0273-2289/00/88/0059/$14.50

The Role of Biodegradation During Bioventing of Soil Contaminated with Jet Fuel

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Abstract

The enhancing removal of kerosene (jet fuel) from contaminated soil during bioventing resulting from biodegradation was compared to the physical removal by evaporation only on bench-scale columns at the controlled temperature of 20°C (± 2.5°C). Carbon dioxide-free air and nitrogen were used as flushing gases, at the constant continuous flow rate of 1 dm^3/h. Kerosene concentrations in soil up to 35000 mg/kg were not toxic for indigenous microbial population. Much slower kerosene biodegradation rates observed for soil from a contaminated site, as compared to soil artificially contaminated with kerosene, were the result of a lower bioavailability of "aged" kerosene, and the presence of compounds that might be persistent or toxic to kerosene-specific degraders. The inhibitory effect of toluene to indigenous microorganisms was found at above 75% of the toluene saturation concentrations in the gas phase.

After 29 d, the overall bioventing efficiency was 17–23%, depending on whether CO_2 production or O_2 uptake was used for calculations, as compared to the removal of 10% when biodegradation was excluded. The increase in efficiency by 50–100% owing to biodegradation would be more spectacular at lower kerosene concentrations during the "tailing" phase, with diffusion-limited desorption, and much lower evaporation of less volatile constituents. Limitation of bioventing as a result of low bioavailability related to intraparticle sorption of residual contamination is discussed.

Index Entries: Kerosene; biodegradation; evaporation; bench-scale columns; unsaturated zone; efficiency; bioavailability; sorption.

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Introduction

Enhancing intrinsic biodegradation of nonvolatile (NVOCs), semivolatile (SVOCs), and residual volatile organic compounds (VOCs) in the unsaturated soil by air injection or vapor extraction is the clean up technique known as soil bioventing (SBV), when evaporation is minimized *(1)*. Experiences showed that indigenous soil microorganisms can degrade most of the hydrocarbons if the environmental conditions (i.e., oxygen, temperature, water content, and nutrients) are not limiting factors *(2–6)*. Increased contribution of biodegradation to the overall removal of hydrocarbons may substantially reduce the amount of air required to evaporate, particularly SVOCs, and lower concentrations of VOCs in off-gases, thus reduce SBV treatment costs *(7)*.

Previous experiments with soil artificially contaminated with model hydrocarbons showed 99% reduction of toluene within 11 d of SBV *(8,9)*. In contrast, 24 d were required to reach the same efficiency when aerobic biodegradation was excluded.

The initial decane concentration of 400 mg/kg decreased below 1 mg after 33 d of SBV, as compared to 60 mg after 36 d when only evaporation was involved.

The main goal of the research was to determine the role of biodegradation during SBV, qualitatively, with respect to process kinetics, and quantitatively, by its contribution to the overall removal of kerosene from soil. SBV was compared with the kerosene removal from contaminated soil exclusively by evaporation, referred to as soil venting (SV), which was realized using N_2, instead of air, as a flushing gas.

Background

Subsoil as a Bioreactor

Transformation processes of organic compounds in subsoil include biodegradation, chemical and physical degradation via oxidation, leaching, and evaporation. The fate of kerosene compounds requires extensive investigations of microbial activity in the subsurface. Modern detection methods confirmed population densities of 10^6 to 10^7 cells/g dry soil in noncontaminated permeable shallow aquifers *(10)* and the occurrence of microbial life and metabolic activity at 200–300 m below ground surface *(11)*. Subsurface indigenous microorganisms are metabolically active, often nutritionally diverse, and the ability to degrade hydrocarbons is widely distributed among microbial populations.

Although experimental data indicate aerobic biodegradation to be generally far more effective than anaerobic *(12,13)*, recent studies showed that effectiveness of anaerobic biodegradation may approach that of the aerobic process under specific conditions *(14,15)*. Aerobic biodegradation of alkanes and cycloalkanes requires molecular oxygen for hydroxylation, i.e., the first metabolic step initiated by microbial enzymes, mono-

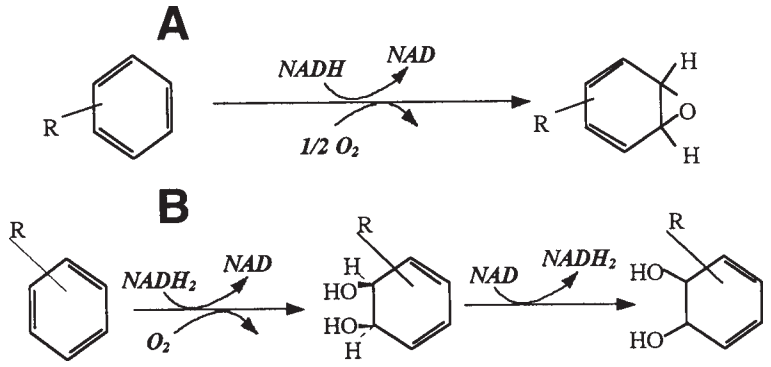

Fig. 1. Hydroxylation of monoaromatics. **(A)** Monooxidation; **(B)** dioxidation.

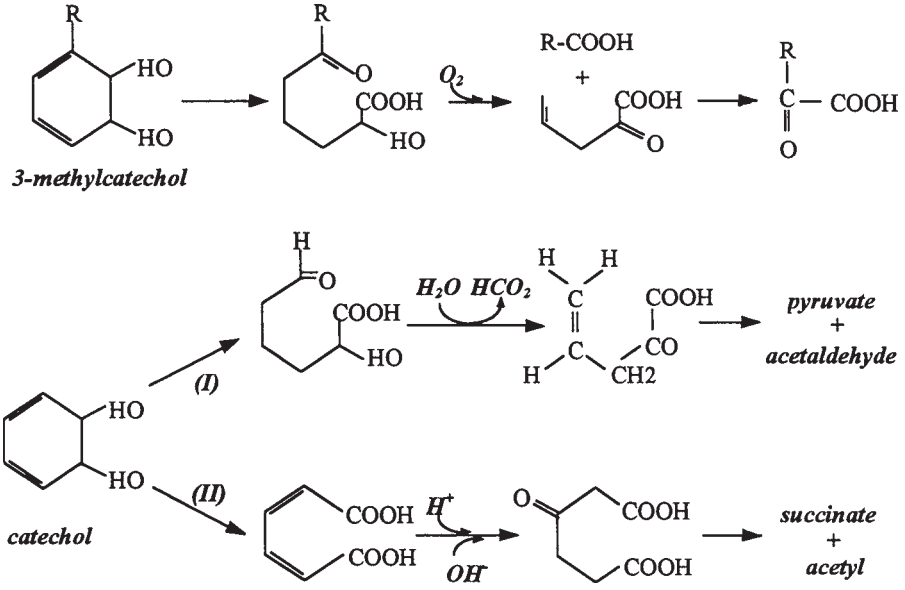

Fig. 2. Catechol decomposition. Metabolic pathways: (I) *meta*, (II) *ortho (12–13,16)*.

oxygenases, whereas further oxidation may be coupled with the reduction of nitrate. The degradation of mono-aromatics (e.g., BTEX) involves oxygenases that also require molecular oxygen for the conversion of side chains and the fission of the aromatic ring. It proceeds via formation of catechols (Fig. 1), which are the intermediates that undergo ring fission (Fig. 2).

Factors that may affect biodegradability include physical behavior and chemical structure of the compound, and environmental conditions, i.e., availability of an electron acceptor, nutrients, and essential elements, type of soil, soil moisture, temperature, and pH, contaminants concentrations, and presence of toxic compounds. Regardless of electron acceptors and nutrient enhancements, porous materials of the unsaturated zone can

limit the extent of hydrocarbons biodegradation by sorption and reduced bioavailability, especially if hydrophobic compounds are present in soil for longer times. The physical–chemical properties of a compound may minimize the susceptibility to microorganisms. The majority of kerosene hydrocarbons are hydrophobic, tend to form insoluble clumps and aggregates, adsorb onto soil organic matter (SOM) and in micropores, decreasing the bioavailability of contaminants to microorganisms.

On the other hand, adsorption may also promote biodegradation when referring to the compound that may be toxic, or may inhibit microbial growth. SOM may have both stimulating and inhibiting effects on biodegradation of kerosene. The former may be due to an extra carbon source, cometabolism, or induction of relevant enzymes, whereas the latter by competition for nutrients and growth factors, or diauxy, leading to preferential metabolism of easily degradable compounds.

For biodegradation to occur contaminants must be available for uptake and utilization by the microorganisms *(17)*. Microorganisms and hydrophobic organic compounds are distributed in the unsaturated zone among solid, liquid, and gas phases *(9)*. In a system with a nonaqueous phase liquid (NAPL) present, bioavailability is partially controlled by a dissolution rate of compounds from NAPL, represented by mass exchange coefficients and mass exchange rates. In the absence of NAPL bioavailability is ultimately controlled by sorption processes.

Higher-molecular-weight kerosene hydrocarbons tend to sorb onto soil, with only a small fraction of them in water and gas phases. Over long contact time, the adsorbed compounds slowly diffuse into the inorganic and organic solid matrix and may also form bound residues.

Sorption of contaminants tends to limit the direct contact between microorganisms and substrates, which is necessary for biodegradation to take place. For porous media with high solid fraction and surface area, sorption is the primary process limiting bioavailability, and the influence can be classified into concentration effects and desorption rate limitations.

Chemicals dissolved in water are available for microorganisms, and the uptake rate is commonly described by the Monod relationship *(18)*. At a very low concentration, the so-called critical water concentration, insufficient energy and carbon may be available for microbial activity, and microbial growth is balanced by decay *(19)*. At high concentrations, many organic compounds become toxic, and the biodegradation rate may be expressed by the Haldane equation *(20)*.

Because of geometrical and mass transfer restrictions, most bacteria are present on the external surface of soil particles and in soil water, and only limited biological activities occur within the intraparticle pores *(21)*. Biodegradation in the unsaturated zone comprises three steps: dissolution, desorption, and biotic or abiotic transformation of the contaminant in the aqueous phase. In the absence of NAPL, the apparent biodegradation rate in a solid–air–water system may be controlled either by the desorption or biodegradation rate.

In case of fast desorption compared to biodegradation, bioavailability is analogous to the retardation factor used to model movement of a sorbing solute in porous media *(22,23)*.

When the biodegradation rate is much faster than the desorption rate, microorganisms may effectively degrade available compounds released from the solid phase. Consequently, the biodegradation rate is approximately equal to the rate of desorption and the mass transfer between soil and water (sorption/desorption) may be described by a first-order reaction.

Kerosene deposited in subsoil is a subject of the so-called "weathering," or "aging," which refers to the changes in the nature of a chemical mixture after its release into the environment *(24)*. The product composition is changing with time, as the more volatile components will partition into the vapor phase, whereas the more soluble components will preferentially dissolve. As a consequence, the remaining kerosene will have a lower vapor pressure, a lower solubility, and higher molecular weight. Weathering has an important implication concerning the contribution of evaporation and biodegradation during SBV.

Although the majority of kerosene hydrocarbons can be degraded easily by soil microorganisms, some compounds may be persistent to biodegradation *(25)*. Branched and condensed cyclic aliphatic constituents of kerosene are slowly degradable, even under optimal conditions. The recalcitrance is their inherent characteristic most probably caused by chemical structures not well-recognized by microbial enzymes, or induction systems. Thus, biodegradability testing is advised prior to each biological treatment *(26)*.

Bioventing Principles

The removal of kerosene constituents from soil during SBV is the result of a combined effect of evaporation and biodegradation. Neglecting the amount of kerosene present in the gas phase between the soil particles, the removal rate can be expressed from a simple mass balance of the complete system under equilibrium, as follows *(9)*:

$$(dm/dt)_{\mathrm{SBV}} = (Q_a \cdot C_a)_{\mathrm{evap}} + [V_s \cdot (dC_s/dt)]_{\mathrm{deg}} \quad (1)$$

where (dm/dt) is the total amount of hydrocarbons removed in time (mg/h), C_a is the hydrocarbon concentration in the outlet gas (mg/m^3), and C_s is the concentration in soil (mg/m^3), Q_a is the volumetric flow rate of air injected or extracted from subsurface (m^3/h), V_s is the volume of soil, including soil water (m^3).

The first term on the right-hand side describes the total amount of hydrocarbons evaporated, and the second term corresponds to the amount biodegraded in soil.

Convective flow of air owing to injection of air to, or extraction from, the subsurface, disturbs the equilibrium of the system. Changes in pressure in the subsurface may increase the evaporation rate as, according to the molecular theory of gases, the air diffusion is inversely proportional to

ambient pressure. Moreover, because of the convective flow of air, hydrocarbons previously volatilized are removed, thus, their concentrations in the gas phase are reduced, and, consequently, the evaporation rate is further increased.

Air injection into subsoil is a practical method to enhance intrinsic aerobic biodegradation of hydrocarbons by sustaining increased O_2 levels *(1,5,27–29)*. Biodegradation may occur in freshly contaminated soil, though a longer exposure of kerosene to microorganisms may increase biodegradation potentials. Aged contamination, however, may slow down both evaporation and biodegradation rates due to lower partial pressures and bioavailability of residues.

The biodegradation rate is proportional to some power of the substrate concentration *(18)*:

$$r_{deg} = -(dC_d/dt) = K \cdot C^n_d \quad (2)$$

r_{deg} is the biodegradation rate (mg/m^3/h), C_d is the substrate (an electron donor) concentration in the water phase (mg/m^3), K is the rate constant (h), and n is the order of the reaction.

For the first-order kinetics (n = 1), often assumed for homogeneous media at low concentrations, the biodegradation rate is the product of the rate constant and the substrate concentration.

At high contaminant concentrations, which is often the case at sites contaminated with kerosene and other oil products, the substrate is not a limiting factor, and the rate does not depend on its concentration. In this case, biodegradation is likely to follow zero-order kinetics, with the rate equal numerically to the rate constant *(4,30)*.

To ensure aerobic biodegradation, the concentration of O_2 in soil water should be higher than 0.2 mg/L *(31)*. Biodegradation rates of hydrocarbons reported in field experiments were linear for O_2 levels in soil vapors down to 2–4%, and concentrations >4% were not considered to limit biodegradation *(29)*.

Materials and Methods

Site Characterization

Contaminated and reference (not contaminated) soil was collected at the military base Volkel, NL, at the depth of 0.2–1.2 m, using a simple random sampling method. Physical characteristics of soil (Table 1) were determined using disturbed samples, homogenized, air-dried, and sieved (fraction <4 mm).

In case of contaminated soil, sieving was done at 0°C to minimize losses of kerosene from soil due to evaporation. For the same reasons columns were also packed at 0°C. Soil was stored in dark at 4°C prior to use.

Contaminant Characteristics

Soil was contaminated by jet fuel (kerosene) from a leaking fuel pipeline, and consisted mainly of the aliphatic hydrocarbon mixture C_{10}–C_{16},

Table 1
Soil Properties

Parameter	Contaminated soil	Reference soil
Measured		
Soil texture (USDA classification)	Sandy	Sandy
sand, (% w/w)	87.8	88.6
clay (% w/w)	9.3	9.3
silt (% w/w)	2.9	3.1
pH	6.0–6.1	5.6–5.8
Gravimetric water content, *w* (%)	5.9–6.4	5.9–6.5
Soil organic matter, *SOM* (% w/w)	0.9–1.0	1.4–1.6
Avg. particle density, *APD* (kg/m^3)	2643	2637
Air conductivity, k_{air} (m/s)	4.5×10^{-2}	4.0×10^{-2}
Field capacity, *FC* (%) at pF = 2.0		
(% v/v)	10	14
(% w/w)	6	9
Porosity, *n* (m^3/m^3), (pF curve)	0.45	0.58
Calculated		
Dry bulk density, r_{db} (kg/m^3)	1588	1593
Wet bulk density, r_{wb} (kg/m^3)	1688	1693
Porosity, *n* (m^3/m^3)	0.40	0.40
Volumetric water content, θ (%)	9.4–10.2	9.4–10.4
Water permeability, k_{water} (m/s)	8.9×10^{-4}	8.0×10^{-4}

BTEX, and naphthalene derivatives. Quantitatively, the average composition comprised 17.2% (v/v) of BTEX and 82.8% (v/v) of alkanes. Contamination was considered old, as weathering was observed.

Batch Tests

Batch biodegradation tests were performed at 20°C in 0.5-L Schott glass bottles, sealed with Viton™ caps to minimize adsorption of hydrocarbons. To study the biodegradation potential of kerosene, bottles were filled with 75 g of contaminated soil with the initial concentration of 2660 m/kg, as extracted with CS_2.

Biodegradation of "fresh" vs "aged" contamination was compared by spiking noncontaminated soil samples with an amount related to the mass of soil to give an initial concentration of approx 2660 mg/kg.

To find kerosene concentration levels in soil that may be toxic to indigenous population, several amounts of kerosene were added to noncontaminated soil samples, yielding the initial concentrations from 5000 to 35,000 mg/kg.

Toxicity of toluene was tested over the range of amounts leading, after adsorption on soil, up to 100% of the saturation concentration in headspace, and the calculated oversaturation of 150%.

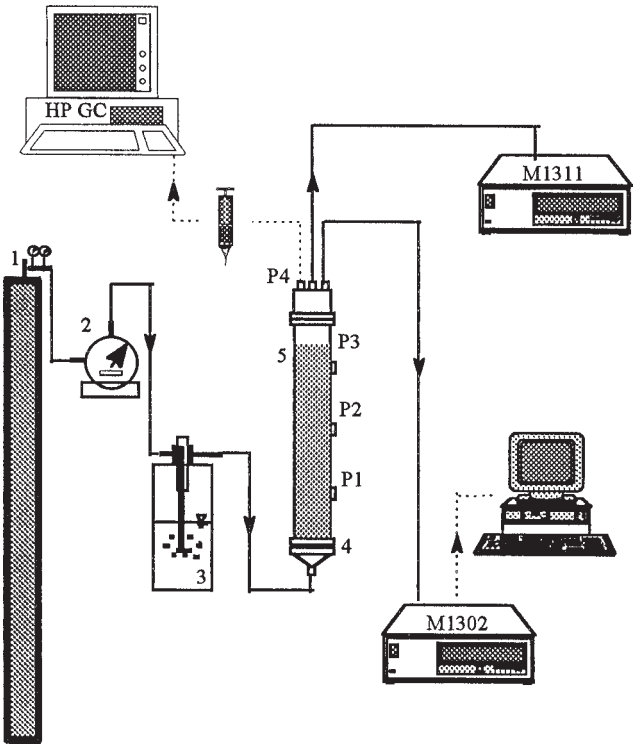

Fig. 3. Installation for simulation of SBV and SV. 1, N_2/CO_2-free air; 2, wet gas meter; 3, gas washer; 4, glass filter; 5, glass column with soil; P1–P4, sampling ports.

To exclude biodegradation and indigenous respiration, γ-ray-sterilized (a dose of 25 kiloGray) and noncontaminated (control) soil samples were used, respectively. The headspace volume maintained aerobic conditions throughout the experiments. Concentrations of hydrocarbons, CO_2, and O_2 could be measured repeatedly through Viton septa without volatile loss, with frequency depending on the process rate. After termination of each test (all in triplicate), residual concentrations were determined by soil extraction.

Column Experiments

SBV was simulated in the installation shown in Fig. 3, in 4.3-L glass columns (60 cm × 9.6 cm i.d.), at the controlled temperature of 20°C (± 2.5°C). Soil of 5 kg (fraction <4 mm) contaminated with kerosene at the initial concentration of 2660 mg/kg, determined by extraction with CS_2, and water content of 6% (w/w), was packed to the height of 45 cm. SV and SBV were simulated using N_2 and CO_2-free air as flushing gases, respectively, with a constant up-flow rate of 40 $cm^3/cm^2/h$ (i.e., 1 dm^3/h).

Soil vapors in ports P2, P3, and P4 (headspace) were sampled for total volatile organic compounds (TVOCs) once a day, and CO_2 and O_2 were monitored continuously in the outlet gas.

A column with the reference (noncontaminated) soil was used as a control for indigenous respiration. Wet gas meters were used to determine the volume of the flushing gas that passed through the columns. To minimize adsorption, all pipe connections having contact with kerosene were made from either glass or Teflon™, and sampling ports were sealed with Viton caps. After termination soil was analyzed for total extractable organic compounds (TEOCs), water content, and pH.

All samples of soil vapors and headspace were transferred by 100-µL gastight syringes and analyzed for TVOCs immediately after collection by HP GC 5890 Series II with flame ionization detector (FID). Headspace samples were analyzed for CO_2 and O_2 on GC 8000 Series (Fisons Instruments) with thermal conductivity detector (TCD).

A Bruel & Kjaer Multi-Gas Monitor Type 1302, and an Industrial Emission Monitor Type 1311, associated with the PC software package BZ5156, were used for continuous measurements of CO_2 and O_2 in the outlet gas.

TEOCs were determined by extraction of 25 g of soil with 50 mL of carbon disulphide (CS_2).

Results and Discussion

Batch Tests

Biodegradation tests with soil artificially contaminated with kerosene showed that concentrations in soil up to 35000 mg/kg were not toxic for the indigenous population. The residual concentrations in soil as a result of kerosene biodegradation, calculated from the cumulative CO_2 production and O_2 consumption after 32 d of incubation, are presented in Table 2. The respiratory quotient, which is the molar ratio of CO_2 produced to O_2 consumed, was of 0.58–0.61.

A comparison of the CO_2 production for "fresh" and "aged" kerosene contamination (Fig. 4) showed much slower biodegradation for soil from the contaminated site. This may be the result of lower bioavailability of "aged" kerosene and/or the presence of some other contamination that may have a toxic effect on kerosene-specific degraders.

The saturation concentration of toluene in the gas phase inhibited biodegradation, as no substantial decrease of toluene concentrations in headspace was observed (Fig. 5A). The CO_2 production (Fig. 5B) and O_2 uptake (Fig. 5C) were lower than the indigenous respiration in control samples.

The inhibitory effect of toluene at high concentrations in soil and soil vapors may be due to its low octanol-water partitioning (log K_{ow} = 2.26–2.57) *(2)* and can be explained by the collapse of energy transduction system of the cytoplasmic membranes *(32)*.

At 75% of the toluene saturation concentration, biodegradation was observed, as the cumulative CO_2 production exceeded the control level, after a lag-phase of about 75 h, reaching approx 130 mg after 216 h (Fig. 5B). The final O_2 content in headspace dropped by 10 times to approx 2%.

Table 2
Results of Kerosene Biodegradation in Soil

C_i (mg/kg)	CO_2 prod. (cumulative in %)	O_2 cons.	C_{final} (mg/kg) CO_2[a]	O_2[a]	$R_{CO2/O2}$ mol/mol
5000	6.0	10.1	515	426	0.59
10,000	7.1	11.6	604	489	0.61
15,000	6.3	10.9	543	460	0.57
20,000	7.4	12.5	633	529	0.59
25,000	7.3	12.4	621	522	0.58
35,000	6.2	10.7	532	451	0.58

[a]Values calculated based on CO_2 and O_2 contents and mineralization reaction; C_i, initial soil concentration; C_{final}, residual concentration; $R_{CO2/O2}$, respiratory quotient.

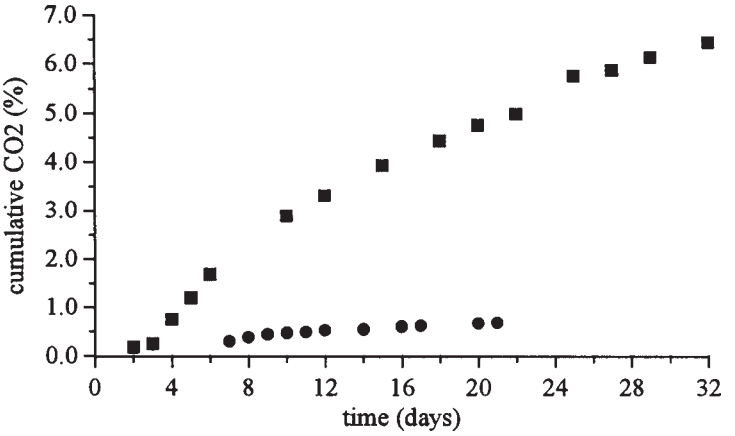

Fig. 4. CO_2 production during biodegradation of "fresh" and "aged" kerosene in soil. ■, Fresh kerosene; ●, aged kerosene.

Simulation of Bioventing

Mass balance of kerosene was based on measurements of TVOCs, CO_2, and O_2 using GC, M1302, and M1311 monitors, under the following assumptions:

1. Chemical formula (weighted average) of kerosene: $CH_{1.8}$ *(33)*, and of biomass: CH_2O.
2. Biomass production yield: $Y = 0.35$ and $Y = 0.5$.
3. Calculations based on the reactions:

for $Y = 0.35$ $$CH_{1.8} + 1.1 \cdot O_2 = 0.65 \cdot CO_2 + 0.55 \cdot H_2O + 0.35 \cdot CH_2O \quad (3)$$

for $Y = 0.5$ $$CH_{1.8} + 0.95 \cdot O_2 = 0.5 \cdot CO_2 + 0.4 \cdot H_2O + 0.5 \cdot CH_2O \quad (4)$$

4. Biodegradation modeled by first order kinetics, with the rate determined as *(9,27)*:

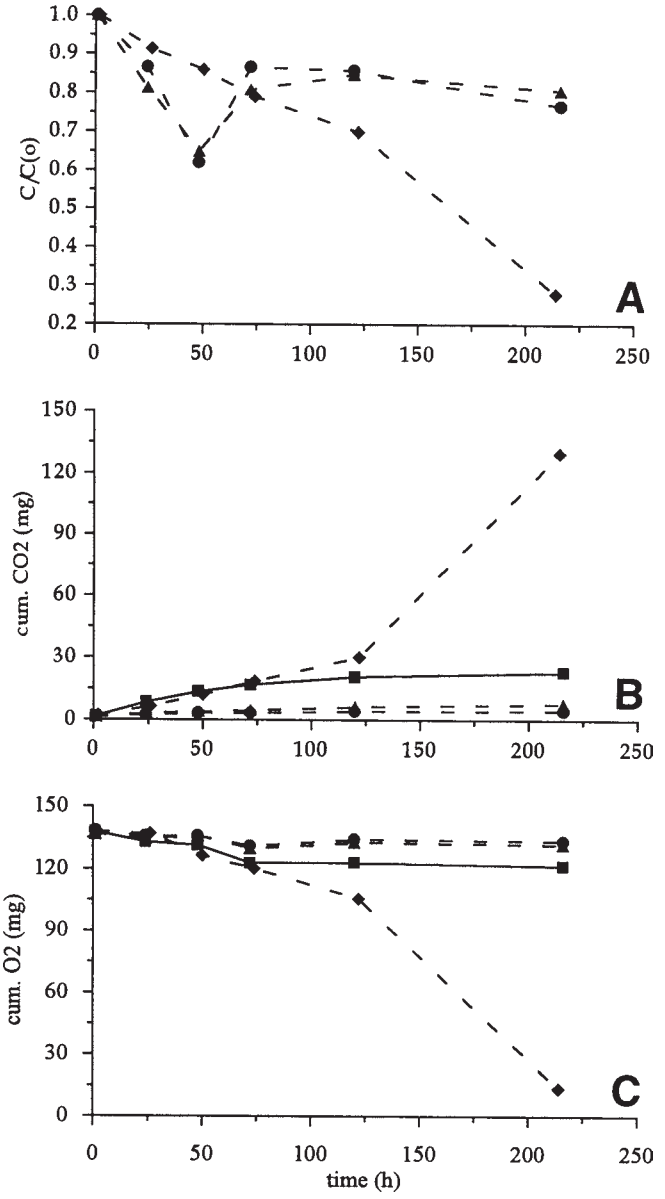

Fig. 5. Biodegradation of toluene at different concentrations. **(A)** Changes of toluene relative concentrations in headspace; **(B)** cumulative CO_2 production; **(C)** cumulative uptake of O_2. ■, control; ◆, 75% sat.; ▲, 100% sat.; ●, 150% sat.

$$r_{\text{deg}} = 1/2 \cdot \{[(CO_2)_{t1} + (CO_2)_{t2}]/100\} \cdot \triangle Q_a \cdot d_{CO2} \cdot (MW_{\text{norm}}/Y) \quad (5)$$

$$r_{\text{deg}} = 1/2 \cdot \{[(O_2)_{t1} + (O_2)_{t2}]/100\} \cdot \triangle Q_a \cdot d_{O2} \cdot (1/R_{O2/\text{ker}}) \quad (6)$$

where r_{deg} is the biodegradation rate (mg/h), $[CO_2]$, $[O_2]$ are CO_2 and O_2 contents (%) in the soil gas at t_1 and t_2, ΔQ_a is air volume that passed through

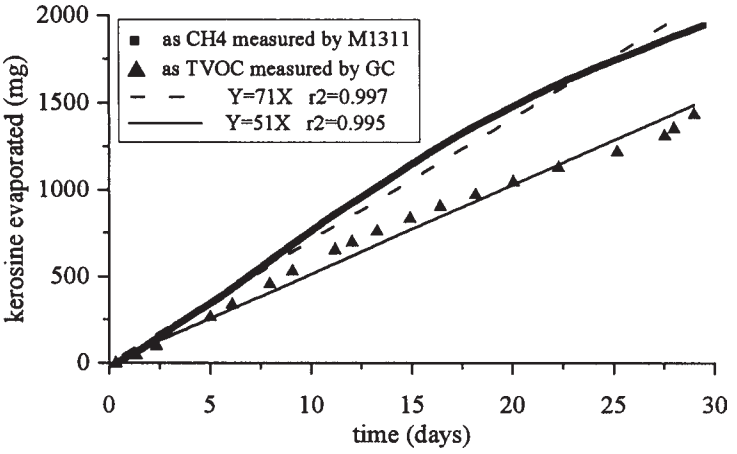

Fig. 6. Evaporation of kerosene during SBV.

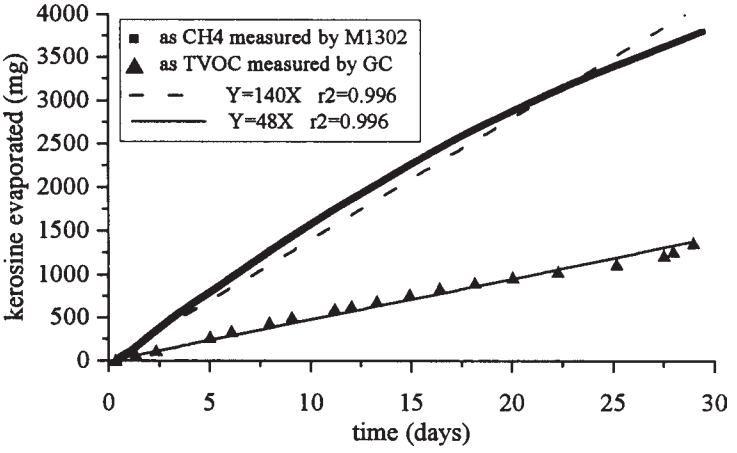

Fig. 7. Evaporation of kerosene during SV.

the column between measurements (L/h), d_{CO2} and d_{O2} are densities of CO_2 and O_2 (mg/L), Y is the biomass production yield (mass of C in biomass per mass of C in substrate), MW_{norm} is molecular weight of kerosene normalized on carbon (mg/mg), $MW_{norm} = 0.31$, $R_{O2/ker}$ is O_2 required for biodegradation (mass of O_2 per mass of substrate degraded), $R_{O2/ker} = 2.21$ (at $Y = 0.5$) and $R_{O2/ker} = 2.55$ (at $Y = 0.35$).

5. Evaporation rates were calculated as:

$$r_{evap} = \tfrac{1}{2} (C_{t1} + C_{t2}) \cdot \Delta Q_a \qquad (7)$$

where r_{evap} is the evaporation rate (mg/h), C_{t1}, C_{t2} are concentrations of kerosene (TVOC), or as the CH_4 signal, in the outlet gas (mg/L) at t_1 and t_2.

The kinetics of kerosene evaporation during SV and SBV are presented in Figs. 6 and 7 and the calculated rates and amounts evaporated are given in Table 3.

Table 3
Evaporation Rates (r_{evap}) and Kerosene Evaporated (m_{evap}) During SV and SBV

Process/method	GC (TVOC) r_{evap} (mg/d)	GC (TVOC) m_{evap} (mg)	M1311 (as CH_4) r_{evap} (mg/d)	M1311 (as CH_4) m_{evap} (mg)	M1302 (as CH_4) r_{evap} (mg/d)	M1302 (as CH_4) m_{evap} (mg)
SV	48	1392	—		104	4060
SBV	51	1479	71	2059	—	

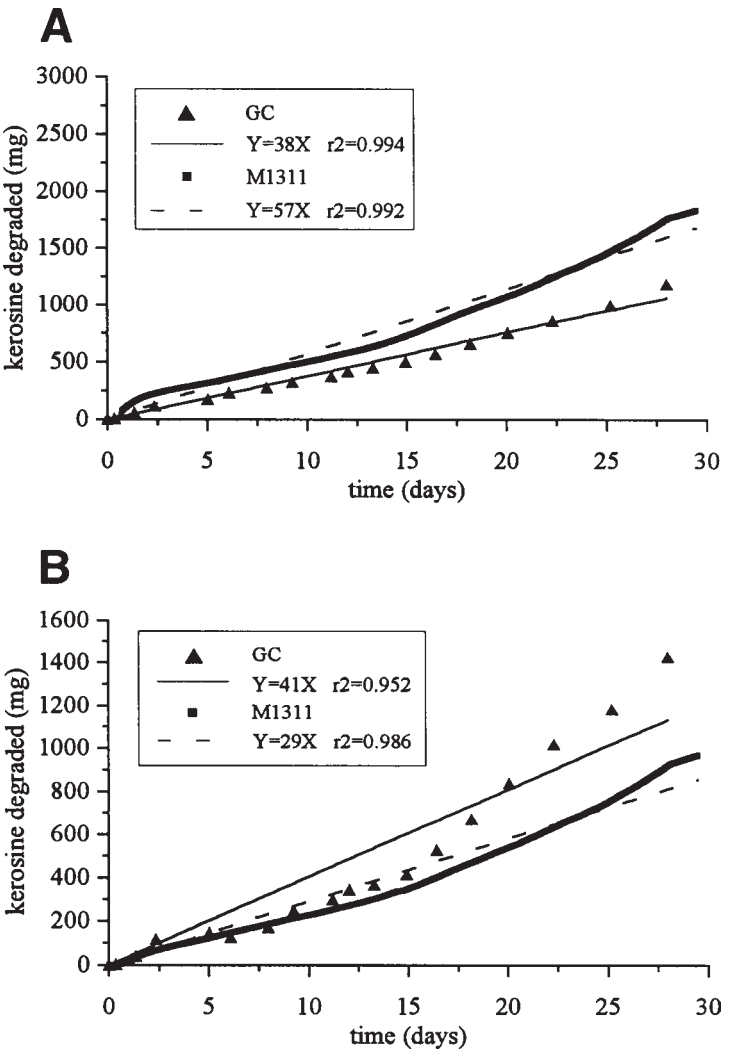

Fig. 8. Kinetics of kerosene biodegradation during SBV based on concentrations of **(A)** CO_2 and **(B)** O_2, in the outlet gas (for biomass production yield $Y = 0.5$).

Biodegradation kinetics for different estimation methods are compared in Figs. 8 and 9.

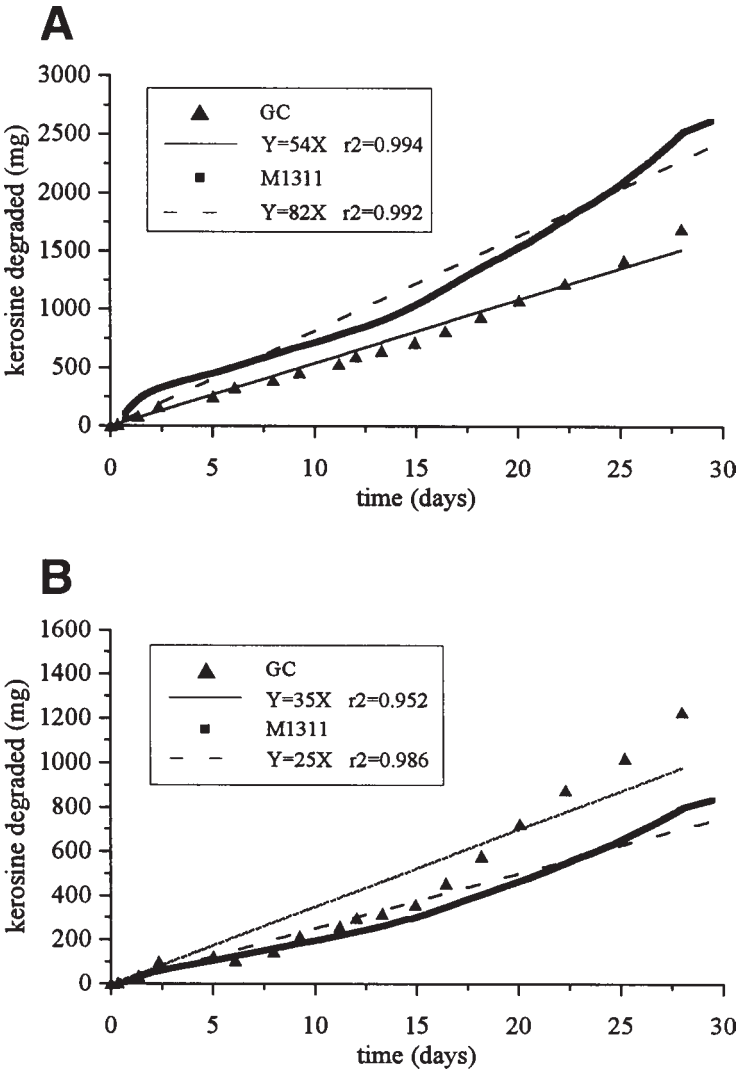

Fig. 9. Kinetics of kerosene biodegradation during SBV based on concentrations of **(A)** CO_2 and **(B)** O_2 in the outlet gas (for biomass production yield $Y = 0.35$).

SV resulted in the removal of 1392 mg of kerosene (Table 3), and in a decrease of the initial concentration in soil by 10% after 29 d, for which 713 L of air was used.

SBV showed comparable evaporation (Fig. 6) and simultaneous biodegradation (Figs. 8 and 9), at the rate of 25–82 mg/d (Table 4), which contributed to the subsequent removal of 6–12% of kerosene initially present in soil.

The overall SBV efficiency was within the range of 17–23% (Table 5), depending on the estimation method used, for which the same time was required, as compared to SV.

Table 4
Biodegradation Rates (r_{deg}) and Kerosene Degraded (m_{deg}) During SBV

Determination method/yield	GC r_{deg} (mg/d)	GC m_{deg} (mg)	M1311 r_{deg} (mg/d)	M1311 m_{deg} (mg)
Calculated from CO_2 measurements				
$Y = 0.35$	54	1566	82	2378
$Y = 0.5$	38	1102	57	1658
Calculated from O_2 measurements				
$Y = 0.35$	35	1015	25	725
$Y = 0.5$	41	1189	29	841

Table 5
Results of SBV

	Biodegraded (%)				Efficiency (%)			
	GC		M1311		GC		M1311	
Evaporated (%)	0.5	0.35	0.5	0.35	0.5	0.35	0.5	0.35
Based on CO_2 production								
11	8	12	12	18[a]	19	23	23	29[a]
Based on O_2 uptake								
11	9	8	6	5[a]	20	19	17	16[a]

[a]Results not taken into account (the highest and the lowest values in the range).

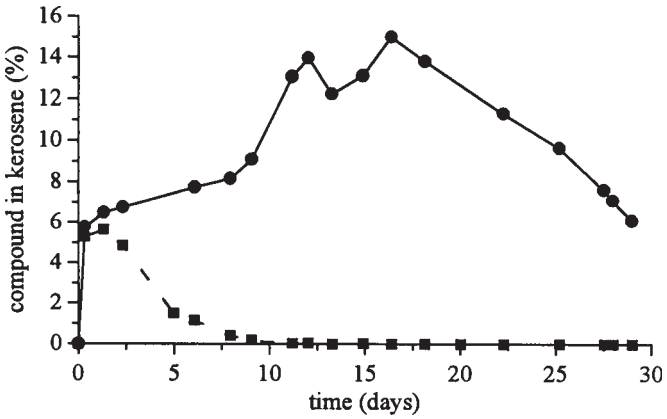

Fig. 10. Evolution of toluene and decane fractions of TVOCs in the outlet gas during SBV. ■, toluene; ●, decane.

Toluene and decane concentrations in the outlet gas were monitored, respectively, to study the behavior of volatile and semivolatile components of kerosene during SBV and SV (Figs. 10 and 11). The results indicate sequential decrease of gaseous concentrations of hydrocarbons according to their volatility. Initial toluene-to-decane ratio in the outlet gas of 80–90% dropped to 5–15% already after approx 6 d of SBV and SV, respectively.

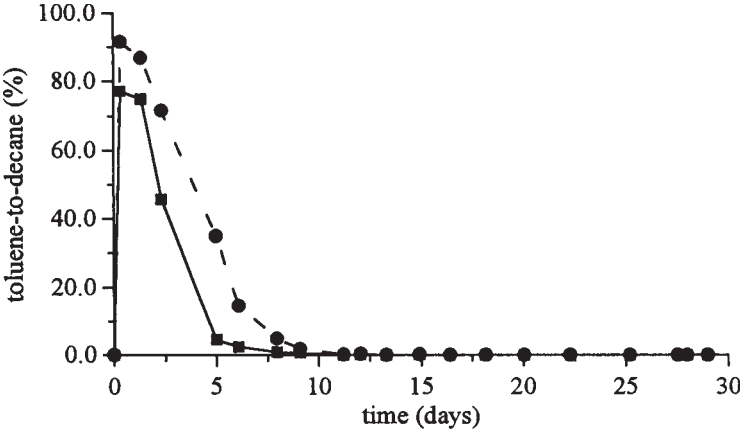

Fig. 11. Evolution of toluene–to–decane ratio of TVOCs in the outlet gas. d, SBV; j, SV.

Table 6
Comparison of SBV vs SV Results

Process	Remediation time (d)	Gas used (L)	Effectiveness of air used (L/mg)	Removal efficiency (%)	E:B[a] ratio (%)
SBV	29	713	0.53	17–23	11:16–11:12
SV	29	738	0.23–0.31	10	—

[a]E, evaporation; B, biodegradation.

From the results presented in Table 6 it may be concluded that the removal efficiency during SV of 10% was comparable to the removal of 11% kerosene by evaporation during SBV. After 29 d of SBV, approx 6–12% of kerosene was biodegraded, depending on the estimation method.

Biodegradation of kerosene increased SBV efficiency by 70–130%, and the evaporation-to-biodegradation ratio was evaluated within the range from 11:16 to 11:12. This contribution to the overall removal of kerosene would probably be even more spectacular at lower kerosene concentrations in soil during the "tailing" phase, with diffusion-limited desorption, and much lower evaporation of less volatile kerosene constituents.

The average effectiveness of gas used for evaporation was 0.53 L/mg of removed kerosene, as compared to 0.23–0.31 L/mg in case of SBV. To increase the effectiveness of the air used, different flow regimes (varying flow rates, intermittent flows) may be preferred, as long as minimum oxygen aeration status in soil that is not limiting biodegradation is ensured. A long-term column and large-scale experiments, under controlled conditions, are recommended to confirm the results of bench-scale tests and to compare the results for different soil and contamination.

A poor predictability of the residual contaminant concentrations is one of the main problems of *in situ* soil remediation techniques, using biodegradation like SBV.

The residual kerosene concentration after SBV is governed by biodegradability and bioavailabilty of contaminants. Only the fraction of kerosene that is both available and degradable can be removed biologically.

The access of degrading microorganisms to contaminants is essential for biodegradation. Hydrophobic kerosene compounds are often present in soil as sorbed and/or separate phases, i.e., not directly available to the microorganisms. Transport of contaminants to the microorganisms is the factor limiting biodegradation, and bioavailability is governed by physical–chemical processes. The potential for bioremediation as a treatment technique is mainly determined by the mass transfer dynamics of kerosene hydrocarbons.

The microbial uptake of the poorly available part of kerosene, present as NAPL, may include compounds from the liquid–liquid interface *(34)*, for which emulsification of the NAPL is essential. In the direct uptake of the NAPL, microorganisms themselves may produce an emulsifying effect as a result of the presence of extracellular emulsifying surface-active agents.

The overall biodegradation rate in the absence of NAPL is controlled by the desorption rate and not by the activity of degrading microorganisms. The practical effect of diffusion out of soil aggregates and other limitations of desorption kinetics is a decrease in the contaminant removal rate and, consequently, the increased clean-up time.

Acknowledgments

The research was carried out at the Department of Environmental Technology, Wageningen Agricultural University, the Netherlands, and financed partially by Arcadis b.v., Research and Development, Waalwijk, The Netherlands. Authors would like to acknowledge Prof. W. H. Rulkens for his scientific support.

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