Environ. Sci. Technol. **2000**, *34*, 3167−3173

Physical versus Biological Hydrocarbon Removal during Air Sparging and Soil Vapor Extraction

C. MARJORIE AELION*,†,‡ AND
BRIAN C. KIRTLAND†

Department of Environmental Health Sciences and Marine Science Program, University of South Carolina, Columbia, South Carolina 29208

Although physical removal of contaminants may account for the majority of mass of petroleum hydrocarbons (PH) removed using air sparging and soil vapor extraction (AS/SVE), biological processes contribute to mass removal both during system operation and during system shutdown. Biodegradation rates are difficult to measure during active AS/SVE due to the forced entry of air. This study examined the relative rates of physical and biological removal of PH during AS/SVE. Before system startup, soil gas CO_2 and O_2 were measured to estimate biodegradation rates based stoichiometrically on the mass of hexane. Biodegradation rates calculated from average CO_2 production (0.08% d^{-1}) were 1.3 times less than those based on average O_2 utilization (0.26% d^{-1}). A simulation model (Stella II) incorporating air injection and microbial respiration measured during AS/SVE shutdown predicted initial O_2 concentrations during AS/SVE well but overestimated steady-state O_2 by up to 2.5% potentially because respiration may be underestimated if more O_2 depletion occurred during AS/SVE than was measured when the system was off. Although biodegradation accounted for 77 times less contaminant mass removal than physical removal, biological contaminant removal may be underestimated using standard respiration tests.

Introduction

The use of in situ technologies to address petroleum hydrocarbon contamination has increased substantially, including bioventing, bioremediation, air sparging, and intrinsic bioremediation (*1*). Of these, air sparging (AS) and soil vapor extraction (SVE) have gained in popularity for volatile contaminants (VOCs). Using this technology, air is injected into the subsurface to strip the contaminants from the groundwater while the soil vapor extraction sucks VOCs from the vadose zone. While AS/SVE is considered a viable technology in highly permeable soils, it is considered less useful in low permeability sediments. Some approaches to improve AS/SVE removal rates in low permeability sediments include enhancing vapor flow with hydraulic fracturing (*2*) and injecting high volumetric flow rates of heated air (*3*). The addition of oxygen during AS/SVE also impacts the biodegradation of VOCs. The relative contribution of biodegradation to contaminant removal is difficult to measure during AS/SVE. It is assumed that, during initial operation of AS/SVE, physical removal will account for the majority of mass removal. As contaminant concentrations decrease, biological removal may play a greater role in contaminant removal.

Biodegradation rates are normally estimated from the consumption of O_2, the production of CO_2, or the decrease in contamination measured when the AS/SVE system is turned off. Each generates different biodegradation rates and may produce variable estimates of mass removal when extended to long time periods. The first objective of this study was to determine whether O_2 utilization rates, and subsequently biodegradation rates, calculated in respirometry tests during AS/SVE system shutdown were comparable to those estimated during AS/SVE in a simulation model (Stella II) (*4*). The second objective was to compare biological and physical petroleum mass removal during AS/SVE in our low permeability sediments for which physical removal was expected to be less than that reported in more permeable sediments.

Methods and Materials

A former gas station in Columbia, SC, is located in the transition zone between the Appalachian Piedmont and the Upper Atlantic Coastal Plain. The sediment consists of low-grade metamorphic rock with alternating laminae of fine sands, silts, and clays. The site contains three general strata: 0−4.6 (approximately) m was dense clay; 4.9−6.2 m was medium sandy with angular pebbles; and 6.2−7.6 m was medium sand with seams of clay (*5*). Water-saturated hydraulic conductivity (K_{sat}) was approximately 1.6−3.4 × 10^{-4} cm s^{-1} from 4.9 to 6.2 m and 6.4 × 10^{-7} to 4.8 × 10^{-5} cm s^{-1} from 6.2 to 7.6 m (*6*). Intrinsic permeability (k) ranged from 1.6 to 3.4 × 10^{-9} cm^2 from 4.9 to 6.2 m and from 6.5 × 10^{-12} to 4.9 × 10^{-10} cm^2 from 6.2 to 7.6 m. The water table fluctuated but was approximately 6.5−6.7 m below land surface (bls). Groundwater flow was northeast at 3.2−9.5 × 10^{-6} cm s^{-1} (*7*).

The AS/SVE system consisted of a series of two parallel sets of wells (Figure 1). One set, SVE 1−6, contained only SVE wells. The second set, AS/SVE 7−12 contained coupled AS and SVE wells. SVE wells were screened over a 3-m interval from 4.3 to 7.3 bls. The SVE wells were constructed of 10 cm diameter PVC piping and connected to a 5.2 kW vacuum pump (pressure, 6 in. of Hg; flow rates, 50 cm h^{-1} after correcting for bleeder air). Six 10 cm (diameter) AS wells were installed 1.5−2.1 m below the water table with 3 m of screened PVC piping extending into the saturated zone. The AS wells were connected to a 2.2-kW compressor, which forced air into the saturated zone (1−2 psi; flow rates, 0.6−7.5 cm h^{-1}), approximately 8 m bls.

A series of soil vapor probes, P-1 through P-8, consisting of four 0.6 cm (diameter) nested sampling tubes was installed at discrete vertical intervals above the water table (4.9, 5.5, 6.1, and 6.7 m bls) to give a more detailed description of gas movement through the vadose zone. P-1 and P-5 lay in the line of probes perpendicular to the SVE wells, P-6 was adjacent to SVE 1, and P-8 was outside the AS/SVE system by approximately 10 m (Figure 1). The probes were point values, and the SVE wells were spatially integrated measures.

O_2 and total combustible hydrocarbons (TCH) (GasTech GT201; O_2 range 0−21%), and CO_2 (GasTech RA411A; range 0−4.975% vol/vol) were measured using hand-held meters and verified by a gas chromatograph (GC) equipped with a thermal conductivity detector (Varian 3400) and a Carboxen 1000 1/8 in. ss packed column. TCH were detected by a hand

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* Corresponding author phone: (803)777-9122; fax: (803)777-3391; e-mail: aelionm@sc.edu.

† Department of Environmental Health Sciences.

‡ Marine Science Program.

10.1021/es9908772 CCC: $19.00 © 2000 American Chemical Society
Published on Web 06/28/2000

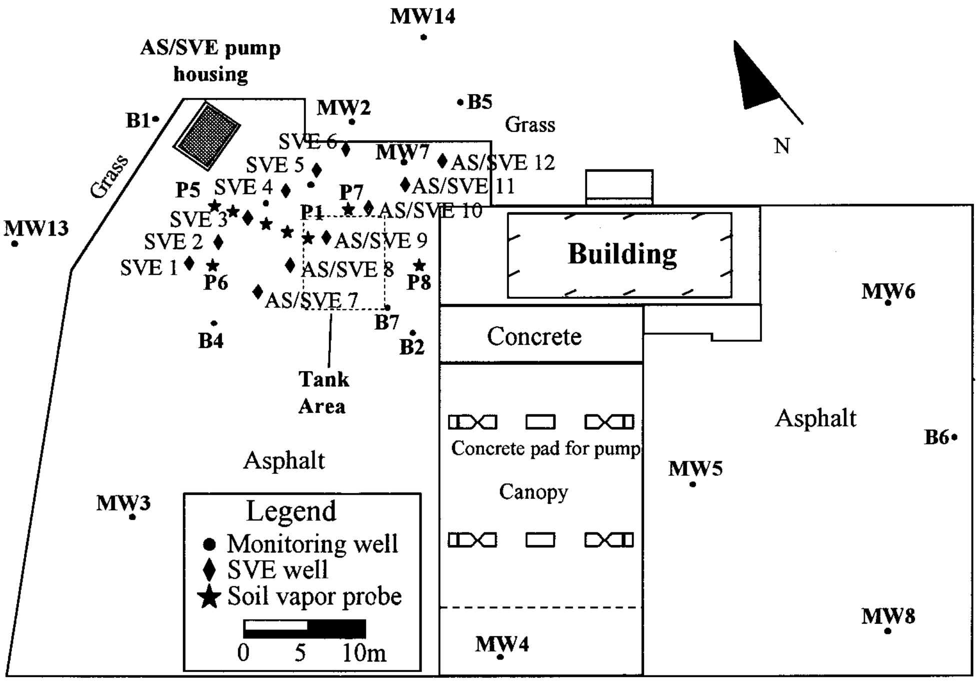

FIGURE 1. Site map showing air sparging and soil vapor extraction (AS/SVE) system including air sparging wells, soil vapor extraction wells, monitoring wells, and soil vapor probes.

meter with a platinum catalyst-type sensor calibrated with a 2.5% methane gas standard. Calibration to another PH could give slightly different TCH values. In previous studies, CO_2 concentration using hand-held meters correlated well with those obtained using GC (r^2 value of 0.96) when both tools were used to measure gases from the same Tedlar bag (*8*).

In situ respiration tests were conducted in 6 SVE wells (SVE 1, 3, 5, and 7−9) by introducing atmospheric air through the series of 6 AS wells for 5 days. The AS/SVE system was then shutoff, and the concentrations of O_2, CO_2, and TCH were measured over 153 days using GC and meters. Samples were collected using a small low-flow vacuum pump. A total of 2−3 L of gas was collected into 5-L Tedlar sampling bags and analyzed within 24 h of collection. The utilization of O_2 and the production of CO_2 were used to calculate zero-order O_2-based and CO_2-based biodegradation rates. The AS/SVE system was subsequently operated for 195 days during which O_2, CO_2, and TCH concentrations were measured in SVE wells, soil vapor probes P-1, -5, -6, and -8 at multiple depths, and the system exhaust stack to estimate the removal of PH. On the basis of the biodegradation rate calculations, the estimated mass of petroleum removed biologically was compared to that removed physically.

Biodegradation rates were calculated using a stoichiometric relation for the degradation of hexane as a typical PH as follows:

$$C_6H_{14} + 9.5O_2 \rightarrow 6CO_2 + 7H_2O \qquad (1)$$

On the basis of the measured O_2 utilization rate (% d^{-1}), the biodegradation rate (mg of hexane equiv (kg of soil)$^{-1}$ d^{-1}) was estimated as

$$K_{BO_2} = -K_{O_2}AD_{O_2}C \div 100 \qquad (2)$$

where K_{BO_2} is the zero-order O_2-based biodegradation rate (mg of hexane equiv (kg of soil)$^{-1}$ d^{-1}); K_{O_2} is the zero-order oxygen utilization rate (% d^{-1}); A is the volume of air per kilogram of soil (L kg^{-1}); D_{O_2} is the density of oxygen gas in air at specified temperature and pressure (kg L^{-1}); and C is the mass ratio of hydrocarbon to oxygen during mineralization based on eq 1 (1:3.5).

On the basis of CO_2 production (% d^{-1}), the biodegradation rate of PH was estimated as

$$K_{BCO_2} = 1.5K_{CO_2}AD_{CO_2}C \div 100 \qquad (3)$$

where K_{BCO_2} is the zero-order CO_2-based biodegradation rate (mg of hexane equiv kg of soil)$^{-1}$ d^{-1}); K_{CO_2} is the CO_2 production rate (% d^{-1}); A is the volume of air per kilogram of soil (L kg^{-1}); D_{CO_2} is the density of CO_2 gas at specified temperature (kg L^{-1}); and C is the mass ratio of hydrocarbon to CO_2 during mineralization based on eq 1 (1:3.1).

Total PH mass biodegraded was calculated using the O_2-based biodegradation rate as

$$B = V_sD_BK_{BO_2}t \qquad (4)$$

where B is the mass biodegraded (mg); V_s is the volume of sediment impacted by the AS/SVE system (m^3); D_B is the bulk density of sediment, measured as 1431 kg m^{-3}; K_{BO_2} is the zero-order biodegradation rate based on O_2 utilization (mg of hexane equiv (kg of soil)$^{-1}$ d^{-1}); and t is the time during which the AS/SVE system was operated (d).

The volume of sediment impacted (1928 m^3) was calculated by assuming that the AS/SVE system (15 m × 3 m well system) had a 10-m radius of influence (ROI), generating an elliptical area of 632 m^2 ($r_1 = 17.5$m; $r_2 = 11.5$m). The majority of contamination was between 5 and 8 m bls (3-m vertical depth), which was oxygenated by AS/SVE and biologically active.

Stella II. The change of vadose zone O_2 concentrations during system operation was simulated over time using Stella II (*4*) to compare to those measured in SVE wells 1, 3, and 8 during AS/SVE as follows:

$$\text{oxygen}(t) = \text{oxygen}(t - dt) + (\text{oxygen input} - \text{respiration})\, dt \qquad (5)$$

$$O_{2t} = O_2(t - dt) + (K_{\text{input}}\,(Cs - O_2) - R)\, dt \qquad (6)$$

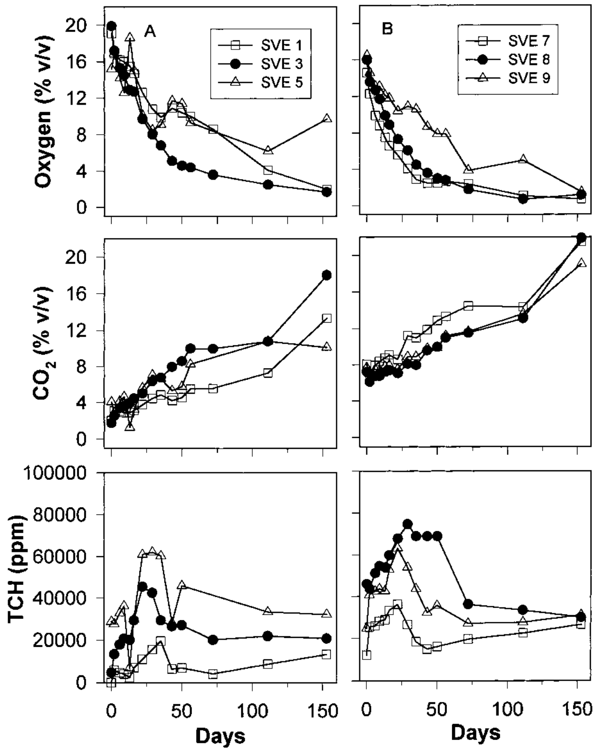

FIGURE 2. Oxygen, CO_2 (% v/v), and total combustible hydrocarbons (TCH) concentrations (ppm) over time prior to AS/SVE system startup in soil vapor extraction wells 1, 3, and 5 (A) and in soil vapor extraction wells 7−9 (B).

where O_{2t} is the vadose zone oxygen concentration at time t predicted by model (%); dt is the simulation time step (0.25 d); t is the time during which the AS/SVE system was operated (195 d); oxygen input due to AS/SVE = $K_{\mathrm{input}}(\mathrm{Cs} - \mathrm{O}_2)$; K_{input} is the rate of O_2 saturation deficit decrease measured in the SVE wells (d^{-1}) during the first day of AS/SVE due to reaeration; Cs is the atmospheric O_2 concentration added to the vadose zone from the AS/SVE system (20.9%); O_2 is the measured O_2 concentration in the vadose zone during AS/SVE (%); R is the zero-order in situ respiration rate constant (% d^{-1}) measured in SVE wells during shutdown.

The rate constant, K_{input}, was determined as the exponential rate of decrease in O_2 saturation deficit from day 0 to day 1 during AS/SVE when aerobic petroleum degradation was at a minimum because O_2 had just been added to the system. As the system became more oxygenated and the calculated vadose zone O_2 concentration approached atmospheric, the rate of decrease in O_2 saturation deficit approached zero because, at the maximum O_2 concentration (20.9%), there was no longer an O_2 deficit.

Results

O_2 Consumption and CO_2 Production during AS/SVE Shutdown. The majority of the vadose zone gases was replaced by the AS/SVE system, but O_2 and CO_2 concentrations in the SVE wells were not atmospheric initially (Figure 2). Either complete displacement of the vadose gases did not occur, or microbial activity was immediately consuming O_2 and producing CO_2. Oxygen concentrations initially ranged from 20% in SVE wells 1 and 3 to 16% in SVE 5, 7, 8. and 9 (Figure 2). All SVE wells showed a decline in O_2 over the first 25−30 d followed by a leveling off of the rate of oxygen depletion. The most rapid and consistent depletion of O_2 occurred in SVE wells 3, 7, and 8. By day 110, most of the oxygen had been removed from the vadose zone, and O_2 concentrations in the SVE wells were approximately 1−2%.

TABLE 1. Zero-Order Rate Constants for Oxygen Consumption and Carbon Dioxide Production during In Situ Aerobic Biodegradation Test in the Soil Vapor Extraction (SVE) Wells

	oxygen (% d^{-1})		carbon dioxide (% d^{-1})	
well	$-k_{O_2}$	r^2	k_{CO_2}	r^2
SVE 1	0.24	0.967	0.068	0.870
SVE 3	0.35	0.961	0.136	0.976
SVE 5	0.23	0.591	0.105	0.470
SVE 7	0.30	0.917	0.109	0.814
SVE 8	0.31	0.964	0.041	0.656
SVE 9	0.15	0.781	0.043	0.693

The average zero-order O_2 utilization rate calculated from 6 SVE wells (1, 3, 5, 7, 8, and 9) was 0.26 (±0.07) % d^{-1} for the 35-d period (Table 1).

CO_2 concentrations were inversely correlated with O_2 concentrations ($r^2 = 0.79$), suggesting that aerobic biodegradation of petroleum was accounting for the majority of CO_2 produced. Consistent with the larger initial O_2 concentrations, the concentrations of CO_2 in SVE 1 and 3 were initially 2% and increased over time (Figure 2A). CO_2 concentrations were initially 4% in SVE 5 and 8% in SVE 7−9, which corresponded to their initial depleted O_2 concentrations. SVE wells 1, 3, and 5 reached maximum CO_2 concentrations (v/v) of 13, 18, and 10%, respectively, after 155 d. SVE wells 7−9 reached maximum CO_2 concentrations (v/v) of 21, 22, and 19%, respectively, after 155 d. In general, SVE wells 1, 3, and 5 had less CO_2 and more oxygen than the coupled AS/SVE wells 7−9 after the 155-d shutdown period. The CO_2 production rate ranged from 0.041% d^{-1} in SVE 8 to 0.136% d^{-1} in SVE 3 with an average zero-order rate of 0.084% d^{-1} (± 0.039) (Table 1).

On the basis of the average O_2 utilization rate = 0.26% d^{-1}, porosity = 0.3, bulk density = 1.43 kg L^{-1}, volume (L) of air/kg of soil = 0.3/1.43, O_2 density = 1330 mg L^{-1}, and mass ratio of 1:3.5 for HC:O_2, the biodegradation rate based on average O_2 utilization rate (K_{BO_2}) was calculated according to eq 2 as 0.21 mg of hexane equiv (kg of soil)$^{-1}$ d^{-1}. On the basis of the average CO_2 production rate of 0.084% d^{-1}, assuming a conversion efficiency of carbon to biomass of 0.5 (or 33% yield; for every 3 carbons used, 2 went to CO_2, and 1 to biomass), a CO_2 density of 1829 mg L^{-1}, and mass ratio of hydrocarbon to CO_2 of 1:3.1, the biodegradation rate based on average CO_2 utilization rate (K_{BCO_2}) was calculated according to eq 3 as 0.16 mg of hexane equiv (kg of soil)$^{-1}$ d^{-1}, or approximately 75% of that calculated for the biodegradation based on O_2 utilization.

The relative fraction that BTEX represented of TCH did not appear to change over the 155-day sampling period, suggesting that microbial degradation was not selective for the BTEX compounds (data not shown). Concentrations of TCH (5000−10 000 ppm) and BTEX (2 ppm) measured in SVE 1 were 2−3 times less than those measured in the other SVE wells (Figure 2C). In general, the SVE wells with the greatest TCH contamination, SVE 7−9, had the greatest biological activity as was shown in previous studies of the soil vapor probes (*9*).

Measured CO_2, O_2, and TCH Concentrations during AS/SVE Operation. SVE wells 1, 3, and 5 were depleted in O_2 concentration initially (0%) and became oxygenated in the first 5 d of AS/SVE (Figure 3A). CO_2 concentrations were reduced during this time period from approximately 12% to less than 4%. TCH concentrations in the SVE wells were initially high, 158 642 (±14 610) ppm and also showed a dramatic decrease to less than 13 080 (±11 878) ppm after 25 d (Figure 3). Initial O_2 concentrations were 0 in SVE 8 and 12, and 2% in SVE 10 (Figure 3B). In SVE wells 5, 10, and 12, O_2 reached atmospheric concentrations soon after the system

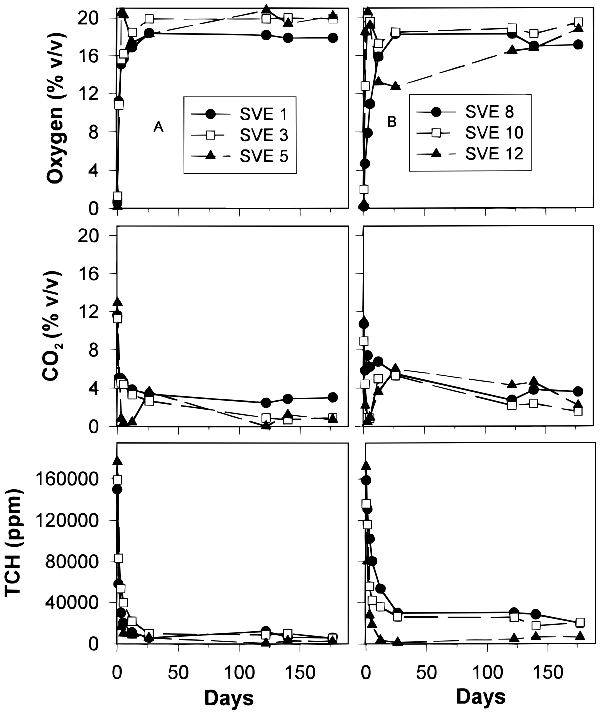

FIGURE 3. Oxygen, CO$_2$ (% v/v), and total combustible hydrocarbon (TCH) concentrations (ppm) over time during AS/SVE system operation in soil vapor extraction wells 1, 3, and 5 (A) and in soil vapor extraction wells 8, 10, and 12 (B).

was turned on. In SVE wells 1, 8, 10, and 12, O$_2$ did not reach atmospheric concentrations, suggesting that bacterial activity was consuming O$_2$ at a greater rate than that of O$_2$ input. Similarly, the concentrations of CO$_2$ were not reduced to zero in these SVE wells initially (Figure 3), suggesting that CO$_2$ production was greater than CO$_2$ removal by the system operation or that the system was drawing air from surrounding areas with nonatmospheric concentrations of O$_2$ and CO$_2$. TCH concentrations in SVE wells 1, 3, 5, and 12 decreased dramatically in the first 3 d of operation (Figure 3) and remained low throughout the 180-d period. TCH concentrations in SVE wells 8 and 10 were reduced by 90%.

As with the SVE wells, in most but not all of the probes, the CO$_2$ and O$_2$ were brought to atmospheric concentrations in the first few days of AS/SVE (Figure 4). Biological activity was observed in P-1 at 4.9 m where O$_2$ decreased with time with a concomitant increase in CO$_2$ (Figure 4A). After the initial infusion of atmospheric O$_2$ and CO$_2$ during the first few days of operation, little change in O$_2$ or CO$_2$ concentrations occurred in P-5 at any of the four depths, and TCH concentrations were reduced to between 4084 ppm (4.9 m) and nondetectable (5.5 m) by the AS/SVE system (data not shown). P-6 had the greatest activity at the deepest probe at 6.7 m with the greatest CO$_2$ production, O$_2$ utilization, and greatest contaminant concentrations (Figure 4B). Initial O$_2$ was approximately 1%, CO$_2$ was 10%, and TCH was 190 000 ppm. All other depths of P-6 remained at atmospheric concentrations of O$_2$ and CO$_2$, and TCH was reduced to zero by the AS/SVE system. P-8 was 10 m east of the line of AS wells. This probe also became oxygenated verifying that the AS system's ROI was at least 10 m. Similar to P-6, the deepest probe at P-8 (6.7 m) was highly active while the system was not operating. Initial O$_2$ concentration was approximately 1%, CO$_2$ was 8%, and TCH was 166 000 ppm (Figure 4C). After 10 d of operation however, the TCH concentrations had been reduced 10-fold, and the O$_2$ and CO$_2$ concentrations were atmospheric. O$_2$ and CO$_2$ concentrations varied over time in P-8 to a greater extent than in the other probes during system operation.

Estimated O$_2$ Concentrations during AS/SVE. The simulation model predicted the initial measured O$_2$ concentrations during the first few days of operation well for all three SVE wells simulated (Figure 5). However, the simulation model overestimated steady-state O$_2$ concentrations by approximately 2.5% in SVE 1 and 8 which were more biologically active than SVE 3 during AS/SVE system operation.

Comparing Physical and Biological Removal. Using eq 3, based on the measured O$_2$ utilization rate of 0.21 mg kg^{-1} d^{-1}, the kg of soil impacted by AS/SVE system and the 195-d period of AS/SVE operation, approximately 111 kg of petroleum was estimated to be biodegraded.

Physical removal was based on TCH concentrations and air flow rates measured in the exhaust gas (Figure 6) (*10*). The spikes in the mass of hydrocarbons extracted (Figure 6A) occurred after system shutdown due to overheating in the summer, which triggered the system's safety feature, or system maintenance and restart. These rest periods, although short, may have allowed volatilization or rebound of the contaminants from residual sediment contamination. The average flow rate was 278 m^3 h^{-1} but fluctuated between 232 and 328 m^3 h^{-1}, which affected the amount of mass extracted (Figure 6C). At higher flow rates more mass was removed. Cumulative hydrocarbon removal was characterized by a high initial rate of removal from 0 to 7 d (627 kg d^{-1}) to a value approximately 5.3 times less (118 kg d^{-1}) within 7 d of operation (Figure 6B). At approximately 10−60 d as the initial rate of removal decreased, the rate of hydrocarbon removal appeared to have stabilized to approximately 35 kg d^{-1}. Average removals were 43.6 kg d^{-1}. TCH concentrations in the exhaust gas decreased 20-fold (36 814 to 1787 ppm) during the first 17 d of operation (Figure 6D). The greatest rate of removal was at the initial time points.

Discussion

Rates of O$_2$ consumption in the SVE wells during system shutdown were initially faster during the first 35 d and then lessened as the oxygen levels fell below approximately 4% (v/v). O$_2$ consumption at long periods showed first-order kinetics, but during the first 35 d was zero order, and more likely to represent rates occurring during AS/SVE when O$_2$ was not limiting. It has been reported that O$_2$ concentrations greater than 5% indicated that rates of biodegradation were not limited by O$_2$ availability (*11*).

CO$_2$ production rates measured during system shutdown corresponded well to zero-order O$_2$ utilization rates. Biodegradation rates based on average CO$_2$ utilization rate (K_{BCO_2}) were approximately 75% of those calculated based on O$_2$ utilization. This difference could be due to errors in the estimated conversion efficiency of carbon to biomass, incomplete mineralization of the PH which consumed O$_2$ without producing CO$_2$, or mineralization of other forms of organic carbon in the vadose zone in addition to PH. It is unlikely that CO$_2$ was removed by precipitation as carbonates due to the acidic nature of the soils, and these soils were devoid of carbonates so they were unlikely to be a source of CO$_2$.

When the AS/SVE system was turned on, all the SVE wells had rapid movement of gases during the first few days of operation. TPH concentrations showed the greatest and most rapid decline in the first few days as compared to CO$_2$ and O$_2$, suggesting that physical gas exchange and biological activity were occurring quickly. Although initial oxygenation was rapid, complete oxygenation was not achieved until almost 35 d. CO$_2$ was removed in the same manner, a rapid decrease in the first few days, followed by a gradual decline in CO$_2$ over the next several months. In some of the SVE wells, atmospheric concentrations of O$_2$ and complete

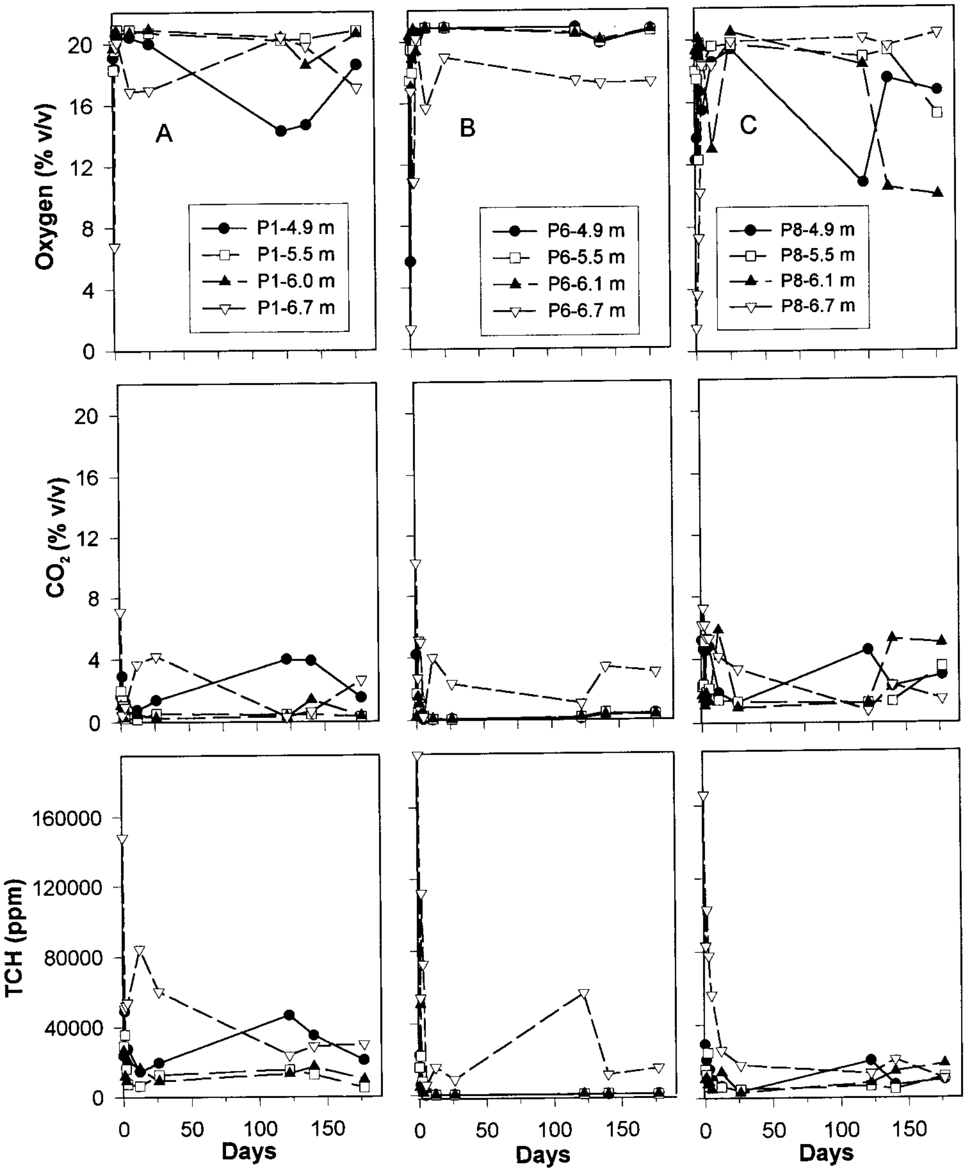

FIGURE 4. Oxygen, CO_2 (% v/v), and total combustible hydrocarbon (TCH) concentrations (ppm) over time during AS/SVE system operation at four depths in (A) soil vapor probe 1; (B) soil vapor probe 6; and (C) soil vapor probe 8.

removal of CO_2 were not reached after 195 d of AS. During longer time periods, degradation of PH accounted for the depressed O_2 and increased CO_2 concentrations despite the active AS/SVE system. Movement of gases in SVE 1 supported this conclusion because initial oxygenation of the vadose zone did not occur more slowly than the other SVE wells, but over time oxygenation was less complete than the other SVE wells, suggesting the impact of biodegradation. These point probe data also suggested that the AS/SVE system impacted areas of the site that had limited biodegradation activity. Thus, biodegradation varied at these discrete spatial scales which were not observable from the SVE data alone.

Using Stella II and respiration rates measured during system shutdown, O_2 concentrations in the vadose zone were predicted to be at atmospheric concentrations after the first few days of AS operation. Actual O_2 concentrations measured in the SVE wells over 195 d of AS/SVE operation clearly did not reach atmospheric concentrations in most of the SVE wells. Oxygenation and gas replacement appeared to be more complete in the point-sample soil vapor probes than in the depth-integrated SVE wells. The discrepancy between the model-predicted values and those measured at long time periods can be attributed to biodegradation. The theoretical zero-order O_2 respiration rate required for Stella II to correctly predict O_2 concentrations at steady state was 0.6−2.0% d^{-1} or 2−8 times greater than that calculated during system shutdown. Thus, O_2 utilization rates calculated during system shutdown, as is commonly done, may be underestimated. Biodegradation rates and mass biodegraded calculated using these rates also may be underestimated.

Using our measured O_2 utilization rate during shutdown, biological removal of PH was estimated at 111 kg over the 195-d AS/SVE operation. On the basis of concentrations of TCH measured in the exhaust stack and accounting for the variations in air flow rates, AS/SVE physically removed 8500 kg of petroleum hydrocarbons (98.7%) from the vadose zone during the 195 days of operation. Calculated biological removal based on O_2 utilization accounted for 1.3% of PH removed. The contribution of biological removal was less than that estimated by Hinchee et al. (*12*), 15−25% of the mass of jet fuel in a mixed sand and gravel aquifer in Utah. Their values were based on a first-order O_2 utilization rate that varied at the site from nondetectable to 10.9×10^{-4} min^{-1} (1.57 d^{-1}), the maximum of which is 5 times our zero-order rate mathematically transformed to a first-order O_2 utilization rate. Given that our sediments were low perme-

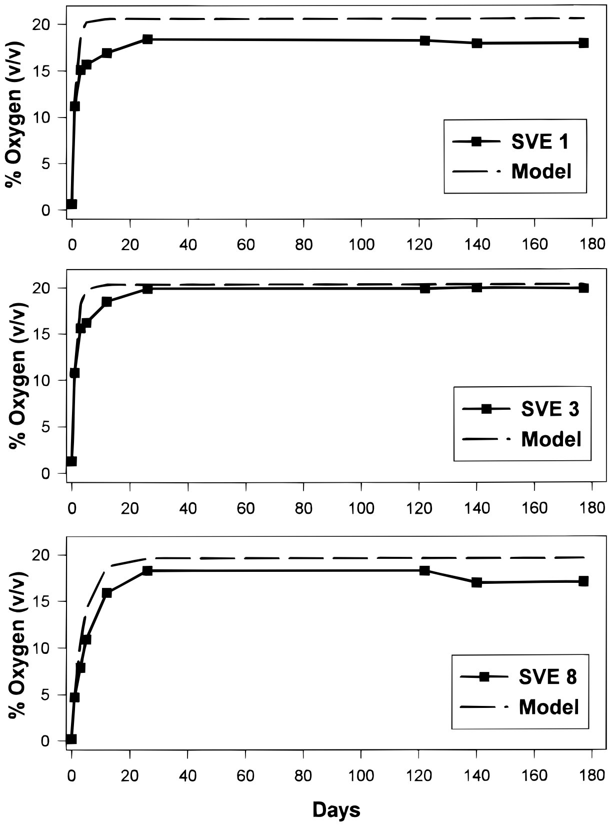

FIGURE 5. Oxygen concentrations (% v/v) over time predicted using Stella II (dashed line) and measured (solid line) during AS/SVE operation in soil vapor extraction wells 1, 3, and 8.

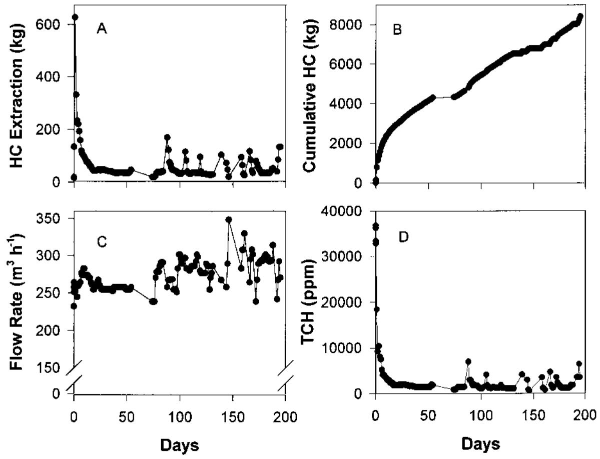

FIGURE 6. (A) Hydrocarbon mass extracted (kg); (B) cumulative hydrocarbons removed (kg); (C) flow rate (m^3 h^{-1}); and (D) total combustible hydrocarbons (TCH) measured in exhaust stack (ppm) during AS/SVE over time.

ability, these values compare well. Hickey (*13*) calculated zero-order O_2 utilization rates of 0.34−0.87% d^{-1} and biodegradation rate of 0.7 mg kg^{-1} d^{-1} in sediments with hydraulic conductivities of 1.9×10^{-2} cm s^{-1}. These hydraulic conductivities were 100 times greater than those measured at our study site, but the biodegradation rate was only 2−3 times our biodegradation rate.

A bioventing field study in low permeability sediments at the foot of the Appalachian Blue Ridge Mountains in Virginia, which was more similar to the geologic setting at our site, estimated zero-order O_2 utilization rates ranging from 0.028 to 0.14% d^{-1} and biodegradation of 5700 kg of contaminant mass during 15 months of operation (*11*). During bioventing, O_2 is input at a slow rate to eliminate off-gas production, and physical removal is minimal. Normalizing for the longer amount of time and the larger mass of sediment impacted (9.3×10^6 kg), the amount biodegraded was approximately 5 times that calculated in our study although the O_2 utilization rate was less than half that calculated in our study (0.26% d^{-1}).

All these studies operated under different flow conditions, lengths of time, hydrogeologic conditions, and contaminant concentrations, making it difficult to compare physical and biological removals. In addition, the relative contribution of physical to biological contaminant removal changes as conditions change with time. Several investigators have used modeling exercises to estimate the physical removal of contaminants as a function of time and under different AS operating parameters. Johnson et al. (*14*) stated that short-term mass removal efficiency, but not long-term cumulative removal, improved with increased flow rates and vapor pressure based on data using physical models in homogeneous and coarse sands. Semer and Reddy (*15*) suggested that volatilization may be the most dominant mass transfer mechanism during AS during short operation periods. However in their study, diffusion of dissolved VOC could be rate limiting, and off-gas VOC concentrations were high initially followed by a drop-off and finally terminal tailing. Predicting SVE cleanup times from short-term field tests was not possible (*16*). In our study, TCH concentrations in the vadose zone were reduced 12-fold in the first 26 d of AS/SVE operation and were reduced sharply at longer time periods but at reduced rates. The cumulative mass removal continued throughout the AS operation in part because of the large concentrations of petroleum in the vadose zone at the thousand ppm levels. On the basis of modeling exercises, Johnson (*17*) estimated that aerobic biodegradation was important when dissolved concentrations in groundwater were <1 mg/L. At concentrations greater than 1 mg/L, physical removal was more important.

Few studies compare biological versus physical removal, and many physical studies are based on modeling simulations. On the basis of our field data of both physical and biological parameters, physical processes and not biodegradation accounted for the majority of petroleum removed even at long time periods. However the determination of biodegradation rates using O_2 utilization rates calculated during periods of system shutdown may underestimate the contribution of biodegradation to petroleum mass removal. Also, although physical removal rates decreased with time, our high contaminant concentrations, as was evident during system PH rebound, favored physical removal even at longer time periods.

Acknowledgments

Research was funded by the National Science Foundation (93-50314), South Carolina Hazardous Waste Management Research Fund, and South Carolina Department of Health and Environmental Control, Underground Storage Tank Program. We thank H. McKellar, R. Ray, and M. Widdowson, and P. Stone, T. Adams, R. Faller, and G. Withycombe (SCDHEC), who assisted at the field site.

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Received for review July 30, 1999. Revised manuscript received March 24, 2000. Accepted May 8, 2000.

ES9908772