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Coupling Transport and Biodegradation of VOCs in Surface and Subsurface Soils

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Volatile organic chemicals present at Superfund sites preferentially partition into the soil gas and may be available for microbial degradation. A simple mass transfer model for biodegradation for volatile substrates has been developed for the aerobic decomposition of aromatic and aliphatic hydrocarbons. The mass transfer analysis calculates diffusive fluxes from soil gas through water and membrane films and into the cell. This model predicts an extreme sensitivity of potential biodegradation rates to the air-water partition coefficients of the compounds. Aromatic hydrocarbons are removed rapidly while the aliphatic hydrocarbons are much slower by orders of magnitude. Furthermore, oxygen transfer is likely to limit aromatic hydrocarbon degradation rates. The model presents results that cast doubt on the practicality of using methane or propane for the co-metabolic destruction of trichloroethylene in a gas phase bioreactor. Toluene as a primary substrate has better mass transfer characteristics to achieve more efficient trichloroethylene degradation. Hence, in sites where these contaminants coexist, bioremediation could be improved. — Environ Health Perspect 103(Suppl 5):75-78 (1995)

Key words: VOCs, mass transfer, gas phase, biodegradation, modeling, soils

Introduction

Subsurface contamination at Superfund sites is dominated by volatile organic chemicals (VOCs) that are initially released as nonaqueous phase liquids. The specific classes of compounds of concern include the aromatic hydrocarbons such as benzene found in petroleum products and the halogenated solvents like trichloroethylene (TCE) used widely in industries for degreasing and heat transfer. When these nonaqueous phase liquids are released to the subsurface, they tend to travel downward through permeable zones in the unsaturated zone; for the halogenated solvents, these liquids can migrate below the water table because they are denser than water. Both in the unsaturated zone and below the water table, nonaqueous phase liquids are left behind as trapped liquids that act as long-term sources of soil gas and groundwater contamination (1). This research focuses on biodegradation of

VOCs in near-surface soils and on how biodegradation can help to minimize human exposure via inhalation.

As an *in situ* or above-ground treatment technology, delivery through the gas phase for biodegradation is recognized as having a number of advantages over groundwater treatment in aqueous phase bioreactors. First, the volatility of the compounds in contrast to their low aqueous solubility suggests that there would be greater availability of the compound and that more rapid removal would be possible. Second, for aerobic degradation pathways, the high potential oxygen content of air is an advantage over the limited solubility of oxygen in water. Air is also much less viscous than water, so oxygen delivery by air is orders of magnitude more efficient than oxygen delivery by water. Third, mass transfer rates for both oxygen and VOCs in the gas phase are also much greater than in the aqueous phase due to a four order of magnitude increase in molecular diffusivity. Finally, there is strong field-scale evidence for VOC degradation above the water table: soil vapor extracted from sites contaminated by petroleum hydrocarbons has low levels of molecular oxygen, and the carbon dioxide level is elevated, but depleted in carbon-14 as are petroleum hydrocarbons (2). Limited mechanistic modeling of gas phase biodegradation is currently available in the literature. Here, some preliminary results are developed to quantitatively evaluate the expected performance of such a system.

Model Development

The initial model developed for gas phase biodegradation considers a single bacterium attached to a much larger sand grain. Rather than attempt to model intrinsic microbial kinetics, the approach assumes that bacterial transformation of substrate is limited by mass transfer external to the cell instead of internal metabolic pathways. There are numerous examples in the natural environment and in engineered bioreactors in which mass transfer limits microbial processes. For example, sediment pore waters show large concentration gradients of oxygen, nitrogen species, and sulfur species over distances of a few centimeters where molecular diffusion limits microbial availability of substrates (3). Chemical profiles in the thermocline of lakes show that substrate delivery is limited by reduced turbulent diffusion in this layer. Bioreactors are frequently limited by oxygen delivery from bubbles or substrate diffusion into flocs and biofilms (4,5).

The idealized bacterium is assumed to be half of a sphere attached to the solid with a radius of 1.0 μm . The Gram-negative bacterium's inner and outer membranes are represented by a 10 nm film of octanol, separated from air by a variable thickness water film. The air and water are assumed to be stagnant when calculating mass transfer rates.

Mass flux to the bacterium is calculated by solving the steady-state diffusion equation for a compound diffusing through air, water, and octanol before being consumed

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by the cell. For each of the three phases, the equation is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D \frac{dC}{dr} \right) = 0 \quad [1]$$

where r is the radial coordinate, C is concentration, and D is molecular diffusivity. Solution of the three coupled differential equations for the three phases requires six boundary conditions. The assumption of mass-transfer limited growth says that the substrate concentration within the cell is zero. The second boundary condition is that in the air far from the cell, the gas phase concentration is at some bulk concentration, $C_{air, bulk}$. The other four boundary conditions require equilibrium and constant flux at the air–water and water–octanol interfaces. The analytical solution is presented in terms of a mass transfer coefficient, k , such that flux is given by

$$flux = k C_{air, bulk} \quad [2]$$

where the *flux* is in terms of mass per area per time. The mass transfer coefficient is a function of mass transfer and partitioning in the three-phase system.

Fluxes to a single bacterium are extended to a column reactor to assess removal along a flow path assuming a bacterial population density of N_b (number per gram of soil) and a bulk soil density ρ_b (g/cm³). The bacterial density is assumed to be substantially less than a monolayer coverage. The soil gas concentration remaining after a flow distance of x is given by

$$C_{air}(x) = C_{air,0} e^{-\frac{2\pi r_b^2 k N_b \rho_b}{U} x} \quad [3]$$

where $2\pi r_b^2$ is the area of the half-spherical bacterium facing the gas and U is the gas approach velocity. This simple model assumes that the bacterial density does not change with time or distance.

Results

The mass transfer model was evaluated for six compounds that span the range of VOCs found in the subsurface. These compounds and some pertinent chemical properties are the first six listed in Table 1. The compounds are ranked in ascending order of their air–water partition coefficient. The first three are aromatic

Table 1. Air–water and octanol–water partition coefficients for selected compounds.^a

Compound	Air–water partition coeff.	Octanol–water partition coeff.
1-Methylnaphthalene	0.018	7,400
Benzene	0.22	140
<i>n</i> -Butylbenzene	0.52	18,200
Methane	27.0	12
Hexane	69.0	8700
Decane	280.0	1.3×10 ⁶
Oxygen	33.0	4.5
Trichloroethylene	0.48	200
Propane	29.0	230
Toluene	0.27	500

^aData from Hansch and Leo (6) and Mackay and Shiu (7).

hydrocarbons with low air–water partitioning, and thus a tendency to partition into water compared with the next three aliphatic hydrocarbons, which strongly favor the gas phase. Of particular note is the four order of magnitude range in air–water partition coefficient for compounds all typically present in fuels, with the exception of methane. The table includes octanol–water partition coefficients with a similarly broad range in values. Besides these chemical properties, molecular diffusivities within a phase were assumed to be identical: 10⁻¹ cm²/sec in the air, 10⁻⁵ cm²/sec in the water, and 10⁻⁶ cm²/sec in the octanol phase.

Figure 1 illustrates the sensitivity of the predicted overall mass transfer coefficients on water-film thickness and the air–water partition coefficient for the six compounds. All mass transfer coefficients decrease as the water-film thickness increases from 0.01 to 1.0 μm because the water phase contributes the most resistance to mass transfer. For water-film thicknesses greater than 4 μm the mass transfer coefficients are level

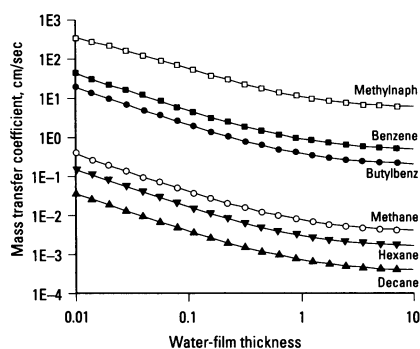


Figure 1. Predicted mass transfer coefficients as a function of water-film thickness.

because, in spherical coordinates, a water film any thicker does not increase the resistance. The aromatic hydrocarbons, methylnaphthalene, benzene, and butylbenzene, have high mass transfer coefficients because of their relative preference for water over air compared to the aliphatic hydrocarbons, methane, hexane, and decane. For equivalent gas phase concentrations, the degradation rate per bacterium for these six compounds would range over four orders of magnitude.

Water-film thicknesses cannot be quantitatively related to water potential. Some soil science research has related water potential with water-film curvature using the Kelvin equation (8). Water can exist as a film coating mineral surfaces and not just in pore spaces (9). The state of water in partially water-saturated soil is an area of continuing interest, particularly as it relates to water potentials that lead to desiccation and reduced microbial activity (10,11). For the remaining model simulations, a water-film thickness of 1 μm is assumed to hold. A water surface with a radius of curvature of 1 μm corresponds to a water potential of -0.15 MPa (-1.5 bar), which does not desiccate soil microorganisms (12).

If these six compounds are injected into a column, the removal along the column can be predicted from Equation 3. Assuming a bacterial population of 10⁴ cells/g medium, a bulk density of 1.5 g/cm³, and a gas approach velocity of 10 m/day, Figure 2 presents the fraction of the compound remaining as a function of distance along the column. Methylnaphthalene is rapidly removed within the first 0.1 m, benzene and butylbenzene are gone after 2 m, but it takes on the order of 100 m to remove the aliphatic hydrocarbons. For the aliphatic

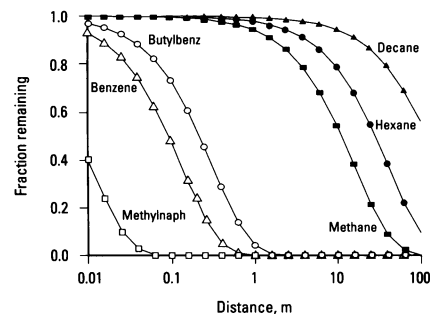


Figure 2. Predicted removal of selected aromatic and aliphatic hydrocarbons along a packed bed column have 10⁴ bacteria per gram of soil and a gas approach velocity of 10 m/day.

hydrocarbons with low mass transfer coefficients, very long flow paths are needed for significant removals.

The predictions thus far have only considered hydrocarbon transport to bacterial cells and not the simultaneous delivery of oxygen that would be required for aerobic decomposition. As seen in Table 1, oxygen has a high air-water partition coefficient similar to methane. Given the high rates of aromatic hydrocarbon mass transfer, oxygen transfer may limit degradation. Oxygen limitations are quantitatively considered in Figure 3, in which the gas phase oxygen concentration is 10 times greater than required by stoichiometry. Even with this excess oxygen, all aromatic hydrocarbons are degraded at the same rate, a rate controlled by oxygen transfer. When oxygen transfer was ignored in Figure 2, complete removal of aromatics was accomplished in 2 m, but when oxygen transfer was included in Figure 3, the necessary length of the reactor increased to 10 m to remove them all. The aliphatic hydrocarbons were not oxygen-transfer limited, and their removal was unchanged from Figure 2.

One final application of this simple model is in consideration of co-metabolic transformation of TCE by aerobic organisms possessing monooxygenases and dioxygenases. Aqueous phase bioreactors have found that primary substrates such as methane, propane, and toluene must be at least 100 times the TCE concentration to avoid enzyme competition and product toxicity. Table 1 includes the properties of TCE, which can be compared with those of methane, propane, and toluene. TCE and toluene partition across the air-water interface similar to benzene and butyl benzene, while propane is similar to methane and oxygen. This suggests that TCE gas delivery to a cell might be far faster than methane or propane delivery, and main-

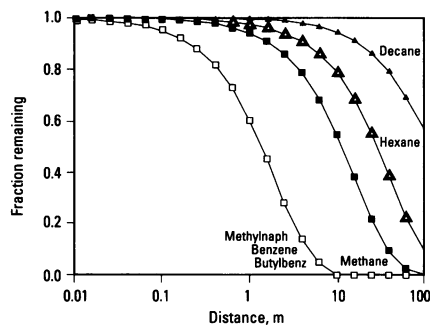


Figure 3. Predicted removal of selected aromatic and aliphatic hydrocarbons along a packed bed column (with 10^4 bacteria/g soil and a gas approach velocity of 10 m/day) for an oxygen influent concentration 10 times greater than required by stoichiometry.

taining a 100:1 degradation rate of the primary substrate to the co-metabolite would require approximately a 6000:1 gas phase concentration ratio using this mass transfer model. In contrast, toluene would only require a 60:1 concentration ratio to initially achieve the 100:1 ratio of degradation rates. In terms of a column reactor attempting to treat TCE by aerobic co-metabolism, the TCE would be rapidly removed, but only if excessively high methane or propane concentrations were imposed. Most likely, engineered reactors would have to cycle between feeding primary substrate and TCE-containing vapors. In the case of toluene as the primary substrate, both TCE and toluene would be removed over comparable distances.

Discussion and Summary

Gas phase biodegradation does occur in soil exposed to petroleum hydrocarbons and offers a number of advantages in remediating sites contaminated by VOCs. In order for petroleum hydrocarbons to be degraded by bacteria, the individual

components must diffuse from the bulk gas phase to the interface of the water film, then partition into the water, diffuse through the water, partition into the cell membranes, and be transported into the cell. A quantitative model for these processes has identified the water film as the critical factor limiting resistance to mass transfer. The limitations imposed by the water film arise from low molecular diffusivities in water and the relatively low air-water partition coefficients characteristic of VOCs. The chemicals considered in Table 1 have a wide range of partition coefficients and are removed at different rates. Consideration of aromatic and aliphatic hydrocarbons revealed that aromatics are rapidly removed, while aliphatics have very slow removal rates due to mass transfer through the water film. Additional consideration of simultaneous oxygen transfer revealed that degradation of aromatic hydrocarbons can be significantly depressed even if oxygen is present in the gas phase at 10 times the amount needed for complete oxidation. When co-metabolic transformations were considered, the mass transfer model predict that, for methane and propane as primary substrates, excessively high substrate concentrations would be required to overcome mass transfer limitations. Toluene as a primary substrate for TCE co-metabolism does not have that limitation.

A model based on mass transfer to a single bacterium attached to a sand grain is highly idealized and is not easily extrapolated to field conditions. Continuing model development and refinement is ongoing with the introduction of bacterial kinetics, microbial development within a biofilm, and the response of biofilms to changing water potential. An experimental program is under way to evaluate the adequacy of our predictive capability.

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