Bioventing to treat fuel spills from underground storage tanks*

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Abstract

Bioventilation is a procedure to cleanse soil gas of volatile fuel hydrocarbons originating from storage tank leaks. The rate of vapor degradation is a controlling parameter in the design of a bioventing system. A laboratory microcosm procedure using sandy soil from an aviation gasoline spill site was used to measure relative kinetics of some fuel vapors.

Introduction

There are thousands of gasoline service stations in this country with residual fuel hydrocarbon contamination. Natural biological activity in the unsaturated zone above a fuel spill rapidly attenuates concentrations of vapors that volatilize from the spill. If moisture and nutrients are adequate, the rate of degradation is controlled by the diffusion of oxygen from the land surface and the diffusion of hydrocarbons from the spill. This natural biological activity can be used to treat off-gas produced during soil vacuum extraction. The gas can be reinjected into the unsaturated zone midway between the water table and the land surface, or alternatively air can be injected into the fuel-contaminated zone rather than extracted. Under appropriate conditions the air that escapes the fuel-contaminated interval will have enough oxygen to allow complete biodegradation of the hydrocarbon fumes. As the air works its way to the surface, biodegradation attenuates the concentration of hydrocarbon vapors to an environmentally acceptable level.

Bioventing is a rather simple bioremediation procedure that can logically be used to clean up many of the contaminated sites. Enhancement of microbial activity for biodegradation of fuel vapors is one of the requirements for a successful operation. The moisture content of the unsaturated zone, and the availability of nitrogen and phosphorus, must be carefully controlled. Figure 1 shows a basic bioventing system.
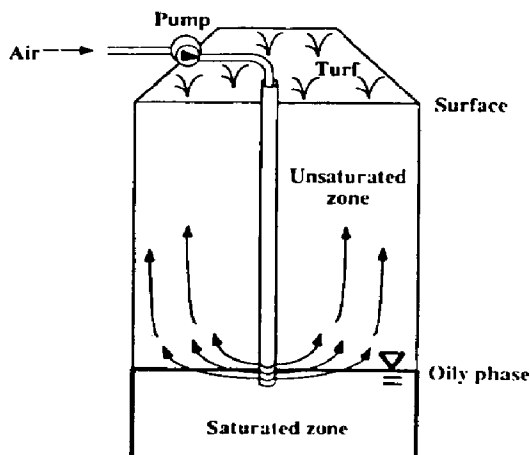
Fig. 1. Schematic of bioventing operation.

The biological breakdown of organic compounds, when biomass is optimum, is commonly expressed as a first-order reaction $dc/dt = -kc$. Other theoretical models have been developed for organic degradation reactions such as Monod kinetics [1]. We will use the first order rate constant as a relative comparison of degradation rates under different experimental conditions. Use has also been made of an integrated rearrangement of the Henri–Michaelis–Menten equation [2] which predicts the maximum reaction rate (V_{max}) and the concentration of substrate at which the reaction rate is half of maximum (K_m).

Laboratory soil microcosms have been used successfully to simulate the ability of the unsaturated zone to bioremediate light hydrocarbon vapors at a gasoline spill site [3]. The objective of these soil microcosm studies was to investigate the possibility of interactions between the vapor components, to determine the degradation kinetics for several fuels, and determine the influence of soil nutrients and temperature on the kinetics of hydrocarbon oxidation.

Experimental

Aerobic soil microcosms (Fig. 2) at 23°C were used to determine the rate of disappearance of vapors of fuels and some of the important components of fuels. Glass serum bottles were used to construct microcosms. They had a volume of 160 mL and contained 32 grams, on a dry-weight basis, of Rubicon Sand. All experimental treatments were carried out in duplicate. The soil was obtained from a gasoline spill site in a uniform sand. A pilot scale bioventing system is being evaluated at the site.

A nutrient solution equivalent to 0.2 mg each of diammonium phosphate and potassium nitrate was added to each microcosm along with ground water to bring the moisture level to 13%. Each bottle was capped with a teflon/silicone septa. The soil microcosms were gradually acclimated for at least a four-
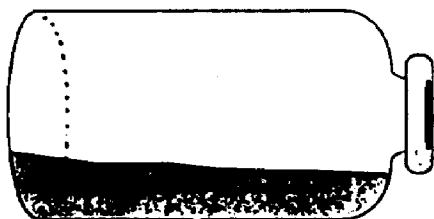
Fig. 2. Soil microcosm.

week period to aviation gasoline fumes. The microcosms were considered to be at steady state when they attained the same rate of fume disappearance on two subsequent days. Control microcosms were included that had not been acclimated. Headspace analysis of the microcosms was done using 100 μL aliquots injected into a gas chromatograph. Rate of disappearance was the difference in headspace concentration between control and test microcosms. Upon termination of the nutrient response study, portions of microcosm soil were removed for total bacterial count by the AODC method [4] and dehydrogenase activity by the Formazan method [5].

Results

Gasoline vapor degradation using the Rubicon Sand microcosms was determined at temperatures of 4, 12, 18, 23, and 37°C (Fig. 3). The highest rate of degradation was obtained at 18°C. Rates of utilization were lowest at 4°C and 37°C. The data suggests that degradation will only be 30% less than optimum at a typical subsurface temperature of 12°C.

A distinct response to added nitrogen, phosphorus, and potassium was obtained (Table 1). Nutrient addition increased by a factor of four the bacterial numbers, degradation rate, and active biomass as indicated by dehydrogenase activity. The addition of nutrients should be considered for each bioventing system.

The disappearance of aviation gasoline and JP-4 jet fuel fumes in the acclimated microcosms was rapid and extensive (Fig. 4). The slopes of the two curves are typical for first-order kinetics. Fumes of unleaded gasoline were much more resistant to degradation. This can be expected because several of the major components were unsaturated alkenes, which are more difficult for microbes to mineralize.

The three most dominant volatile organics in fresh aviation gasoline have been shown by chemical analyses to be 2,4- dimethylpentane, 2,3-dimethylpentane, and 2,2,4-trimethylpentane or iso-octane. All three compounds were readily degraded when injected singularly into microcosms acclimated to aviation gasoline (Table 2). Iso-octane had the lowest rate. The compounds degraded more slowly when introduced as a mixture. The reduction in rate was
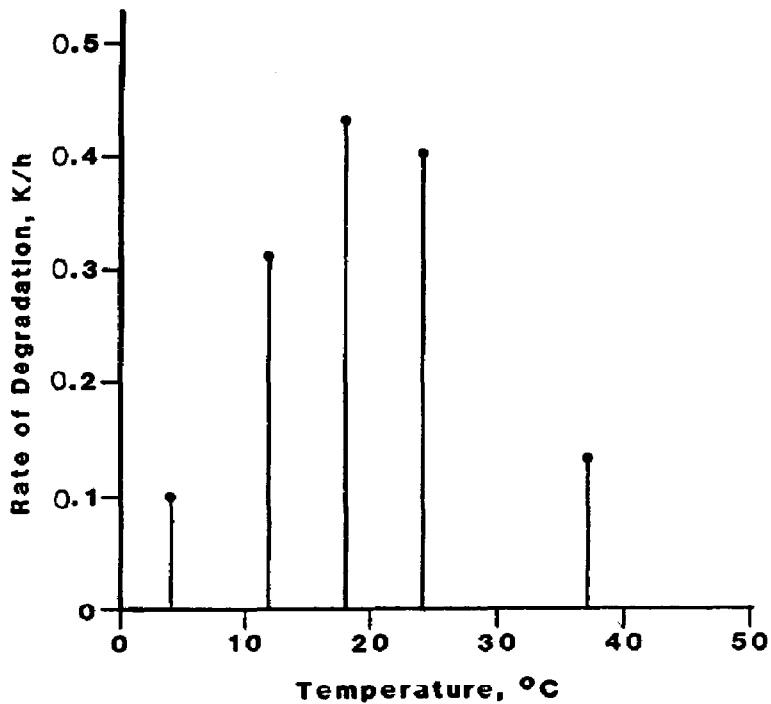
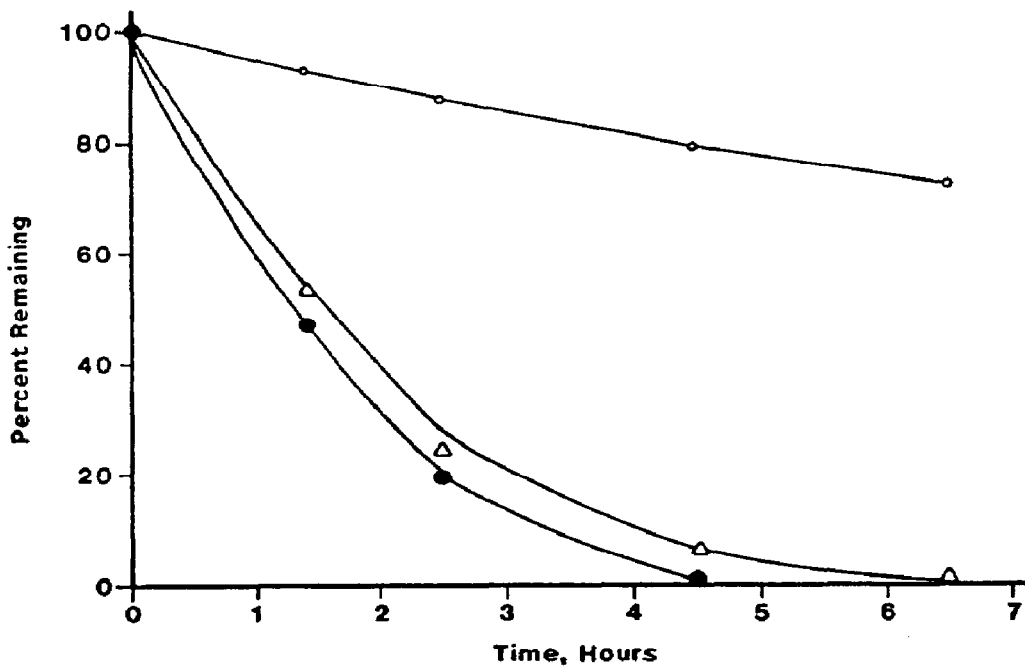Fig. 3. Influence of temperature on removal of gasoline vapor.

Fig. 4. Disappearance of headspace fumes in soil microcosms: (O) 12.3 mg unleaded/kg soil, (◇) 8.4 mg JP4/kg soil, and (●) 14.5 mg aviation gasoline/kg soil.

TABLE 1

Response to added nutrients

Treatment	First-order rate of disappearance	Dehydrogenase activity (mg Formazan/kg-day)	Bacteria count (cells/g)
−NPK	0.13	5.4	8.8×10^8
+NPK	0.58	27.8	37×10^8

TABLE 2

Relative degradation rate of methylpentanes

Compound	As single compound		As a mixture	
	Initial conc. (mg/kg soil)	Rate (h^{-1})	Initial Conc. (mg/kg soil)	Rate (h^{-1})
2,4-DMP[a]	28	0.60	12.5	0.18
2,3-DMP	28	0.67	9.0	0.47
2,2,4-TMP[b]	28	0.27	6.5	0.21

[a]DMP = dimethylpentane.
[b]TMP = trimethylpentane.

TABLE 3

Calculated values for half-saturation constant (K_m) and maximal rate (V_{max})

Fuel	K_m (mg fuel/kg soil)	V_{max} (mg fuel/kg soil-hour)
Aviation gasoline	39	31
Unleaded gasoline	30	0.9
JP-4 jet fuel	17	12

greatest for 2,4-dimethylpentane. The data suggests an inhibition effect on degradation in mixtures with the influence greatest for the dimethylpentanes. A similar suppressive influence has been reported that the same n-alkanes in two crude oils [6].

The experiment was repeated at a constant initial concentration of fuel vapors (31 mL of vapors/ kg soil at 22°C). The first order rate for fume disappearance was 0.74, 0.63, and 0.05 /hour for aviation gasoline, JP-4 jet fuel, and unleaded motor gasoline respectively.

Biodegradation at higher vapor concentrations is limited by the microbial capacity to metabolize the organic vapor. Once the rate becomes independent

of vapor concentration, it follows a straight line integrated rearrangement of the Henri–Michaelis–Menten kinetic equation [2]) represented by a Lineweaver–Burk reciprocal plot. The plot is commonly used as a linear transformation of velocity for biochemical reaction kinetics. Maximum velocities and half saturation constants (K_m) for the three fuel vapors are listed in Table 3. Data shown in Fig. 4 and Tables 2 and 3 are actual headspace concentrations. Extrapolation of biodegradation from soil microcosms to field subsurface conditions may increase by several hundred fold based on derived assumptions of soil pore volume dilution, relative activity, and transport phenomena.

The maximum rate of biodegradation was attained on aviation gasoline. Rates were 39 and 3% of maximum for JP-4 jet fuel and unleaded gasoline, respectively. Values similar to those obtained for aviation gasoline have been reported for propellant mixtures for aerosol cans, that contain propane, iso-propane, and n-propane [7].

The rates are adequate to consume all the vapors produced during vacuum extraction or air injection at the pilot demonstration site, if the extraction or injection rate exchanges all the air in the unsaturated zone every eight hours.

References

1   S.K. Schmidt, S. Simkins and M. Alexander, Models for the kinetics of biodegradation of organic compounds not supporting growth. Appl. Environ. Microbiol., 50 (1985) 323.
2   I.H. Segal, Biochemical Calculation, Wiley, New York, NY, 1976, p. 245.
3   D.W. Ostendorf and D.H. Kambell, Bioremediated soil venting of light hydrocarbons. Haz. Waste Haz. Mat., 7(4) (1990) 319–334.
4   J.T. Wilson, J.F. McNabb, D.L. Balkwill and W.C. Ghiorse, Enumeration and characterization of bacteria indigenous to a shallow water table aquifer. Ground Water, 21 (1983) 134–142.
5   L.F. Din, Standard Operating Procedure for Dehydrogenase Activity, RSKSOP-100, U.S. EPA/RSKERL, Ada, OK, 1990.
6   G.J. Mulkins-Phillips and J.E. Stewart, Distribution of hydrocarbon-utilizing bacteria in northeastern atlantic waters and coastal sediments. Can. J. Microbiol., 20 (1974) 955–962.
7   D.H. Kampbell, J.T. Wilson, H.W. Read and T.T. Stocksdale, Removal of volatile aliphatic hydrocarbons in a soil bioreactor. J. Air Pollut. Control Assoc., 37 (1987) 1236–1240.