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Push−Pull Tests to Quantify In Situ Degradation Rates at a Phytoremediation Site

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Nine push−pull tests (PPTs) were performed to determine in-situ aerobic respiration rates at a creosote-contaminated site and to assess the contribution of hybrid poplar trees to the remediation of polynuclear aromatic hydrocarbons (PAH) in groundwater. PPTs were conducted by injecting a solution containing dissolved oxygen and naphthalene (reactive tracers) with bromide (nonreactive tracer) into wells constructed in a shallow unconfined aquifer. The objective of this study was to determine seasonal variation and spatial differences (contaminated versus uncontaminated areas and treed versus untreed areas) in the rate of consumption of dissolved oxygen. First-order aerobic respiration rates varied from 0.0 (control well) to 1.25 hr^{-1}, which occurred at a planted area in early summer (June). Rates measured in winter at treed areas were greater by a factor of 3−5 when compared to winter rates determined at nontreed areas of the site. Rates at treed regions were found to increase by over 4 times in summer relative to winter at the same location.

Introduction

Quantification of contaminant degradation rates is necessary to assess risk, optimize remedial design, and predict the remediation time frame. Site-specific data that support design decisions are critical to the success of remediation technologies including phytoremediation systems. In-situ degradation rates more accurately characterize the attenuation capacity of an aquifer when compared to rates derived using laboratory microcosms, the merits of which are discussed by Chapelle (*1*). Generally, in-situ degradation rates are considered more representative of the actual aquifer conditions since a larger volume of aquifer can be investigated (*2*). Approaches to quantify in-situ degradation rates include the analysis of plume data (e.g., inverse modeling and regression analysis) and controlled experiments (e.g., tracer tests).

Push−Pull Tests. Single-well injection−withdrawal tests, or push−pull tests (PPTs), involve the injection ("push") of a well-mixed solution consisting of a nonreactive, conservative tracer and a reactive, biodegradable tracer (electron donor and/or electron acceptor) into the saturated zone. Following injection, extraction ("pull") of groundwater from the well occurs. The conservative tracer is subject only to advection and dispersion, whereas the other reactive solute(s) are additionally presumed to be subject to constant, irreversible attenuation processes. Solute concentrations are measured throughout the injection and extraction phases, and the resulting concentration breakthrough curves are used to quantify degradation rates.

PPTs are widely applicable to determining in-situ properties, including hydrogeologic parameters and degradation rates, as well as allowing the determination of microbial degradation pathways. PPTs have been used to determine the hydraulic properties of aquifers, primarily hydraulic conductivity (*3*−*8*). PPTs are also useful in determining degradation rates for a variety of contaminants and attenuation processes, including metals, chlorinated solvents such as trichloroethene, and other organics such as benzene, toluene, ethylbenzene, and xylene (BTEX), and other petroleum products (*9*−*19*). Researchers have also applied PPTs to a range of microbial processes (*2*, *10*, *13*, *20*−*22*), including aerobic and anaerobic (e.g., denitrification, sulfate reduction, methanogenesis) biodegradation rate determination. In contrast to indirect methods to quantify degradation rates using mathematical models, PPT analysis methods are relatively less difficult than inverse modeling and require no previous knowledge of regional groundwater flow or hydraulic parameters (*23*−*24*). However, the cost and feasibility of PPTs at field sites relative to other methods is largely site specific, particularly at sites where hydrogeology limits the rate of injection and recovery.

Snodgrass and Kitanidis (*23*) and Haggerty et al. (*24*) each developed methods for determining zero and first-order reaction-rate coefficients. Key assumptions to the methods of Snodgrass and Kitanidis (*23*) and Haggerty et al. (*24*) include the following: (1) the injected solutes are simultaneously introduced as well-mixed slugs; (2) the dominating processes are advection, dispersion, and spatially homogeneous, constant coefficient, zero or first-order irreversible reactions; (3) other processes such as sorption are negligible; (4) the retardation factors and boundary conditions of the conservative tracer and injected reactive solutes are similar; and (5) the background concentration of the conservative tracer and reactive solutes are negligible. In addition, Haggerty et al. (*24*) showed that complete tracer recovery is not necessary for accurate quantification of rate coefficients.

Phytoremediation. Phytoremediation, or the use of plants to remove or degrade soil and groundwater contaminants, occurs through both direct and indirect mechanisms. Specific applications of phytoremediation are explained in greater detail by McCutcheon and Schnoor (*25*). Polycyclic aromatic hydrocarbons (PAHs) are subject to two primary phytoremediation mechanisms: (1) direct plant uptake of contaminants and subsequent accumulation of either the contaminant or nontoxic metabolites within the plant tissue, and (2) rhizosphere degradation, which involves both (a) the stimulation of microbial activity and transformation of xenobiotic contaminants caused by the release of enzymes and exudates into the rhizosphere, and (b) enhanced mineralization of contaminants by microrhizal fungi and rhizosphere microbial consortia (*26*).

Degradation rates can be expected to increase when plants are used because plants provide tremendous root surface area for microbes to attach to and grow on, and some species of plants transfer oxygen to the rhizosphere enabling aerobic mineralization of organics. Increased microbial mineralization can also be attributed to the release of soluble exudates that include enzymes, aliphatics, aromatics, amino acids, sugars, and low-molecular-weight carbohydrates (*27*−*28*). Symbiotic relationships with fungi and plant roots provide

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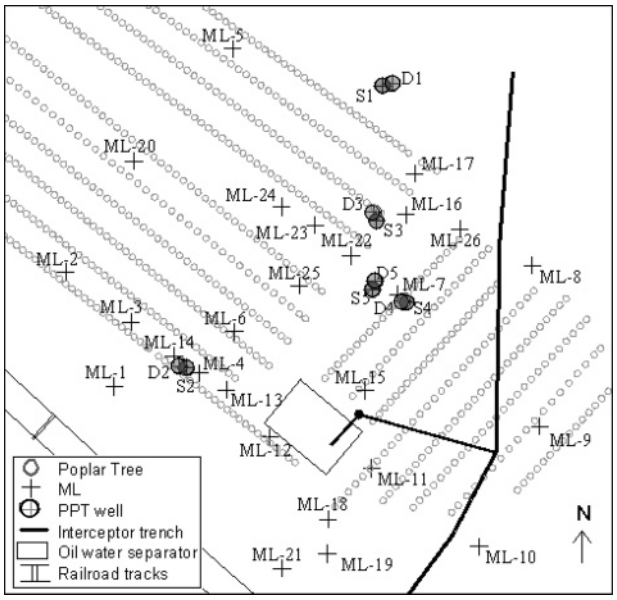

FIGURE 1. Site map showing location of push−pull test wells in relation to the phytoremediation system and monitoring network.

a wider array of enzymatic pathways that are not possible with bacteria alone (*26*). Reilley et al. (*29*) reported 30−44% lower concentrations of anthracene and pyrene, two PAHs found in creosote, in vegetated soil, and microbial activity in the rhizosphere can be enhanced up to 100 times when compared to unvegetated soil. Robinson et al. (*30*) reported increased degradation of pyrene and fluoranthene relative to controls in microcosm experiments using vegetated soil from a PAH-contaminated site.

Scope of Study. The goal of this project was to assess the contribution of a phytoremediation system to the remediation of PAHs at a creosote-contaminated site. To the best of our knowledge, PPTs have not been applied to assess degradation rates at a phytoremediation site. The objective of this study was to determine in-situ aerobic respiration rates using the PPT method in different locations within a phytoremediation system comprised of hybrid poplar trees. The study was designed to compare rates in areas impacted by trees to control areas of the site and to assess seasonal variation in rates.

Experimental Section

Site Description. A creosote-contaminated site in Oneida, TN has been the subject of extensive monitoring and research since installation of a phytoremediation system comprising 1146 hybrid poplar, *Populus deltoides x* nigra DN34, in 1997. The site is underlain by an unconfined aquifer consisting of sand and sandy clay to a depth of 3.0−3.5 m below land surface. Over the past seven years, researchers conducted biannual groundwater and annual soil boring monitoring of 10 PAHs including 2-, 3-, 4-, and 5- ring PAHs that are representative of the contaminants detected in the initial site characterization (*31*). A map detailing the layout of the phytoremediation system, soil boring transects, monitoring wells, multi-level samplers (MLs), and push−pull test wells is shown in Figure 1.

Historic Data and Observed Trends. Marked drops in PAH groundwater concentration and plume size over time have been observed in both shallow and deeper regions of the plume resulting from implementation of the phytoremediation system (*31*). The enrichment of high-molecular-weight compounds has also been observed at the site (*31*). Naphthalene comprises about 65% of the PAHs found in the groundwater at the Oneida site (*32*). Widdowson et al. (*31*) reported field degradation rates of naphthalene ranging from 3.4×10^{-5} h^{-1} to 5.5×10^{-5} h^{-1} using concentration versus time data over a six-year period from two multilevel sampling ports located in an anaerobic zone within the PAH plume. However, quantification of in-situ rates that compare treed and nontreed regions, as well as seasonal variation of in-situ rates, had not been conducted.

TABLE 1. Push Pull Test Well Description of Each Test Variation Performed

well	contamination	proximity to trees	screen depth[a] (m)
D1	none	nontreed	2.50
D3	moderate	treed	2.53
D4	high	treed	2.16
S5	high	nontreed	1.75

[a] All depths measured from the ground surface at each well.

Experimental Design. Ten push−pull wells were installed in upper and lower depth pairs at the five locations shown in Figure 1 (denoted as S for shallow or upper and D for deep or lower, followed by the well number). Well placement was designed to enable comparison between contaminated and noncontaminated locations, as well as comparisons between locations with and without trees. Control wells S1/D1 are located in an uncontaminated region of the site without trees. Well pairs S3/D3 and S4/D4 are located in contaminated treed areas, while S5/D5 is located in a contaminated, nontreed area. Table 1 lists the location, depth, and characteristic of each PPT well where tests were conducted. The well pairs were constructed in separate boreholes with a relative small vertical separation (0.30 m) between screens. Tests were primarily limited to the deeper wells due to drought-related lower water table conditions during the period of push−pull testing. No tests were performed at well pair S2/D2.

Well Construction. Wells were constructed by advancing a 5.1-cm-diameter sterilized hand auger to bedrock and consisted of 2.54-cm-diameter PVC with well screens 30.5-cm long. The annulus of each well was filled with approximately 45 cm of filter sand followed by 30 cm of bentonite clay, and backfilled to the surface with a mix of soil and bentonite. Newly constructed wells were conditioned by injecting 50 L of clean water at a flowrate of approximately 0.5 L/min. Soil samples corresponding to the screened depths for the shallow and deep pairs were collected for later microcosm construction. A detailed description of well construction, including logs of soil borings, is reported by Pitterle (*32*).

Push-Pull Test Method. Bromide, dissolved oxygen (DO), and naphthalene were injected and monitored throughout the PPT duration. Injection solutions were prepared by diffusely aerating 35 L of tap water, allowing the solution to equilibrate, and adding bromide to produce a final bromide concentration of 750 mg/L. Naphthalene was added to the solution following addition of bromide to produce a final naphthalene concentration of 2 mg/L. Naphthalene was not used for rate determinations because of the high background concentrations of naphthalene in most of the wells; however, the compound was included in the injectate for consistency in the test procedure. The effect of naphthalene on aerobic respiration rates was evaluated by excluding naphthalene from the solution in two PPTs. Before the feed tank was sealed with Parafilm to prevent volatile losses, a submersible mixing pump was placed in the injection solution container to ensure the solutes were well-mixed.

Triplicate background samples were collected from the wells prior to injection for analysis of bromide, DO, and naphthalene concentrations. Dissolved oxygen was measured immediately after sample collection using a HACH kit that

TABLE 2. Summary of Push−Pull Test Parameters

	background concentration		injection		extraction		recovery	
push-pull test (well ID-month)	DO (mg/L)	naphthalene (μg/L)	Q_{inj} (L/min)	V_{inj} (L)	Q_{ext} (L/min)	V_{ext} (L)	Br (%)	DO (%)
D1-Feb[a]	3.3	BDL	0.50	35	0.34	76.7	74.9	72.0
D1-April	3.1	BDL	0.32	35	0.32	108.2	66.4	113.8
D1-June	0.3	<9.5	0.54	35	0.38	110.0	91.1	88.0
D3-Dec	BDL	379	0.50	35	0.30	42.4	87.8	65.7
D3(1)-April[a]	BDL	1517	0.50	35	0.31	105.2	96.0	53.9
D3(2)-April	BDL	388	0.55	35	0.36	107.4	101.2	62.7
D3-June	BDL	1595	0.55	35	0.29	116.6	91.7	45.8
D4-Dec	0.1	8604	0.50	35	0.30	62.6	94.6	65.9
S5-Feb	BDL	2502	0.50	35	0.26	61.1	99.5	82.5

[a] Naphthelene not injected.

utilizes the Winkler titration method with a detection limit of 0.1 mg/L. Samples were collected in 20-mL scintillation vials and 40-mL volatile organic analysis EPA amber vials for analysis of bromide and naphthalene, respectively, stored on ice, and analyzed in the laboratory. Bromide concentrations were determined using ion chromatograph analysis with a method detection limit of 0.5 mg/L. Naphthalene samples were extracted using methylene chloride and analyzed on a gas chromatograph with a flame ionization detector with a DB5-MS fused silica capillary column. The naphthalene method detection limit was 9.5 μg/L.

Following collection of the background groundwater samples, 35 L of the injection solution was injected at a flowrate of approximately 0.5 L/min. This volume of water corresponded to a radius of 30−40 cm of aquifer volume centered about the injection well. Injection samples for analysis of bromide, DO, and naphthalene were taken every 10 min. Immediately following completion of injection, extraction was initiated at a flowrate ranging from 250 to 400 mL/min. Extraction samples for analysis of bromide and DO were taken every 10−20 min. Extraction continued until either three times the injected volume was collected or until the DO stabilized to background levels.

First-Order Rate Determination. Solute concentrations were normalized by dividing the extraction concentrations values (C_{ext}) by the average injection concentration (C_{inj}). In cases where background solute concentrations (C_B) were detected (for example, DO at control wells), concentrations were normalized using $(C_{ext} - C_B)/(C_{inj} - C_B)$. Data were then analyzed to determine first-order degradation rates using the method of Haggerty et al. (*24*). The method is based upon tracer and reactant transport as the radial flow field fluctuates from divergence during injection and convergence during extraction. The solution for the ratio of the normalized concentrations of the tracer and reactant is

$$\ln\left[\frac{C_r^*(t^*)}{C_t^*(t^*)}\right] = \ln\left[\frac{(1 - e^{-kt_{inj}})}{kt_{inj}}\right] - kt^* \qquad (1)$$

where C_r^* is the normalized concentration of the reactant; C_t^* is the normalized concentration of the tracer; t^* is the elapsed time from the end of the injection phase (min); t_{inj} is the total time of the injection phase (min); and k is first-order degradation rate (min^{-1}). If the reactive solute decays at a first-order rate, a plot of $\ln(C_r^*(t^*)/C_t^*(t^*))$ versus t^* produces a straight line with a negative slope k and y-intercept of $\ln[(1\text{-}e^{-kt_{inj}})/(kt_{inj})]$. The variance of the first-order rate (σ_k^2) was calculated to determine a 95% confidence interval for k so that $k = \pm 2\sigma_k$ (*22*):

$$\sigma_k^2 = \sigma^2\left\{\sum_{i=1}^{n}\left[\frac{1 - e^{kt_{inj}} + kt_{inj}}{k(e^{kt_{inj}} - 1)} - t^*\right]^2\right\}^{-1} \qquad (2)$$

where n is the total number of observations and σ^2 is the variance of errors in $\ln(C_r^*/C_t^*)$.

Results and Discussion

General Trends in PPT Results. A summary of the PPT test parameters and mass recovery for bromide and DO is shown in Table 2. Background DO was only above detection limits at the control well, D1, while detectable naphthalene was found at contaminated wells D3, S5, and D4, in respective order of increasing magnitude. Recovery of bromide was typically 90% or greater, while the percent recovery of DO was variable. Schroth et al. (*22*) noted that unlike analysis techniques that are based on the method of moments to determine k, the approach used here does not require complete mass recovery of either tracer.

Breakthrough curves of bromide and DO (Figure 2) demonstrate that little to no consumption of oxygen occurred at the uncontaminated control well with no trees (Figure 2a), while substantial DO consumption was observed at a contaminated, treed area of the site (Figure 2b). This is shown by comparing the plots of relative concentrations and mass recoveries of bromide and DO at each location (Figure 2). In the control well, the percent recovery of mass for each tracer was nearly identical (74.9 versus 72.0%, respectively). Mass recoveries of bromide and DO in the contaminated well were 96.0 and 53.9%, respectively.

A comparison of bromide and DO breakthrough curves for PPTs conducted in the PAH plume also showed greater oxygen consumption at treed areas (Figure 3a) when compared to nontreed areas (Figure 3b). For a PPT conducted adjacent to trees during June, mass recoveries of bromide and DO were 91.7 and 45.8%, respectively, resulting in a 46% difference. In contrast, a PPT conducted in an area not directly impacted by the poplar trees (S5) showed less difference (17%) in the recovery of the mass of bromide and DO (99.5 and 82.5%, respectively).

First-Order Rate Analysis. The first-order rate results for aerobic respiration for the nine PPTs are shown in Table 3 in chronological order by well. First-order rates were determined by plotting the log of the ratio of normalized concentration of DO to the normalized concentration of bromide versus the elapsed recovery time (t^*). Figure 4a and b show plots corresponding with the DO breakthrough curves in Figure 3a and b, respectively, for wells in the treed and untreed areas of the PAH plume, respectively. For the PPT labeled D3-June (Figure 4a), the DO decreased from an

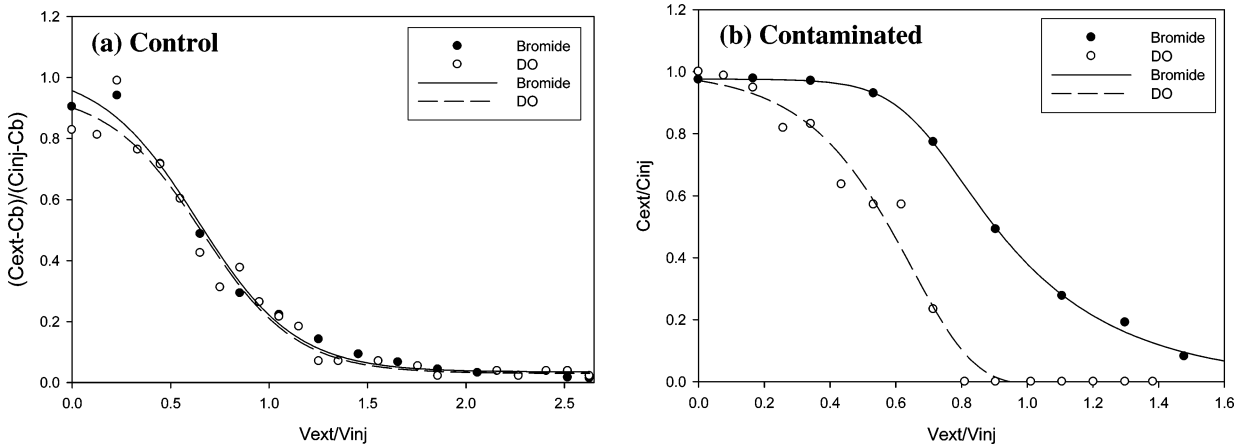

FIGURE 2. Comparison of push-pull test DO and bromide breakthrough curves for (a) the February test at control well D1, and (b) the April test 1 at well D3 in the contaminated area.

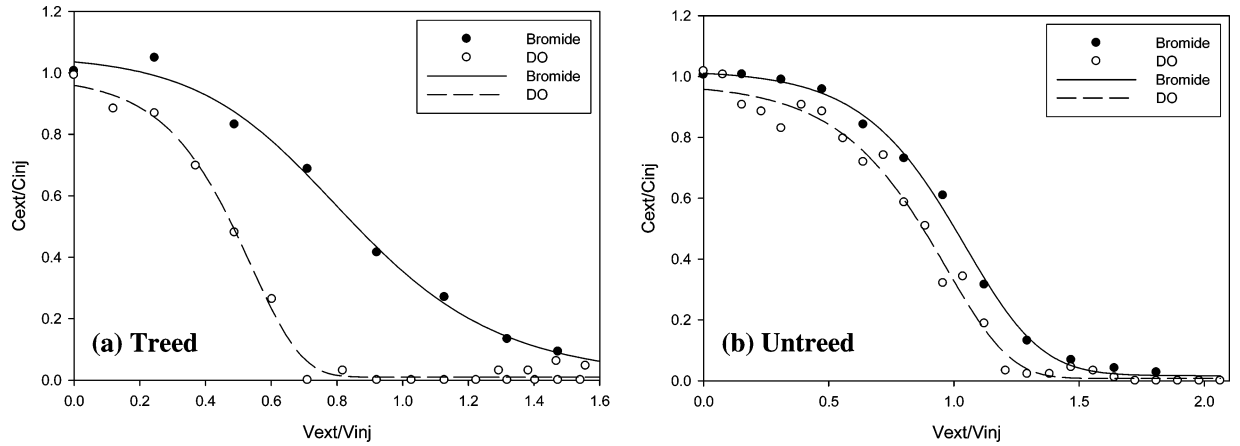

FIGURE 3. Comparison of push-pull test DO and bromide breakthrough curves in contaminated areas for (a) the June test at well D3 (treed area of site), and (b) the February test 1 at well S5 in the area without trees.

TABLE 3. Summary of Push-Pull Test First-Order Aerobic Respiration Rates

push-pull test (well ID-month)	first-order rate (h^{-1})	temperature (°C)	95% confidence interval[a]	R^2
D1-February[a]	0.002	9.9	0.005	0.01
D1-April	0.000[b]	14		
D1-June	0.000[b]	23		
D3-December	0.302	10	0.070	0.93
D3 1-April[a]	0.773	no data	0.198	0.81
D3 2-April	0.601	17	0.168	0.73
D3-June	1.25	20	0.380	0.78
D4-December	0.486	no data	0.104	0.99
S5-February	0.098	no data	0.022	0.87

[a] Naphthalene not injected [b] Near zero, positive slope found. [c] 95% confidence interval for $k = k \pm 2\sigma_k$.

injection concentration of 6.45 mg/L by approximately 90% within the first 60 min of the extraction phase of the test. In contrast, the DO concentration measured during extraction at well S5 in February (Figure 4b) remained above 10% of the injection concentration through the first 150 min. The concentration of bromide decreased to approximately 10% of the injection concentration within the first 130 min and the first 170 min, respectively.

The three control well tests at D1 were conducted in winter, spring, and summer, and resulted in the detection of little or no consumption of oxygen. Only one control well test, D1 February, resulted in a detectable oxygen respiration rate, 0.0024 h^{-1}; however, this low rate was outside of the 95% confidence range of all noncontrol well rates. Control well results indicate that aerobic respiration rates did not require any adjustment for consumption of natural organic carbon or inorganic species. Total organic carbon (TOC) in the aquifer sediment collected during installation of the control well (1.9%) was nearly equal to the largest TOC measured in samples collected at the other PPT wells, which ranged from 1.0% to 2.0%, indicating that the loss of oxygen was due to the contaminant and not organic or inorganic matter associated with the soil. The inclusion of naphthalene in the latter two PPTs at D1 did not increase the aerobic respiration rate at the control well. The potential for chemical reactions of oxygen with inorganic species was mitigated by the positioning of the well screens, which were located in a zone of mixed aerobic and mildly reducing anaerobic conditions. In addition, if the chemical oxygen demand in the PAH plume was significant, then an initial rapid DO depletion would be observed at all test sites. The pattern of oxygen depletion observed at contaminated wells S5 did not suggest chemical depletion (see Figure 3) and was similar to the control well outside of the area of contamination where no rapid drop in DO was seen.

Four PPTs were conducted at D3 to determine the extent to which the rates varied seasonally. Results from PPTs at D3 showed that rates increased by a factor of 4 from nonactive winter months to active summer months (dashed box in Figure 5). The lowest rate (0.30 hr^{-1}) occurred in the winter, and the highest rate (1.25 hr^{-1}) occurred in June when the poplar trees are most active. Spring PPT rates for D3, conducted on different days in April under similar weather

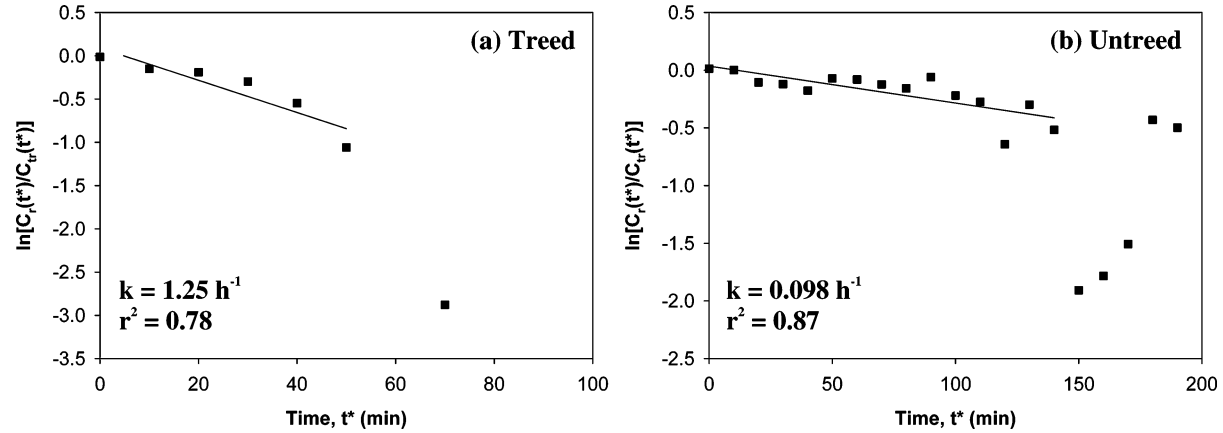

FIGURE 4. Regression plots for first-order rate analysis of the push-pull tests shown in Figure 3: (a) the June test at well D3 (treed area of site), and (b) the February test 1 at well S5 in the area without trees.

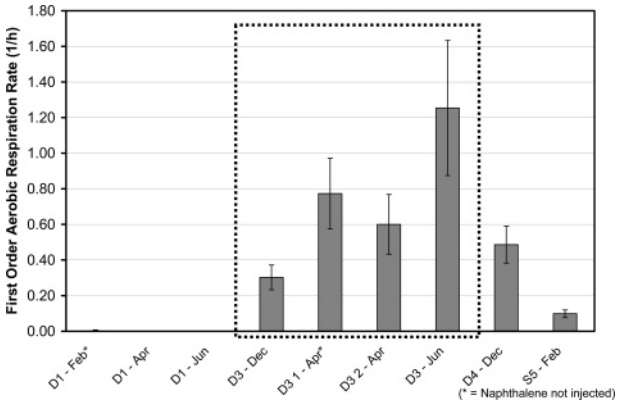

FIGURE 5. First-order degradation rates for aerobic respiration for push-pull tests. Dashed box highlights seasonal variation at the well D3 (treed area).

conditions, did not vary significantly (0.77 and 0.60 hr^{-1}, respectively), demonstrating that results can be replicated. A comparison of the results from the April PPT tests shows that the inclusion of naphthalene in the injection solution had no significant impact on the rates.

Groundwater temperature increased from 10 to 17 °C and to 20 °C at D3 from December to April and then to June, respectively. Temperature effects were evaluated using the common equation for temperature effects on the rate of biological activity in the mesophilic range:

$$k = k_{T_o}\Theta^{T-T_o} \quad (3)$$

where k is the reaction rate at temperature T; k_{T_o} is the reaction rate at temperature T_o; and Θ is the temperature coefficient. The values of Θ for the biodegradation of wastewater range from 1.047 to 1.072 (*33*) if the rate of biological activity doubles with a 15 and 10 °C increase, respectively, and 1.08 for unlimited heterotrophic growth (*34*). For well D3, the increase from 0.302 to 1.25 hr^{-1} for the 10 °C increase would require a value of 1.26 for Θ. This simple analysis suggests that temperature effects on biological activity alone do not account for the differences in rates from winter to spring to summer.

The apparent influence of trees on aerobic respiration rates is demonstrated by comparing results from wells D4 and D5 to rates from well S5. Figure 5 shows that first-order winter rates from PPTs in treed areas (D4-Dec and D5-Dec) were greater by a factor of 3−5 when compared to PPTs in a nontreed area (S5-Feb). For these winter rates, it is interesting to note that the difference in rates (D4 > D3 > S5) did not appear to be related to differences in the background concentration of naphthalene where D4 ≈ S5 > D3 (see Table 2).

A comparison of the aerobic respiration rates from this study and those reported by Schroth et al. (*22*) shows very similar results. The study by Schroth et al. (*22*) took place in a former gasoline and diesel fuel storage area that was highly contaminated with petroleum hydrocarbons. PPT-derived rates in contaminated areas of their site ranged from 0.08 to 1.69 hr^{-1} compared to 0.098 to 1.25 hr^{-1} (contaminated wells) in our study. Conversion of these rates to naphthalene degradation rates using a stoichiometric factor of 2.007 $g_{O_2}/g_{naphthalene}$ (*35*) yields values approximately 4 orders of magnitude greater than the range of naphthalene degradation rates reported previously at our study site (*31*). This rate was derived using long-term naphthalene data in oxygen-limited groundwater where iron and sulfate respiration are contributing to the biodegradation of naphthalene. Furthermore, pockets of creosote, present as a separate phase, reduce the apparent naphthalene degradation rate through dissolution of naphthalene to the groundwater.

Schroth et al. (*22*) discussed the validity of push−pull field rates, and their interpretation was that these represent maximum rates for conditions where the electron acceptor concentration is nonlimiting. In this research, the zones targeted with PPT wells (depth = 1.75−2.53 m) were exposed to both highly reducing conditions in the winter and to mildly reducing and aerobic conditions in other seasons when the water table was lower. Widdowson et al. (*31*) showed that increased microbial populations are present in the treed areas, including aerobic bacteria, actinomycetes, and fungi. For purposes of comparing rates in different areas of the site, and also for ease of measurement, oxygen was selected as an electron acceptor. Aerobic conditions produce the least limiting conditions for microbial degradation, thereby eliminating variability associated with the use of different electron acceptors. This technique will also produce the highest respiration rates at hydrocarbon-contaminated sites, which can be interpreted as the peak respiration rate when DO concentrations are at their highest level.

Engineering Significance. The push−pull test results indicate that not only can the PPT method discern differences between treed and untreed areas, but it can also show seasonal variations in the rate of oxygen uptake. The largest first order rate occurred in June at D3, located adjacent to the largest trees at the site. This may suggest that not only will the presence of trees increase naphthalene degradation, but it is probable that the size of the tree is an important factor, likely because larger trees will have a more extensive root system. The seasonal variation in degradation rates at the same PPT well in a treed area increased by a factor of 4

from winter to summer. This is important because microcosm tests conducted in a controlled temperature environment would not be expected to differentiate between rates from soils collected during different times of the year. This finding also suggests that poplar-tree-based phytoremediation systems remain active, but at a lower rate, during months of the year when transpiration is inactive.

At most remediation sites, the time to completion of the remediation process is an important consideration in the selection of the remediation method. For phytoremediation sites, estimating the time to remediation has not been possible, due to both the lack of extensive monitoring data and the inability to quantify rates of contaminant loss associated with the various mechanisms attributed to phytoremediation processes. The PPT results from the Oneida site, coupled with the overall rates measured by Schroth et al. (*22*) suggest that these rates can be estimated, at least for moderately to highly contaminated sites. Our data also indicate that winter rates of degradation are significant, although the rates could be impacted more at colder locations. Our data permit estimation of in situ microbial degradation rates of naphthalene over the year.

Results from our site show that poplar trees are effective in ameliorating PAHs, particularly naphthalene, which is supported by site data showing enrichment of the PAH plume with higher molecular weight compounds over time (*31*), as well as increased degradation rates in contaminated regions. Results from this study indicate that push−pull test results show enhanced microbial activity during the winter period compared to control areas, indicating that benefits of phytoremediation using poplar trees is not limited to growth seasons. Further, by using the data from treed and nontreed locations, a comparison of phytoremediation with natural attenuation without intervention can be made.

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