moisture (pore water), where microbes can degrade the organic compound; and (3) resultant creation of a reducing environment that can facilitate contaminant immobilization or degradation. Additional understanding of the underlying chemistry is needed for certain contaminants to determine the robustness of the remedy against the return of oxidizing conditions. This work focused on investigating the organic gas injection, vadose zone transport, and equilibrium partitioning to soil moisture.

A version of the HYDROBIOGEOCHEM finite element numerical code [5] modified for gas transport was used to simulate organic gas injections. A two-dimensional finite-element grid was constructed to represent the Hanford geological formation in the Hanford 200 West Area. The model configuration is described in TABLE I.

TABLE I. Numerical Model Configuration Information

Parameter	Symbol	Units	Value
Numerical code	—	—	HYDROBIOGEOCHEM v. 4.0 (customized)
Model type	—	—	2D Finite element (10,000 elements)
Modeled vadose zone thickness	VZT	cm	3050
Material	—	—	Hanford formation
Hydraulic conductivity	K	cm/s	0.00573
Total porosity	θ_T	—	0.3
Residual soil water content	θ_r	—	0.0175
Dry bulk density	ρ_{bulk}	g/mL	1.855
van Genuchten inverse air entry suction	α	1/cm	1
van Genuchten shape parameter	n	—	2.5

Eight organic gases were assessed in the simulations, representing candidate amendments with a range of physio-chemical properties. TABLE II lists relative metrics of the unitless Henry's law constant (indicating gas volatility in equilibrium with water), the aqueous solubility (mg/L), and the gas density (kg/m³). TABLE III lists the gases used in the numerical scoping simulations. In these scoping simulations, gas injection lasted for 48 hours with a unit normalized mass concentration.

TABLE II. Relative Property Values

Relative Value	Henry's Law Constant (—)	Aqueous Solubility (mg/L)	Gas Density (kg/m³)
Very low (VL)	< 1.0 E-3	Immiscible	< 0.5
Low (L)	1.0 E-3 to 2.0	.01 to 2.0	0.5 to 1.0
Medium (M)	2.0 to 20.0	2.0 to 500.0	1.0 to 2.0
High (H)	20.0 to 40.0	500 to 20,000	2.0 to 3.0
Very high (VH)	> 40.0	> 20,000 / miscible	> 3.0

TABLE III. Organic Gases Used in Simulations and Their Relative Properties

Organic Gas	Relative Henry's Law Constant	Relative Aqueous Solubility	Relative Gas Density
Pentane	VH	M	H
Propane	H	M	M
Ethane	H	M	M
Butane	M	M	H
1-Hexene	M	M	L
Butyl acetate	L	H	VH
Ethyl acetate	L	VH	VH
Ethanol	VL	VH	M

RESULTS

Simulations were conducted to investigate injection and distribution of organic gases having different physio-chemical properties into the vadose zone. Given the variations in chemical properties (TABLE III), a range of results were obtained, with pentane and butane being representative of the two extremes in the outcomes. Fig. 1 shows the relative concentration distribution for butane and Fig. 2 shows the corresponding distribution for pentane. The results for ethyl acetate and butyl acetate were similar to those for pentane, while the propane and ethane results were similar to those for butane.

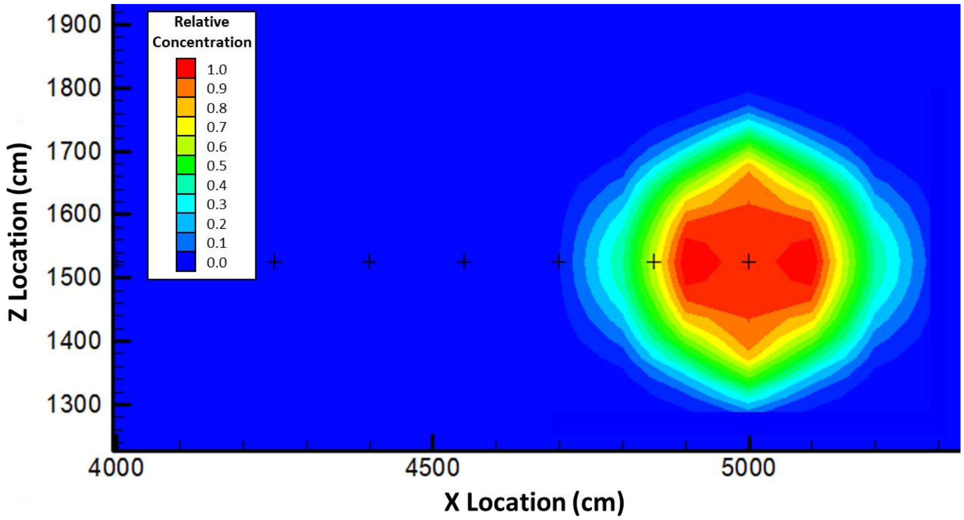

Fig. 1. Relative Concentration Distribution for Butane

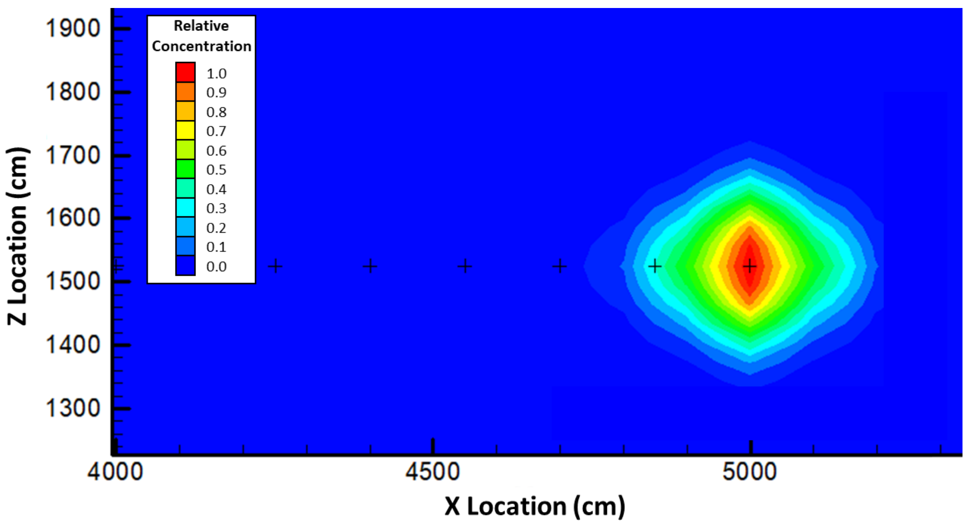

Fig. 2. Relative Concentration Distribution for Pentane

The distribution results are also presented as an XY plot of concentration versus distance, with Fig. 3 showing the relative gas concentrations and Fig. 4 showing the corresponding equilibrium aqueous concentrations. The Henry's law constants of the organic gases were used to determine the partitioning into the aqueous phase. Here, ethanol has the most mass in the aqueous phase, followed by ethyl and butyl acetate, while ethane and pentane have the least mass in the aqueous phase.

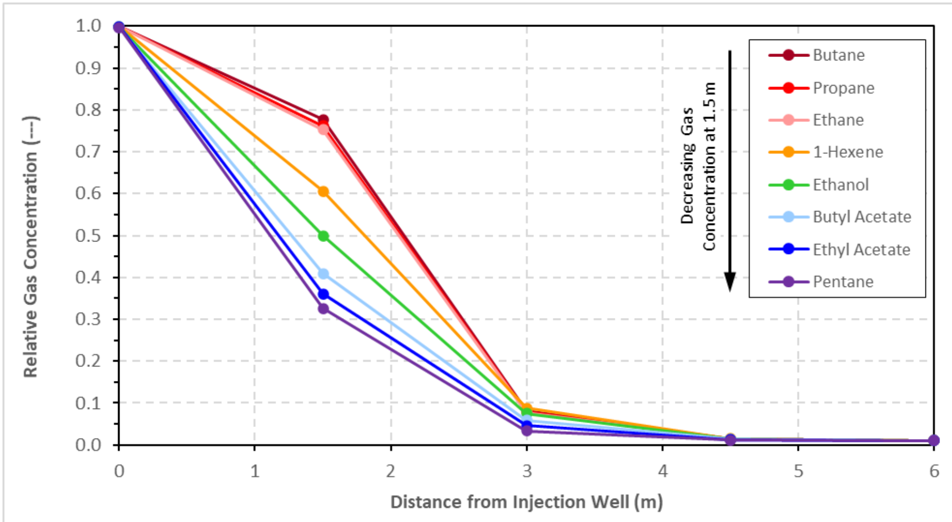

Fig. 3. Gas Concentrations of Organic Amendments over Distance from the Injection Well

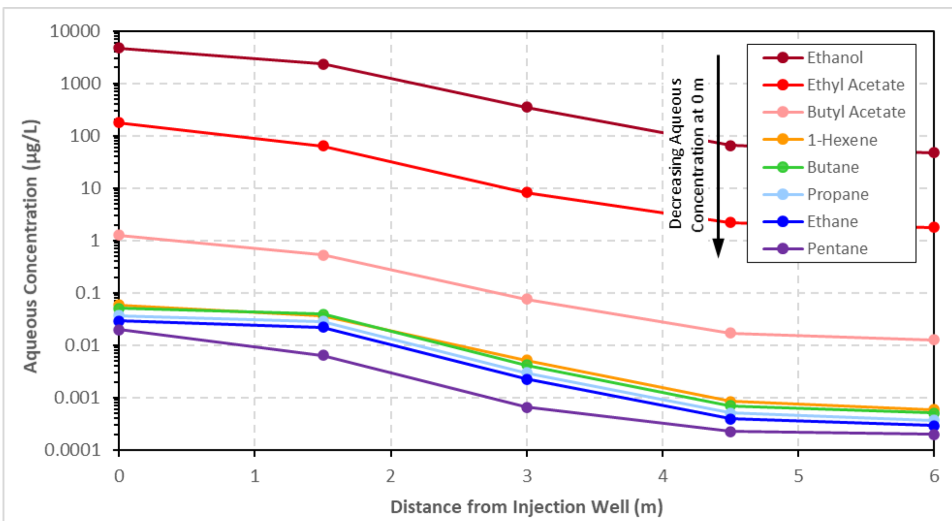

Fig. 4. Aqueous Concentrations of Organic Amendments over Distance from the Injection Well

One consideration beyond just mass in the aqueous phase could be potential toxicity to microbes or inhibition of microbial metabolism. This could be a particular concern for ethanol, which is used as a sterilant in other settings. As a starting point, one reference [6] indicates that ethanol concentrations of up to 3% (on the order of 23 g/L) have minimal impact on subsurface microbial activity (in the context of gasoline remediation). Information on organic compound aqueous concentrations that are toxic or inhibitory to microbial activity will be important to consider in future work to determine suitable injection concentrations that result in viable aqueous concentrations.

CONCLUSIONS

Results of the simulations were evaluated to determine how organic gas and porous media properties affected the spatial distribution and mass partitioning of the amendment between gas and aqueous phases in the vadose zone. These scoping simulations indicate that selection of a suitable organic gas is not a simple matter because the distribution and mass availability for microbial reduction is complicated by different physio-chemical properties of the potential amendments. It is the combination of partitioning, solubility, gas density, and subsurface properties that results in the mass distribution in the pore water. Additional work is needed to evaluate impacts of gas density on vertical distribution of amendment mass, the effects of variations in porous media properties, and variations in the injection operational strategy. A better understanding of gas amendment delivery to the subsurface will facilitate feasibility study technology evaluations and system design for implementation to achieve successful remediation by providing broad insight into the combined effects of amendment and subsurface properties.

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