

Use of Groundwater Circulation (UVB) Technology and Integrated Bioreactors for Chemical Containment and *in-situ* Bioremediation of Subsurface Environments Contaminated by Coal Tar Creosote: Full-scale Field Validation

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are present in many fossil fuels, including coal and crude oil. The wide-scale, multiple-purpose use of these fuel sources throughout the industrialized world has resulted in the inadvertent contamination of myriad environments. On a world-wide basis, the scale and magnitude of PAH environmental contamination problems is unmatched by any other group of organic chemicals.

Given the scope and magnitude of these environmental contamination problems, bioremediation often represents the only practical and economically feasible solution (Mueller *et al.*, 1993, 1995). Accordingly, the removal (e.g. biodegradation) of PAHs from impacted environments has become a ubiquitous component of effective site amelioration. However, because of intrinsic chemical stability, the higher-molecular-weight (HMW) PAHs, defined herein as those chemicals containing four or more fused rings, commonly resist biological catalysis and thus persist in certain environments (Mueller *et al.* 1989). This seems to be especially true under anoxic or anaerobic settings. Hence, *in-situ* remediation of sites, particularly those contaminated by HMW PAHs (e.g. creosote, coal tar, manufactured gas plants), is complicated significantly when the subsurface environment is impacted.

Despite the recognized limitations to PAH biodegradation, *in-situ* bioremediation is frequently recommended. This is

especially true when depth of contamination, magnitude of the problem, and nature of contaminated material preclude other remedial actions, short of the no-response alternative. From our perspective, the effective, safe and scientifically-valid employment of *in-situ* bioremediation technologies for PAH impacted sites requires cost-efficient and effective *in-situ* implementation strategies *in combination with* unequivocal approaches for monitoring *in-situ* bioremediation of target contaminants.

With these goals, we have completed the full-scale installation of a microbiologically-enhanced groundwater circulation (UVB) system coupled with an *in-situ* bioreactor (patent pending) at an operating wood preserving site in the southeast United States where constituents of coal tar creosote are present in soil and groundwater. Data collected from a continuing sampling and analysis plan include conventional measurements of bioremediation performance (PAH analysis of soil and water, *in-situ* respiration measurements, and nutrient utilization profiles) along with more innovative measurements of *in-situ* biodegradative activity including: (1) bacterial productivity measurements; (2) gene frequency responses; (3) biosurfactant production; and (4) stable isotopic ($\delta^{13}\text{C}$) analyses of the fate and effect of organic compounds. The validity of using $\delta^{13}\text{CO}_2$ measurements in monitoring the *in-situ* bioremediation of environments impacted by creosote and related chemicals will be simultaneously demonstrated.

DESCRIPTION OF FIELD DEMONSTRATION SITE

The Cabot Carbon/Kopper's Superfund Site is located in the City of Gainesville, Florida. Since the mid-1920s, the former Cabot Carbon Company operated a 34-acre pine tar and charcoal generation facility, both which are now discontinued. During the same time, the Kopper's Industries, Inc. plant occupied about 90 acres as a wood treatment facility. Historically, the facility used creosote, pentachlorophenol (PCP), and chromated copper arsenate (CCA) to preserve wood utility poles and timbers. The facility continues to operate, but using only CCA on site.

Topographically, the site is relatively flat at an elevation between 175 to 185 feet above mean sea level. Adjacent to the west and northwest of the site is residential property consisting primarily of single-family housing. Commercial facilities are located to the south and east of the site, and an industrial park is located to the north. Stratigraphic formations encountered in the vicinity of the site consist of the Lake City Formation, the Avon Park limestone and the Suwannee limestone. Overlying these formations is the Hawthorn Formation (25 to 65 feet below ground surface [bgs]) which is a marine clay interbedded with limestone and sandy phosphatic limestone, with a dense dolomite and limestone unit at the base. Overlying the Hawthorn Formation are Pleistocene Terrace deposits consisting of organic matter, clay and sand. There are three aquifers identified in the plant vicinity: (1) surficial unconfined aquifer in the Pleistocene sands (3 to 10 feet bgs); (2) intermediate aquifer of limestone and sandy beds of the Hawthorn Formation (25 to 175 feet bgs); and (3) Floridian Aquifer (>150 feet bgs).

Multiple process and storage areas associated with past facility operations have been identified as potential sources of organic wood preserving constituents. Results obtained from a remedial investigation conducted in 1989 indicated that groundwater in the shallow aquifer had been impacted by phenolic compounds, creosote, volatile organics and chromium; PCP was not detected. The former north lagoon area (which has since been filled and levelled) has been identified as a potential source of creosote constituents (Figure 1). More recent analysis of soil and groundwater samples recovered during the installation of monitoring well 10 (Figure 1) showed Constituent of Interest (COI) concentrations near this area (Table 1). Thus, this location was chosen for field demonstration of the *in-situ* bioremediation and efficacy monitoring technologies.

TECHNOLOGY BASED *IN-SITU* BIOREMEDIATION SOLUTIONS

In an effort to overcome recognized limitations of *in-situ* PAH bioremediation technologies for saturated soils and groundwaters, we have modified proven vertical groundwater circulation (UVB) systems by incorporating *in-situ* bioreactors into the center of the groundwater circulation cells (U.S. Patent 1992; patent pending). The groundwater circulation system is based on patented Vacuum-Vaporized Well (German: Unterdruck-Verdampfer-Brunnen; abbreviation UVB)

Table 1. Summary of analytical data for soil and groundwater samples near the former North Lagoon Area

Constituent of Interest	Water (µg/L)	Soil (mg/Kg)
acenaphthene	400	27.6
acenaphthylene	20	0.76
anthracene	280	19.5
*benz[a]anthracene	<20	10.9
*benzo[b]fluoranthene	<20	5.7
*benzo[k]fluoranthene	<20	4.1
benzo[g,h,i]perylene	<20	1.0
*benzo[a]pyrene	<20	3.4
*chrysene	<20	9.7
*dibenz[a,h]anthracene	<20	<0.4
fluoranthene	100	58.1
*indeno[1,2,3-c,d]pyrene	<20	1.4
naphthalene	3560	7.4
phenanthrene	390	154.0
pyrene	20	32.7

* potential carcinogens as defined by US EPA/600/R-93/089

technology (U.S. Patents 4,892,688; 4,943,305; 5,095,975; 5,143,606; 5,143,607; 5,171,103) originally designed for *in-situ* treatment of the capillary fringe, unsaturated and saturated zones contaminated with volatile organic compounds (VOCs), including NAPLs. The UVB system represents a proven technology for simultaneous *in-situ* remediation of contaminated soil and groundwater, especially those contaminated with volatile and semi-volatile organics (Borchert and Sick 1992; Herrling *et al.* 1993).

The basic principle of UVB operation can be summarized as follows: as the water level rises within the UVB well casing due to a reduced atmospheric pressure generated by an above-ground blower, ambient air is drawn into the system through a pipe leading to the stripping reactor. Air bubbles leaving the diffuser plate meet water initially in counter-current flow streams, loop through the stripping reactor, then exit back into the aquifer. The rising air bubbles cause an air-lift and suction effect at the well bottom, drawing water from the aquifer through the lower screen. The upward movement of water through the well casing creates a difference in total head which causes water to exit the well casing into the upper portion of the aquifer. This results in a vertical groundwater flow downward through the aquifer. A groundwater circulation cell therefore develops with water entering at the base of the well and leaving the upper screened section, or vice versa, depending on the desired flow direction.

As a result of the turbulent water flow and the high air:water ratio in the stripping reactor, rapid mass transfer of volatile organics from water to air is achieved. Contaminants vaporized into the air are subsequently removed from the well by the suction effect of the blower (*in-situ* air stripping). The continuous expansion of the air bubbles causes adiabatic

Figure 1. Gainesville, Florida UVB and *in-situ* bioreactor installation

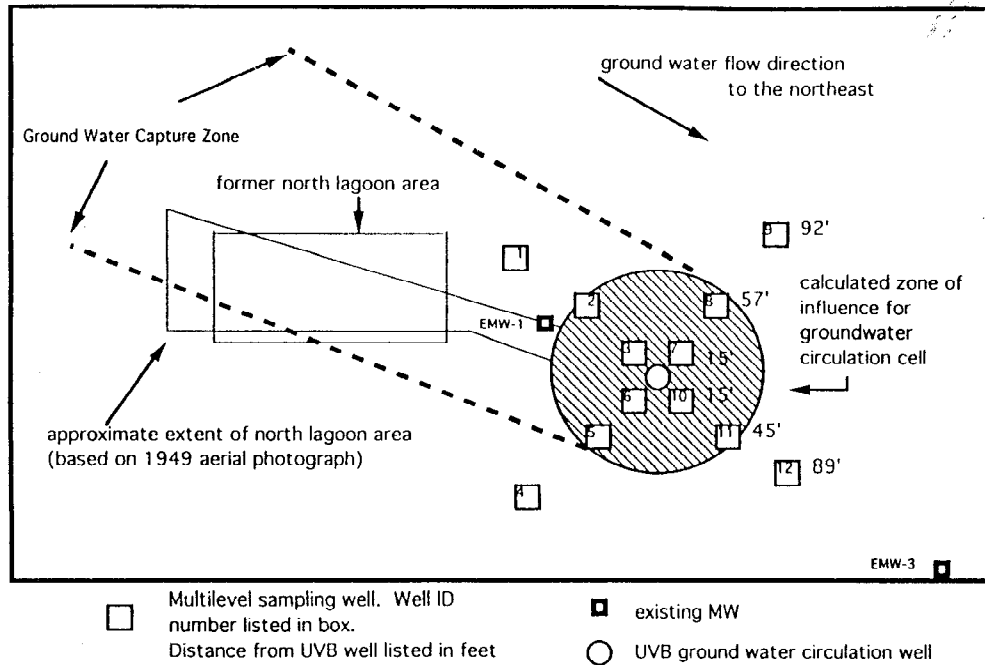
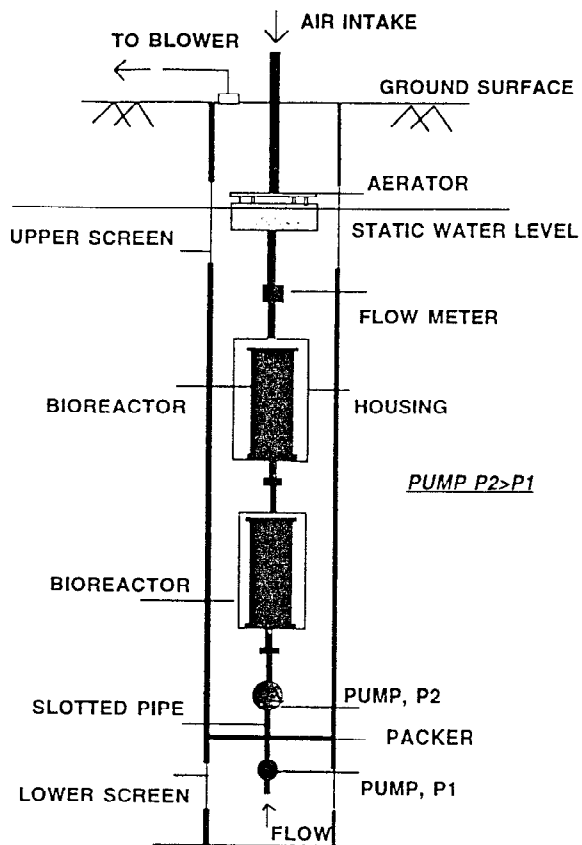


Figure 2. Schematic diagram of *in-situ* bioreactors in a groundwater circulation well



SCHEMATIC DIAGRAM OF IN SITU BIOREACTORS IN A GROUNDWATER CIRCULATION WELL

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cooling which decreases the relative humidity of the withdrawn air. Thus, as the exhaust air passes through the above-ground treatment unit (activated carbon or vapor-phase bioreactor), condensation is minimized. By adding various combinations of support pumps (mechanical or air-lift) to the UVB system, a specific groundwater flow direction can be induced in the aquifer which produces a vertical flow either upward (reverse circulation mode) or downward (standard circulation mode). Reverse flow systems would be desired in the presence of LNAPL (prevents smearing of free product through the soil profile) whereas the presence of DNAPL would encourage the use of standard circulation (pulls free product to a DNAPL recovery sump within the UVB well). UVB systems are readily converted in the field from standard- to reverse-flow mode of operation.

Biodegradation of COI can occur under several settings depending on the mode of UVB operation (stripping or groundwater circulation or both). For example, stripped COI can be treated in above-ground bioreactors and aqueous-phase VOCs can be treated by immobilized cells within an *in-situ* bioreactor. Therefore, overall remedial efficacy of the UVB system is accomplished through a combination of physical and biological processes further described below:

i. ***In-situ* circulation of air and water**

The UVB system produces a 3-dimensional groundwater flow net around the remediation well encompassing both horizontal and vertical components. This circulating water constantly transports both contaminants, nutrients, oxygen, and, presumably, indigenous bacteria through the soil profile to the well. Likewise, air is radially pulled from the unsaturated zone into the well through the screened section. This *in-situ* 'bioventing' is maximized as the UVB system moderates automatically the desired balance of air and water by adjusting to the changing groundwater level (floating).

ii. **Stimulated *in-situ* bioremediation by indigenous microflora via the introduction/distribution of electron acceptor (oxygen) and nutrients (nitrogen)**

Groundwater circulation stimulates *in-situ* biodegradation by continuously providing dissolved oxygen and nutrients (when supplemented) to the native soil microflora. To further stimulate the biological degradation of targeted organics, the systems can be used to introduce into the soil environment inorganic nutrients and/or alternative electron acceptors in either liquid (*e.g.* nitrate) or gas form (*e.g.* oxygen, ammonia). *In-situ* biodegradation of resident organic contaminants can be further enhanced via soil heating (injected air is warmed) which also serves to enhance desorption and movement of VOCs as well as increase the period of active bioremediation in climates subject to seasonal temperature limitations.

iii. ***In-situ* air stripping of volatile organics**

In-situ air stripping aids in the overall removal of COI from the groundwater. This allows for more stringent remedial goals for monitored organics to be

more readily achieved. The contribution of stripping compared to biological removal varies according to site specific conditions. If necessary, treatment of exhaust air containing stripped VOCs can be accomplished through the use of above-ground, gas phase bioreactors and/or carbon adsorption. If the amount of VOCs in exhaust gas is predictably low, then the use of activated carbon versus a bioreactor may be preferred from an economic perspective.

iv. ***In-situ* biotreatment of aqueous VOCs via fixed-film bioreactors**

In-situ biotreatment of aqueous, dissolved-phase COI may also be accomplished using fixed-film bioreactors (Figure 2). The *in-situ* bioreactors at this site are specifically designed to house specially-selected bacteria (*Sphingomonas [Pseudomonas] paucimobilis* strain EPA505) that utilize (mineralize) HMW PAHs as sole sources of carbon and energy for growth (Mueller *et al.* 1990). In the field the HMW PAH-degrading bacteria are immobilized on an inert support in the form of a removable 'cassette' that is inserted into the core of the UVB well yielding an *in-situ* bioreactor in the flow path of the circulating groundwater. These cassettes are replaceable and may also contain slow-release inorganic nutrient sources to expand the activity of the systems. Previous results with these systems showed effective bioremediation of BTEX and pesticides with an *in-situ* bioreactor and indigenous microflora (Herrling *et al.* 1993). When properly designed and operated, the combined technologies offer, uniquely, the many advantages of *in-situ* bioremediation such as cost-effective, non-invasive, no water pumping, low operational and maintenance costs while providing *in-situ* chemical containment, mineralization of persistent chemicals (*i.e.* HMW PAHs), and protection of human health and the environment. Thus, for many environmental contamination problems, these systems offer practical, reasonable and feasible remedial options.

EFFICACY MONITORING

In addition to weekly monitoring, soil, groundwater and gas samples will be analyzed quarterly over a minimum two-year period as described in Table 2. The stable isotope approach to monitoring biodegradation of fuels involves using natural abundance measurements of carbon and nitrogen isotopes. Petroleum-derived materials are comprised of many different chemical components. The $\delta^{13}\text{C}$ values of many of these components have been measured in petroleum products of various origins and maturities. In summary, petroleum products have been found to have distinct suites of carbon isotope ratios associated with them. In other words, a specific source has a distinct 'fingerprint' of $\delta^{13}\text{C}$ values. Therefore, $\delta^{13}\text{C}$ analytical methods can be used to trace carbon in creosote into bacterial biomass and into gases resulting from biodegradation. A combination of gas chromatography-mass spec-

Table 2. Identification of analytical measurements and frequency of analyses conducted to assess *in-situ* bioremediation at the Gainesville, Florida site

Analysis	Soil	Water	Gas
Semivolatiles PAH	4x/yr	4x/yr	4x/yr
Semivolatile PAH SI	4x/yr	4x/yr	4x/yr
AODC	4x/yr	4x/yr	N/A
Phenanthrene degraders	4x/yr	4x/yr	N/A
Humic extraction	4x/yr	N/A	N/A
C Humic SI	4x/yr	N/A	N/A
C/N Humic []	4x/yr	N/A	N/A
pH	1x/yr	4x/yr	N/A
Ammonia-N	1x/yr	4x/yr	N/A
Nitrate-N	1x/yr	4x/yr	N/A
Nitrite-N	1x/yr	4x/yr	N/A
Total phosphorus	1x/yr	N/A	N/A
Soluble phosphorus	1x/yr	N/A	N/A
Phosphate	N/A	4x/yr	N/A
Organic C []	4x/yr	4x/yr	N/A
Organic C SI	4x/yr	4x/yr	N/A
Organic N []	4x/yr	4x/yr	N/A
Organic N SI	4x/yr	4x/yr	N/A
Nucleic acids	4x/yr	N/A	N/A
Bacterial productivity	N/A	4x/yr	N/A
Bacterial A SI	4x/yr	4x/yr	N/A
Inorganic C []	4x/yr	N/A	N/A
Inorganic C SI	4x/yr	N/A	N/A
O ₂ []	N/A	4x/yr	4x/yr
CO ₂ []	N/A	N/A	4x/yr
CO ₂ SI	N/A	N/A	4x/yr
CH ₄ []	N/A	N/A	4x/yr
CH ₄ SI	N/A	N/A	4x/yr
Temperature	4x/yr	4x/yr	4x/yr
Dissolved organic C []	N/A	4x/yr	N/A
Dissolved organic C SI	N/A	4x/yr	N/A
Dissolved inorganic C []	N/A	4x/yr	N/A
Dissolved inorganic C SI	N/A	4x/yr	N/A
Dissolved inorganic N SI	N/A	4x/yr	N/A
Total organic N []	N/A	4x/yr	N/A
Dissolved iron	N/A	4x/yr	N/A
Cations	N/A	4x/yr	N/A
Cl, SO ₄ , pH,	N/A	4x/yr	N/A
Total dissolved solids, conductivity	N/A	4x/yr	N/A
Bicarbonate	N/A	4x/yr	N/A

Abbreviations:

[] – Concentration

SI – Stable isotopes

AODC – Acridine orange direct count

AA – Amino acids

trometry (GC/MS) and carbon isotope ratio mass spectrometry (GC/C/IR/MS) will offer insight into the fate and effect of removed creosote. Moreover, stable carbon isotope ratios of amino acids specific to bacteria will be used as a biomarker for bacterial biomass. Together with $\delta^{13}\text{C}$ measured in gases (e.g. CO_2 , CH_4), these data will provide an isotopic fingerprint of carbon being degraded by bacteria. These values will be compared to $^{13}\text{C}/^{12}\text{C}$ of the potential bacterial substrate sources, indicating which compounds are being degraded. Carbon isotope ratios are reported in the standard $\delta^{13}\text{C}$ notation:

$$\delta^{13}\text{C} (\text{‰}) = [(R_{\text{sample}}/R_{\text{std}}) - 1] \times 1000$$

where R_{sample} and R_{std} are the $^{13}\text{C}/^{12}\text{C}$ isotope ratios of the sample and the conventional PeeDee Belemnite standard, respectively.

CRITICAL ANALYSIS

Groundwater remedial guidelines identified by the State of Florida and the US EPA, Region IV (Atlanta) are summarized in Table 3. The overall success of the *in-situ* bioremediation system will be evaluated, in part, according to its ability to meet these stringent criteria. But the advantages of *in-situ* chemical containment, economics, and implementability will also be considered. Moreover, the validity of using stable C isotope analysis for near-real-time monitoring of *in-situ* bioremediation performance will be documented.

Table 3. Groundwater remedial guidelines for the Gainesville, Florida site

Chemical	Identified clean-up criteria ($\mu\text{g/L}$)
Phenol	2630
Anthracene	1310
Fluorene	323
Acenaphthene	260
Acenaphthylene	130
Phenanthrene	130
Pyrene	130
Arsenic	50
Chromium	50
Naphthalene	18
Benzene	1
pcPAHs	0.003

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