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BTEX degradation in a cold-climate wetland system

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Abstract

A pilot scale subsurface vertical-flow wetland system was constructed at the former BP Refinery in Casper, Wyoming in order to determine BTEX degradation rates in a cold-climate application. The pilot system, consisting of 4 cells, each dosed at a nominal flow rate of 5.4 cubic meters per day, was operated between August and December 2002. The pilot was designed to test the relative effects of operating the cells with wetland mulch (obtained from a natural wetland) and with aeration (believed to enhance volatilization and aerobic biodegradation). Areal rate constants (k_A values) were calculated based on an assumed three tanks in series (3TIS). The presence of wetland sod and aeration both improved treatment performance. Mean k_A values were ~240 m/yr for cells without sod or aeration, and improved to ~360 m/yr with sod and aeration.

Based on the results of the pilot system, a full-scale wetland (capable of operating at 6,000 m^3/day) was constructed at the site and started up in May 2003. The full-scale system achieved permit compliance within one week of startup, but is currently being loaded at only 45% of the design hydraulic load, and 15% of the design BTEX mass load, resulting in a mean k_A value of ~350 m/yr.

Keywords
Aeration; benzene; BTEX; cold-climate; subsurface–flow wetland

INTRODUCTION

The British Petroleum (BP) refinery in Casper Wyoming operated from 1912 to 1991. As a result of common operating practices during the first 50 years of operation, much of the site is underlain with residual hydrocarbons. Remediation efforts were complicated because the North Platte River serves as the northern border of the 140-ha site. Historically, the elevation of the water table has fluctuated in response to the water stage of the North Platte River. These fluctuations have produced a "smear zone" containing residual hydrocarbons that extends from approximately 1.5 meters above the water table to 3 meters below the water table. Since 1981, over 37,000 cubic meters of light non-aqueous phase liquids (LNAPL) have been removed from the groundwater. In 1998, the Wyoming Department of Environmental Quality (WDEQ) finalized a Consent Decree establishing the framework for site remediation. Under the Consent Decree, BP and the City of Casper agreed to convert the former refinery site into a golf course and office park with a trail system along the North Platte River.

Because of the time required for remediation (50 to 100 years), BP became very interested in biological treatment processes due to the potential cost savings. A constructed wetland was identified as a low-maintenance system compatible with the intended golf course use of the property. The WDEQ permit requires that effluent benzene levels be less than 0.05 mg/L.

Existing Information on BTEX Hydrocarbon Treatment in Wetlands

Petroleum wastes are documented to naturally degrade in natural wetland environments (Wemple C. *et al.,* 2000). The microbial community associated with the plant rhizosphere creates an environment conducive to degradation of many volatile organic compounds (Schnoor J. *et al.,* 1995, Pardue J.H. *et al.,* 2000). Both surface-flow and subsurface-flow constructed wetlands have been used to treat petroleum wastewaters (American Petroleum Institute, 1998).

Surface-flow constructed wetlands have been used to treat petroleum wastewaters from Amoco's Mandan, North Dakota facility since the early 1970's (Litchfield D.K. *et al.,* 1989, Litchfield D.K., 1993). For higher strength wastes, surface-flow wetlands have been used in conjunction with mechanical treatment systems (Lakatos G., 2000).

Due to the higher surface area present in a gravel bed, subsurface-flow wetlands can achieve more biological treatment in a given unit area (Kadlec R.H. *et al.,* 1996). Initial work on the use of subsurface-flow wetlands to treat industrial organic compounds was completed in Germany (Seidel K., 1973). The Seidel approach has been successfully used in a full-scale system at the Mobil Oil AG terminal in Bremen, Germany (Vymazal J. et al., 1998). Subsurface-flow wetlands have also been used to treat coke plant wastewaters (Jardiner N. et al., 2000). A study in Arizona (Wass R.D. *et al.,* 1993) indicated that wetland vegetation plays an important role in the removal of oil & grease in stormwater-driven subsurface-flow wetlands. A study in the United Kingdom (Omari K.O. et al., 2001) demonstrated improved removal of BP diesel-range organics (C-10 to C-26-range) in vegetated vs. unvegetated subsurface-flow wetland cells, and the improved removal could be correlated to the vertical distribution of root/rhizomes in the wetland cell.

Kadlec (Kadlec R.H., 2001) concluded that aeration would be an important component of subsurface-flow wetland design, as an active aeration system would enhance both volatilization and aerobic degradation of hydrocarbons. A subsurface-flow wetland was used at the Gulf Strachan Gas Plant, approximately 200 km northwest of Calgary, Alberta to treat hydrocarbon-contaminated groundwater (Moore B.J. et al., 2000). This study demonstrated successful treatment of hydrocarbon waste under winter conditions. An aeration system was used during the winter months, which resulted in improved removal of both total petroleum hydrocarbon (TPH) and benzene-toluene-ethylbenzene-xylene (BTEX) compounds. An aerated subsurface-flow wetland in Watertown, South Dakota, demonstrated essentially complete BTEX removal in the first 40% of the wetland bed (Wallace S.D., 2001a).

PILOT SYSTEM

Based on a review of the existing literature, Kadlec (Kadlec R.H., 2001), estimated a 3-tanks-in-series (3TIS) areal rate constant (k_A) of 115 m/yr for BTEX and benzene. For the initial design criteria of 8,000 m^3/d, this would have required 11 ha of subsurface-flow wetlands, which could not be accommodated at the site. This initial feasibility study also recognized the need for cascade oxygenation for iron control, together with a settling basin for iron precipitate collection. Further, all examples available in the literature were for non-aerated wetlands, and since aeration is believed to improve treatment of petroleum hydrocarbons, a pilot system was constructed to assess aerated wetland performance.

Pilot System Design

Four subsurface-flow treatment cells (operating in parallel) were established. Each cell was 1.7 m wide by 7 m long by 1.1 m deep (Ferro A.M. et al., 2002). Cells were loaded at a nominal flow rate of 5.4 m^3/day, resulting in a nominal hydraulic retention time of one day.

In each pilot cell, influent was introduced across the bottom area of the wetland, flowed upward through the (lower) gravel and (upper) sand bed, and then across the upper portion of the sand bed to the outlet. This flow path was selected based on intellectual property constraints in the United States, although Kadlec (Kadlec R.H., 2001) noted that this is a potentially unstable flow regime, and short-circuiting problems were observed with this flow path.

Various species of wetland plants were transported from the University of Wyoming-Laramie greenhouse for the pilot systems, including species of willows (*Salix*), reed (*Phragmites*), bulrush (*Schoenoplectus*), rush (*Juncus*), and dogwood (*Cornus*). Two of the four cells were vegetated using a 15-cm thick sod layer consisting of plant detritus interlocked with roots and rhizomes harvested from a nearby wetland (Soda Lake) which had a mature assemblage of wetland vegetation adapted to alkaline conditions (Ferro A.M. *et al.,* 2002).

Pilot System Results

The pilot system was operated between August and December 2002. The pilot was designed to test the relative effects of operating the cells with wetland sod and with aeration. Some problems (non-uniform flow due the upward flow path and non-uniform air distribution) were noted. During the course of operation, all four pilot cells were operated with aeration for at least part of the study period. Data from each of the pilot cells was segregated into periods with and without aeration. The presence of wetland sod and aeration both improved treatment performance. The water temperature decreased throughout the period of pilot operation, however no impact on removal rates was observed (θ = zero). Mean rate constants based on assumed 3TIS flow were established for benzene, BTEX, TPH, and methyl *tert*-butyl ether (MTBE) as summarized below:

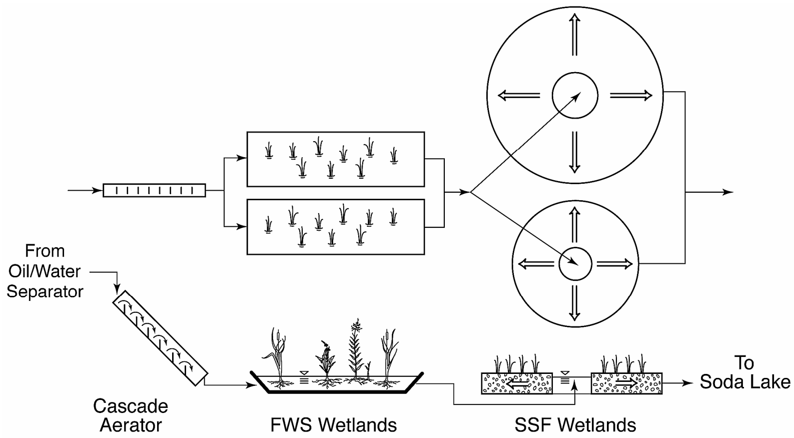
Table 1. Pilot system areal rate constants (k_A, m/yr, based on 3TIS)

	Aeration		No Aeration	
Compound	Wetland Mulch	No Mulch	Wetland Mulch	No Mulch
Benzene	518	456	317	226
BTEX	356	311	257	244
TPH	1058	965	725	579
MTBE	64	60	35	22

FULL-SCALE SYSTEM

The full-scale system was designed to treat 6,000 m^3/day of contaminated groundwater. Because potential fouling of the subsurface-flow (SSF) wetland media was identified during the pilot operation, a cascade aeration system (for iron oxidation) and free-water-surface (FWS) wetland (for iron precipitation) was added to the system.

Figure 1. Schematic of full-scale wetland treatment system at Casper, Wyoming. The FWS wetland cells have a combined area of 0.6 ha. The SSF wetland cells have a combined area of 1.3 ha with 90-cm deep gravel beds.



Cascade Aerator

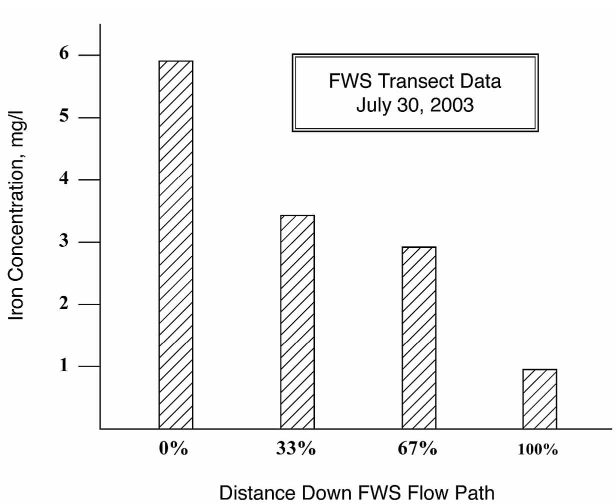
Federal regulations require that the benzene concentration of the water released to the wetland treatment system be less than 0.5 mg/L. An enclosed, ventilated cascade aerator was designed to reduce benzene levels in the oil/water separator effluent. Volatile organics stripped from the water column are routed to a soil-matrix biofilter for degradation. Average benzene reduction in the cascade aerator to date has been 54 percent.

Free Water Surface Wetlands

The primary function of the FWS wetlands is to precipitate and remove iron to prevent fouling of the SSF wetland media. Reduced iron present in the groundwater is oxidized in the cascade aerator. Due to the pH of the water (8.3), oxidized iron rapidly forms ferric oxyhydroxide precipitates.

The FWS wetland is divided into two parallel treatment cells with a combined surface area of 0.6 ha. The water depth in each cell can be independently adjusted from 0 to 60 cm, with a typical operating depth of 30 cm. The FWS wetland cells were planted with Hardstem Bulrush (*Scheonoplectus acutus*), Cattail (*Typha angustfolia*) and Bur-reed (*Sparganium eurycarpum*). Transect data indicates the FWS wetlands are effective in removing iron.

Figure 2. Iron reduction in FWS wetland cell.



Subsurface-Flow Wetland Cells

The thousand-fold scale-up from the pilot until to the full-scale treatment system presented a number of design challenges, first and foremost of which was flow distribution. In order to apply the rate constants developed from the pilot, the full-scale system had to be designed such that the degree of short-circuiting and dispersion was less than that observed in the pilot study. The vertical flow path was abandoned in favor of a center-feed, horizontal, radial-flow configuration.

In order to operate ice-free in the severe Wyoming winter, a 15 cm insulating mulch layer was installed on top of the SSF wetland cells. The insulation layer was designed using energy balance methods described elsewhere (Wallace S.D. et al., 2001), and the wetland cells remained ice-free during the winter of 2003/2004. The SSF wetland cells were constructed with an aeration system (Wallace S.D., 2001b) capable of uniformly distributing air throughout the wetland basins. Air distribution to the wetland bottom was via aeration tubing on 60 cm spacing. Thirty-seven kilowatts of blower capacity are employed. However, since the aeration system uses variable-frequency drives, actual power consumption is usually much less.

The full-scale system was started up in May, 2003. Since startup, the system has been hydraulically loaded at approximately 2,700 m^3/day (45% of design). System performance to date for benzene, BTEX, and gasoline-range organics (GRO) is summarized below:

Table 2. Mean influent and effluent concentrations for the full-scale wetland treatment system, May 2003 – March 2004.

Compound	Wetland Influent	Wetland Effluent
Benzene, mg/L	0.17	Non-detect (0.01)
BTEX, mg/L	0.47	Non-detect (0.01)
GRO, mg/L	2.02	Non-detect (0.05)

Although the system is producing non-detect levels of petroleum hydrocarbons, the current BTEX mass load is only about 15% of the design mass load. Because actual effluent concentrations are likely significantly less than the detection limit, the low mass loading has resulted in lower observed removal rate constants:

Table 3. Mean areal 3TIS rate constants for the full-scale treatment system.

Compound	k_A, m/yr
Benzene	~ 240
BTEX	~ 350
GRO	~ 325

Rate constants summarized in Table 3 are approximate in nature. Due to the location of sampling points, this represents the combined removal in the FWS and SSF wetland cells, and the combined detention time has been used.

CONCLUSIONS

This project demonstrated, through the application of both pilot-scale and full-scale wetland treatment systems, that removal rates for petroleum hydrocarbons in aerated subsurface flow wetlands is considerably higher than in non-aerated wetlands. Areal rate constants (3TIS k_A values) BTEX degradation was measured in the pilot system to be 244 m/yr for cells operating without aeration and mulch, and increased to 356 m/yr for cells with aeration and mulch. The full scale system, which uses aeration and mulch, has a 3TIS k_A value of ~ 350 m/yr. Based on data from the pilot and the full-scale system, there appears to be little, if any temperature effect on petroleum hydrocarbon degradation rate constants.

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