

Enhancing biodegradation of petroleum hydrocarbons through soil venting

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Abstract

Aerobic bioremediation of jet fuel in contaminated soil in an unsaturated vadose zone at Hill Air Force Base, Utah, was stimulated by soil venting. *In situ* respiration studies conducted at the contaminated site revealed that microbial respiration was occurring as a result of oxygen introduced by the venting process. Stable isotopic ratios (¹³C/¹²C) in soil gas were measured to confirm a biogenic source of carbon during venting of the contaminated soil. Although volatilization was the primary mechanism of removal, from 15 to 25% of the jet fuel was biodegraded *in situ*, making soil venting a promising approach for enhancing the aerobic remediation of contaminated vadose zones.

Introduction

After decades of neglect, the U.S. now faces the task of cleaning soil and groundwater contaminated by hydrocarbon fuels [1]. Many petroleum hydrocarbons biodegrade if indigenous soil bacteria have adequate oxygen and nutrients. Because of oxygen limitations, however, natural biodegradation is frequently too slow to prevent the spread of contamination. Virtually all sites require enhancement of natural processes to accelerate biodegradation.

Over the last 20 years, enhanced biodegradation of hydrocarbons has been investigated as a means of treating petroleum distillate hydrocarbon components in contaminated groundwater [2]. Less emphasis has been placed on enhancing biodegradation of fuel residues in the unsaturated zone. Conventional enhanced bioreclamation uses water to carry oxygen or alternative electron acceptors to the contaminated groundwater or unsaturated zone. However, a recent field experiment using aqueous H₂O₂ for oxygen transfer at a site

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contaminated by jet fuel was unsuccessful because of rapid H_2O_2 decomposition and resulting poor oxygen distribution within the contaminated zone [3]. Soil samples from the site also revealed that little or no reduction in hydrocarbon concentration, either by biodegradation or hydraulic flushing, occurred even though up to 190 pore volumes of the nutrient-amended groundwater had passed through the soil [4].

One important limiting factor in bioremediation of soils contaminated with hydrocarbons is the lack of oxygen to support microbial metabolism [5,6]. Soil venting is a promising method for overcoming this limitation for supplying oxygen.

The Texas Research Institute [7,8] conducted laboratory studies indicating that as much as 38% of the removal of gasoline from vented soils may have been the result of biodegradation and that venting did stimulate microbial degradation. Wilson and Ward [9] discuss the potential for using air as an oxygen carrier to stimulate hydrocarbon biodegradation in the vadose zone. They point out that this could potentially be 1,000 times more efficient for oxygen transfer than using water as a carrier.

Bennedsen et al. [10] conclude that soil venting provides large quantities of oxygen to the vadose zone and may therefore be used to enhance biodegradation. Connor [11] claims to have induced biodegradation by venting a gasoline-contaminated soil pile; however, his conclusion was based only on temperature increase in the treatment zone, and no other supporting evidence was presented.

Soil gas oxygen and hydrocarbon measurements were used to demonstrate vadose zone *in situ* biodegradation as the result of passive oxygen diffusion at a fuel hydrocarbon-contaminated site in Traverse City, Michigan [12]. Based upon these observations, Ostendorf [12] concluded that biodegradation may be further stimulated by the injection of air into the vadose zone in the areas of highest concentration.

Field applications using soil venting to enhance biodegradation have been reported by Steps [13,14], Hinchee et al. [15], and Ely and Heffner [16]. Ely and Heffner of the Chevron Research Company have patented a process that involves extracting gas from a hydrocarbon-contaminated site to stimulate biodegradation. Unfortunately, the majority of the data on the Chevron research remains proprietary [17]. Steps [13,14] describes a similar Dutch process; however, no supporting data are published. Hinchee et al. [15] also describe a process with little supporting data.

The objective of this study was to describe an application of the soil venting technique at a jet fuel-contaminated site and to present evidence for biodegradation.

Site description and process design

In January 1985, an estimated 27,000 gallons (100,000 liters) of JP-4 jet fuel

were released when an automatic overflow prevention device failed at Hill Air Force Base near Ogden, Utah. The contaminated area is in a delta outwash of the Weber River known as the Provo Formation. This surficial formation extends from the surface to a depth of approximately 50 feet (15 m) and is composed of mixed sand and gravel with occasional clay stringers. Because of limited atmospheric precipitation and high evaporation rates in this area, groundwater in the Provo Formation occurs only in discontinuous perched zones, with soil moisture averaging less than 6% in the vadose zone that extends to a depth of approximately 600 feet (190 m). Approximately 20,000 cubic yards (15,000 m³) of soil were contaminated by this JP-4 spill at Hill Air Force Base. Soil samples collected from the contaminated zone indicated hydrocarbon concentrations up to 15,000 mg/kg, with an average concentration of approximately 1,500 mg/kg [18]. Contaminants were unevenly distributed to depths of 50 feet (15 m).

Figure 1 shows the 15 vertical vents installed on a 40-foot (12-m) grid across the contaminated site. A background vent was installed in an uncontaminated location in the same geological formation approximately 700 feet (200 m) north of the site. Vent wells were drilled to approximately 50 feet (15 m) below the ground surface and screened from 10 to 50 feet (3 to 15 m) below the surface. The plastic liner covering a portion of the site was used to prevent surface air from short-circuiting the system. In addition to the vents, monitoring points were installed throughout the sites at various depths to allow vacuum and soil gas composition measurements to be taken during the field study.

Venting was initiated on 18 December 1988 at a rate of approximately 26

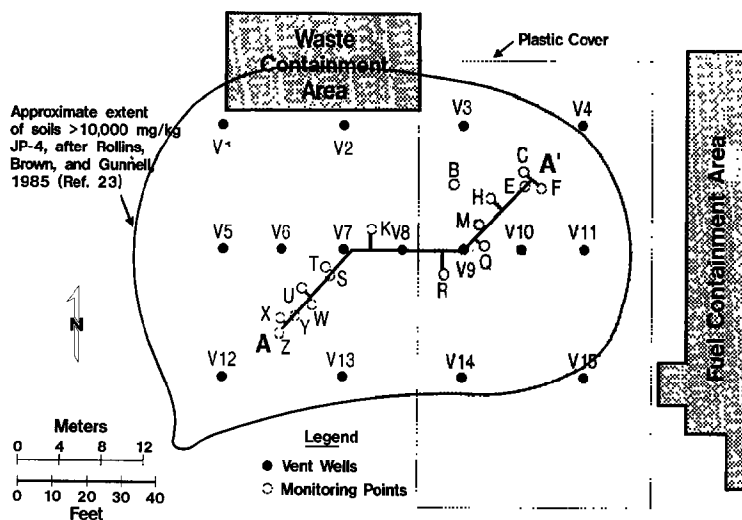


Fig. 1. Site map illustrating the locations of vent wells and monitoring points.

acfm ($44 \text{ m}^3/\text{h}$). The off-gas was treated by catalytic incineration, and it was initially necessary to dilute the highly concentrated vent gas to remain below explosive limits and within the incinerator's hydrocarbon operating limits. The venting rate was gradually increased to approximately $1,500 \text{ acfm}$ ($2,500 \text{ m}^3/\text{h}$) as hydrocarbon concentration levels dropped during venting. During the period between 18 December 1988 and 26 May 1989 approximately $45,000,000 \text{ acf}$ ($1,300,000 \text{ m}^3$) of soil gas were extracted from the site.

In situ respiration studies

To determine site-specific oxygen utilization rates, *in situ* respiration tests were conducted at the monitoring points throughout the site during periods of venting system shutdown. These tests were conducted three times during system operation corresponding to vented air volumes of $42,000 \text{ acf}$ ($1,200 \text{ m}^3$), $540,000 \text{ acf}$ ($15,000 \text{ m}^3$), and $45,000,000 \text{ acf}$ ($1,300,000 \text{ m}^3$). A test was conducted by shutting down the venting system, evacuating three volumes of each vent well, and collecting vent well gas samples for oxygen and carbon dioxide measurement periodically over time at a number of vent wells.

Prior to soil venting, soil gas oxygen concentrations throughout the site were below 1 vol.% (Fig. 2) for all but the shallow monitoring points (X, U, S, C, and Z), while oxygen levels in the background well were essentially at the atmospheric levels. After 6 months of venting and the extraction of approximately $45,000,000 \text{ acf}$ ($1,300,000 \text{ m}^3$) of soil gas, oxygen levels throughout the site increased significantly at all monitoring points (Fig. 3).

Figure 4 shows the site oxygen concentrations after 14 days of system shutdown following venting of $42,000 \text{ acf}$ ($1,200 \text{ m}^3$) of soil gas. The decline in

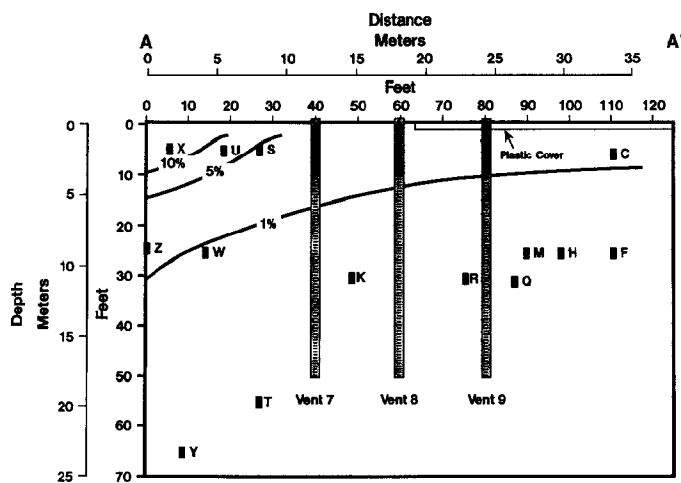


Fig. 2. Oxygen concentrations in soil gas on 7 December 1988 prior to venting.

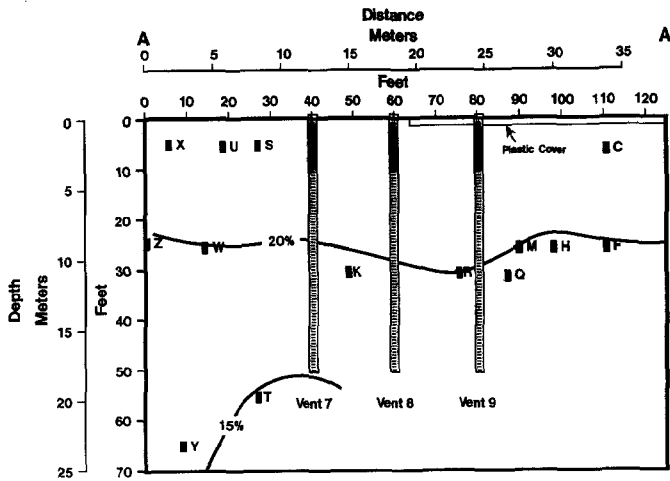


Fig. 3. Oxygen concentrations in soil gas on 26 May 1989.

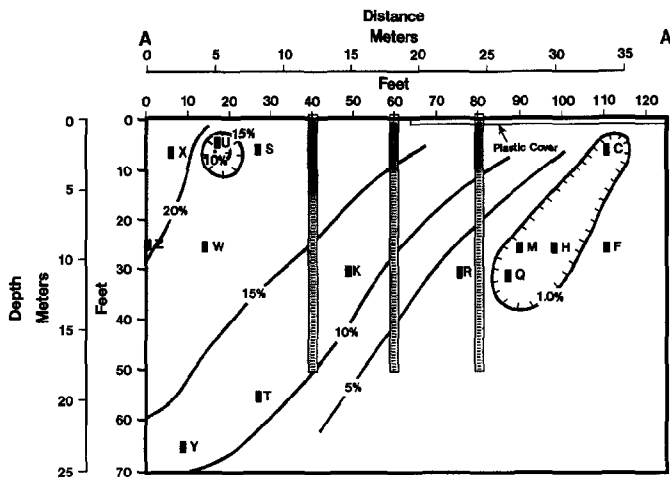


Fig. 4. Oxygen concentrations in soil gas on 9 June 1989 at the conclusion of *in situ* respiration tests.

oxygen concentration is consistent with first order kinetics and calculated oxygen uptake rates throughout the site range from $10.9 \times 10^{-4} \text{ min}^{-1}$ to non-detectable. Figure 5 illustrates typical profiles of oxygen decline at Monitoring Point Y (65 ft or 20 m below the land surface), which is located in one of the least contaminated areas of the site. Results from Monitoring Point Y indicate that during the incremental treatment of the contaminated soil over the venting period, the microbial activity, as observed from oxygen uptake rates, gradually declined to nondetectable levels at the end of the study.

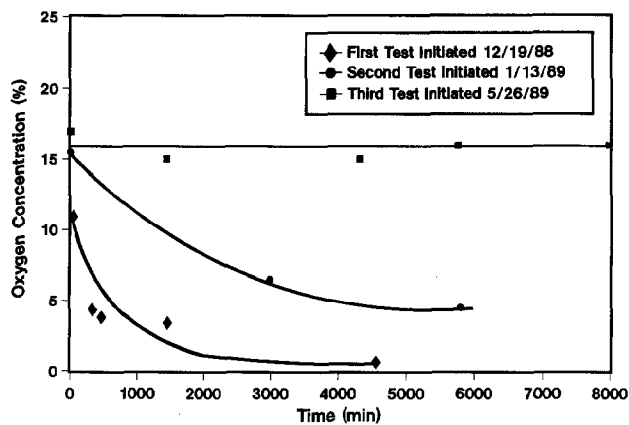


Fig. 5. Results of *in situ* respiration tests at Monitoring Point Y.

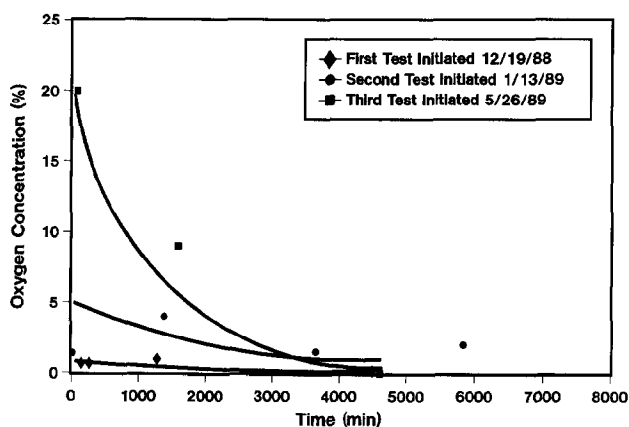


Fig. 6. Results of *in situ* respiration tests at Monitoring Point M.

TABLE 1

Soil gas oxygen and carbon dioxide levels measured in the background vent

Date	O ₂ (Vol.%)	CO ₂ (Vol.%)
6 December 1988 ^a	21.0	< 0.25
17 December 1988	-	< 0.2
23 February 1989	20.8	0.2
1 March 1989	-	< 0.2
20 April 1989	20.8	0.25
26 May 1989	20.5	< 0.25
5 June 1989	20.5	0.5
14 June 1989	-	0.2

^aThis sample was collected prior to any venting, and was considered typical of background uncontaminated soil gas.

In contrast, results at Monitoring Point M (25 ft or 7.6 m below the land surface), which was in a more contaminated portion of the site, indicate that initially higher respiration rates may have prevented significant oxygenation at this location (Fig. 6). Table 1 summarizes some of the oxygen and carbon dioxide concentrations measured in the background vent. It is apparent that significantly more respiration was occurring in the JP-4 contaminated areas than at the uncontaminated location.

Biodegradation estimates

Oxygen (O_2), carbon dioxide (CO_2), and hydrocarbon concentrations were measured in the undiluted off-gases during the first 70 days of the project. During this period, 8,600,000 acf (240,000 m^3) of air had been vented. Figure 7 illustrates the O_2 and CO_2 concentrations in the off-gas. The large drop in O_2 and rise in CO_2 concentrations at approximately 50 days were related to conditions at the site following a 9-day shutdown period. These O_2 and CO_2 concentrations differ markedly from those measured in the uncontaminated background vent where steady-state oxygen and carbon dioxide levels were measured at 20.9 and 0.1 vol.%, respectively.

To quantify the extent of biodegradation at the site, all vent gas constituents were converted to an equivalent carbon (C) basis. JP-4 fuel-C was converted to an equivalent carbon (C) basis. JP-4 fuel-C was determined based on direct readings of a total hydrocarbon analyzer calibrated to hexane, corrected by the ratio of C to hexane (72 g C/86 g hexane).

Calculations for CO_2 were similar, with CO_2 -C calculated by the product of the CO_2 concentration and the molar mass fraction of C in CO_2 (i.e., 12 g C/44 g CO_2). Oxygen equivalent C, defined as the theoretical oxygen demand for

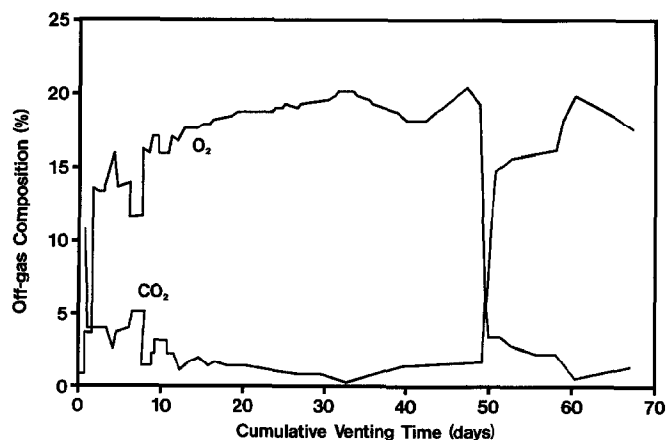


Fig. 7. Oxygen and carbon dioxide concentrations versus time in the venting of off-gas.

complete mineralization of hexane, was determined based on the oxygen deficit (O_2 level below that in the gas vented from the uncontaminated location) measured in the vent gas over time, the oxygen equivalent required to mineralize hexane ($3.53 \text{ g } O_2/\text{g hexane}$), and the C-hexane ratio given above. Note that estimates of biodegradation are based on oxygen consumption and carbon dioxide production. These estimates only account for the JP-4 actually mineralized, JP-4 converted to biomass, or that which may have been partially degraded to intermediate products during the test period was not accounted for.

Based on these calculations, the mass of JP-4 as carbon removed and degraded between 18 December 1988 and 1 April 1989 was 25,000 pounds (11,300 kg) volatilized and 4,700 to 4,800 pounds (2,100 to 2,200 kg) biodegraded (calculated from CO_2 production and O_2 consumption, respectively). Because of possible inorganic sources and sinks of CO_2 , it is believed that biodegradation estimates based upon O_2 utilization are more accurate than those derived from CO_2 production values.

The fraction of JP-4 that was biodegraded dropped rapidly from initial values of approximately 30% to steady-state values of approximately 15% within 30 days after venting began. This decline may be an artifact of increasing venting rates, which would increase volatilization but would have little effect on biodegradation. It is also possible that this decline could be due to the initial removal of the more biodegradable components of JP-4 leaving more recalcitrant residuals or to decreasing soil moisture, and therefore microbial habitat during the venting period. In a laboratory study of composited soils from this site, to which 5,000 mg/kg JP-4 had been added, Hinchee and Arthur [19] found a biodegradation rate increase of up to 50% when soil moisture content was increased from 6% to 18% (on a weight basis).

Carbon isotope studies

To confirm the source of carbon dioxide in the vent gas, the isotopic ratios of carbon ($^{13}C/^{12}C$) were determined. Four gas samples were collected in May and June of 1988 — one from the background vent, one from a bioactive sampling location at Monitoring Point M, one from vent 10 during active vent, and one atmospheric sample. The samples were collected in Tedlar™ bags after passing through activated carbon filters to remove any hydrocarbon vapor. Carbon dioxide in the gaseous samples was isolated from other components by a series of freeze-thaw steps at dry ice-alcohol and liquid oxygen temperatures [20]. The carbon dioxide gas was analyzed using a mass spectrometer and the isotopic ratios, R , are reported as parts per thousand (per mil) deviation from an isotopic standard (PDB) [21] using the “ δ ” notation

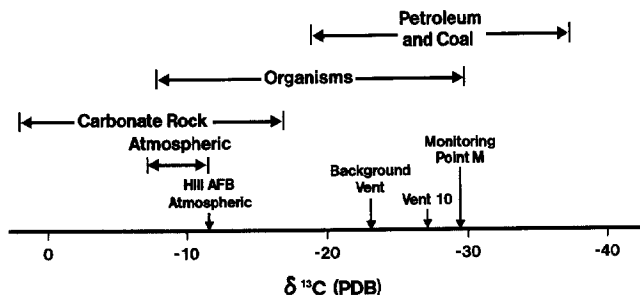


Fig. 8. Carbon isotopic composition of various sources of carbon (adapted from Ref. [22]). Also shown are the isotopic compositions of samples from the Hill Air Force Base site.

$$\delta^{13}\text{C} = \frac{R_{\text{sample}} - R_{\text{std.}}}{R_{\text{std.}}} \times 1000 \quad (1)$$

where R is the $^{13}\text{C}/^{12}\text{C}$ ratio in the sample or the standard.

The carbon isotopic ratios of the four gas samples taken from the Hill Air Force Base site are shown in Fig. 8. Isotopic compositions of the atmospheric sample and the sample from the background vent are similar to those reported for atmospheric CO_2 and plant respiratory CO_2 , respectively [22]. Vent 10 and Monitoring Point M samples have lower (more negative) $\delta^{13}\text{C}$ values compared with background CO_2 . These lower $\delta^{13}\text{C}$ values suggest a source of carbon such as petroleum hydrocarbons [20], confirming the mineralization of JP-4 constituents at the site.

Summary and conclusions

The results of this study indicate that aerobic biodegradation of JP-4 fuel did occur in the vadose zone at the Hill Air Force Base site. Biodegradation was increased by soil venting at this site because, prior to venting, biodegradation appears to have been oxygen limited. The soil venting system, which was designed to volatilize the JP-4, stimulated *in situ* biodegradation with no added nutrients or moisture. In this study, approximately 15% of the documented JP-4 removal observed at the field site was the result of microbial-mediated mineralization to CO_2 . Additional biological JP-4 removal by conversion to biomass and degradation products no doubt occurred, but was not quantified.

Based on this study, the following recommendations are made for monitoring conventional soil venting of fuel hydrocarbon-contaminated soil: (1) soil gas hydrocarbon, CO_2 , and O_2 profiles should be determined prior to venting; (2) hydrocarbon, CO_2 , and O_2 in the off-gases should be measured to document biodegradation and to aid in identifying the end point for venting; and (3) an

estimate of noncontaminate respiration should be developed either through background measurements of CO₂ and O₂ in an uncontaminated location or by means of carbon isotopic analyses.

Further studies of fuel biodegradation in unsaturated soils are needed to develop a better understanding of the effects of such variables as oxygen content, nutrient requirements, soil moisture, contaminant levels, and soil type on the limitation and optimization of soil vacuum extraction-augmented bioremediation of contaminated field sites. In addition, further studies of gas transport in the unsaturated vadose zone are needed to ensure adequate design of air delivery systems. A major goal of these optimization steps should be to reduce overall volatile emissions.

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