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Long Term Hydrocarbon Removal Using Treatment Wetlands

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Abstract

This study focuses on the treatment performance of two full-scale treatment wetlands constructed by BP for groundwater remediation. The first is in Casper, Wyoming (commissioned in 2003); the second is located in Wellsville, New York (commissioned in 2008). Treatment wetlands were selected in both cases due to low operating costs, which result in favorable life-cycle costs when managing legacy contaminants associated with former refining operations.

Both treatment systems have been highly effective and have met regulatory compliance objectives. System performance can be measured by a first-order, area-based rate coefficient (k), that can be applied to future wetland design projects. For the full-scale Casper wetland, rate coefficients were measured as 0.66, 0.96, and 0.89 m/d for benzene, BTEX and gasoline-range organics, respectively. The wetland system removes essentially 100% of these constituents, with non-detect concentrations in the effluent.

For the full-scale Wellsville wetland, rate coefficients were measured as 0.37 and 0.33 m/d for aniline and nitrobenzene. The wetland system has removed 94% of the aniline and 93% of the nitrobenzene (based on mean influent and effluent concentration values over the period of record). Treatment performance has been very stable after the initial winter start-up period. Excursions above non-detect concentrations typically occur during the winter months when water temperatures are at a minimum and the wetlands are partially iced over. The Wellsville system has also been very effective in iron removal, removing 98% of the iron (based on mean concentration values), despite relatively high influent concentrations (mean value of 33.3 mg/L).

Both systems operate under cold climate conditions. The Casper wetland operates at temperatures as low as -35˚C; the Wellsville wetland operates at temperatures that can drop below -20˚C. The multi-year performance history of these two wetland systems demonstrates that wetlands are a viable and cost-effective treatment alternative, even under cold climate conditions.

Development of Wetland Technology in the Oil and Gas Industry

Petroleum hydrocarbons are known to naturally degrade in natural wetland environments (Wemple and Hendricks, 2000). The microbial community associated with the plant rhizosphere creates an environment conducive to degradation of organic compounds (Schnoor *et al.*, 1995; Pardue, 2002). Both surface flow and subsurface flow constructed wetlands have been used to treat petroleum wastewaters (Knight *et al.*, 1999)

Surface flow constructed wetlands have been used to treat petroleum wastewaters from the Mandan, North Dakota refining facility since the early 1970's (Litchfield, 1990). For higher strength wastes, surface-flow wetlands have been used in conjunction with mechanical treatment systems (Lakatos, 2000). Initial work on the use of subsurface-flow wetlands to treat industrial organic compounds was completed in Germany (Seidel, 1973). The Seidel approach has been successfully used in a full-scale system at the Mobil Oil AG terminal in Bremen, Germany (Vymazal *et al.*, 1998).

A study in Arizona (Wass and Fox, 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 *et al.*, 2003) demonstrated improved removal of diesel range organics (C-10 to C-26-range) in vegetated subsurface flow wetlands cells when compared to unvegetated cells. The improved removal was correlated to the vertical distribution of root/rhizomes in the wetland cell. The important role of vegetation in hydrocarbon degradation has also been documented in surface flow wetlands (Al Mahruki *et al.,* 2006).

The development of wetland technology in the oil and gas industry has lead to a number of different application areas, which include groundwater remediation (Moore *et al.*, 2000; Wallace and Kadlec, 2005), treatment of refinery effluents (Litchfield, 1990, Duda 1992), management of tank farm runoff and tank bottoms (Wallace, 2002), and treatment of low-salinity produced water (Gurden and Cramwinckel, 2000, Jackson and Myers, 2003, Al Mahruki *et al.,* 2006, Gill *et al.,* 2006).

Kadlec (2001) concluded that aeration would be an important component of subsurface flow wetland design, because 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 *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 hydrocarbons (TPH) and benzene, toluene, ethylbenzene, and 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, 2002). Aeration has been designed into produced water treatment wetlands in Oman (Sluijterman *et al.,* 2004).

Treatment wetlands are known to have very low operating costs relative to other treatment technologies (Jackson and Myers, 2003). These low operating costs result in favorable life-cycle costs when dealing with legacy contaminants, which can be present for decades. This makes treatment wetlands a preferred technology for groundwater remediation systems when adequate land is available (Wallace and Kadlec, 2005).

Characterization of Wetland Performance

It is recognized that wetlands, being natural treatment systems, do not behave as plug-flow reactors. As a result, most modern wetland design methods use a tank-in-series (TIS) hydraulic model to account for short-circuiting and dispersion within the wetland. The number of tanks in series is a mathematical characterization of hydraulics and can also be adjusted to account for pollutant weathering (where the most easily degradable compounds are removed first) and is commonly denominated as P. Most treatment reactions in wetlands follow first-order kinetics, which is characterized by a rate coefficient, k. For certain compounds, such as chemical oxygen demand and organic nitrogen, there is a background concentration that is inherent to the wetland ecosystem, which is commonly denominated as C^*. Combining these parameters to characterize wetland performance is commonly called the P-k-C^* model (Kadlec and Wallace, 2009):

$$\left(\frac{C-C^*}{C_i-C^*}\right)=\frac{1}{(1+k/Pq)^P}=\frac{1}{(1+k_V\tau/P)^P}$$

Where: C_i = inlet concentration
C = outlet concentration
k = area-based first order rate coefficient, m/d
k_v = volumetric-based first order rate coefficient, d^{-1}
q = hydraulic loading rate, m/d (flow divided by wetland area)
τ = hydraulic residence time, days
P = apparent number of TIS

Expression of wetland treatment performance can be characterized by either volume-based calculations (k_v) or area-based calculations (k). However, many treatment processes in wetlands (such as particle settling or air/water gas exchange) are dependent on the wetland area, so area-based calculations (k) are usually preferred in the wetland design field.

Casper, Wyoming Wetland Treatment System

The Casper system was developed from a pilot-scale subsurface flow (SSF) wetland that was operated in 2002. Pilot system results indicated that the aerated SSF configuration (with a surface mulch layer for insulation) was the most effective in hydrocarbon removal. The full-scale treatment system includes a cascade aerator for iron oxidation and surface flow (also termed free water surface, FWS) wetlands for iron removal prior to the SSF wetland cells, as indicated in Figure 1:

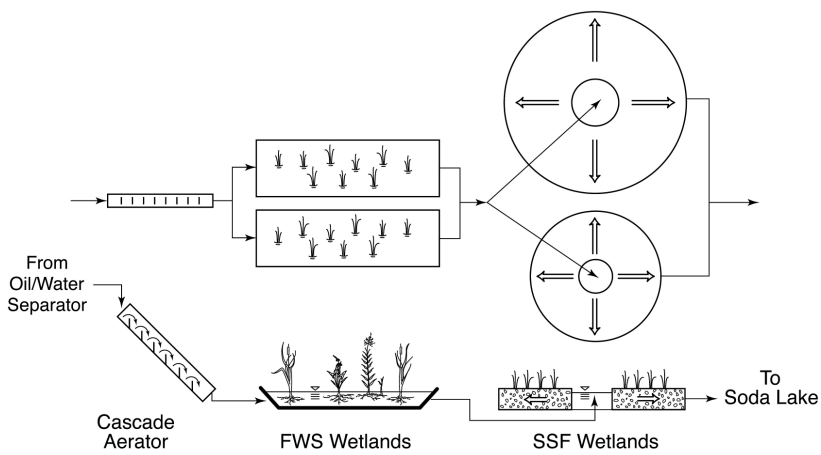

Figure 1. Schematic of the full-scale treatment wetland at Casper, Wyoming

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. The design flow rate for the system is 6,000 m^3/d, although actual flows are approximately 2,700 m^3/d (45% of design). Due to the cold winter temperatures (-35˚C), the SSF wetland cells are covered by 15 cm of mulch insulation, as shown in Figure 2:

Figure 2. Insulated SSF wetland at Casper, Wyoming

At the actual flow rate of 2,700 m^3/d, the overall hydraulic residence time (τ) is approximately 2.3 days. System performance for benzene, toluene, ethylbenzene, and xylene (BTEX), and gasoline-range organics (GRO) was monitored in detail during 2003 and 2004; results are summarized in Table 1:

Table 1. Mean influent and effluent concentrations for the Casper wetland system

Compound	Influent	Effluent	Removal Percentage
Benzene, µg/L	170	Non-detect	~100%
BTEX, µg/L	470	Non-detect	~100%
GRO, µg/L	2,020	Non-detect	~100%

Since 2004, treatment results have been consistent with Table 1, although the monitoring frequency has been reduced. The flow rate, wetland areas, and treatment performance can be combined to determine a first-order area-based rate coefficient (k) that can be used to design other wetland treatment systems, as summarized in Table 2:

Table 2. Mean areal (3TIS) rate coefficients for the Casper wetland system

Compound	k, m/d
Benzene	0.66
BTEX	0.96
GRO	0.89

Wellsville, New York Wetland Treatment System

At the project site in Wellsville, New York, an oil refinery was operated by Sinclair from circa 1901 though 1958. Although refining operations ceased over 50 years ago, legacy contaminants persist at the site. The Wellsville treatment facility consists of four major unit processes that are designed to reduce metals, organic compounds, and buffer the pH of the recovered groundwater:

A cascade aeration system (four 45 cm diameter corrugated metal pipes in parallel) to oxidize iron to the Fe^{+3} state.

A sedimentation pond (0.16 ha) to settle and remove ferric hydroxide precipitates.

A series of surface flow wetlands (3 in parallel) to further remove iron and also to remove residual organic compounds (notably aniline and nitrobenzene). The surface flow wetland cells have a combined area of 0.7 hectares.

A series of vertical flow wetlands (5 in parallel) with a reactive limestone media to add alkalinity to the water and buffer the effluent pH. The vertical flow wetland cells have a combined area of 0.07 hectares.

The system is designed to operate at 840 m^3/day, but actual flow rates have exceeded this by 20%. A schematic of the facility is shown in Figure 3:

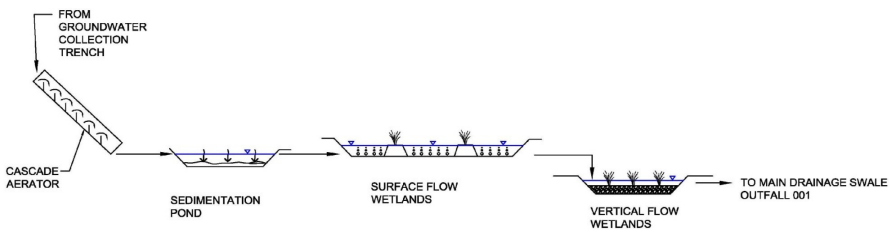

Figure 3. Wellsville, New York treatment wetland process schematic

Due to the cold climate (-20˚C), the surface flow wetland cells are aerated to create ice-free zones during the winter, as shown in Figure 4:

Figure 4. Wellsville, New York treatment wetland operating under winter conditions

The wetland system was placed into operation in December 2008 and was monitored weekly through August 2009. Due to the high level of treatment occurring in the system, the sampling frequency was reduced to monthly monitoring in September 2009. At the design flow rate of 840 m^3/d, the overall hydraulic residence time (τ) is approximately 4.8 days. The system has been monitored for a variety of volatile organic compounds (VOCs) semi-volatile organic compounds (SVOCs) and metals, including: benzene, ethylbenzene, toluene, xylene, acenapthene, aniline, 2-methynapthalene, nitrobenzene, phenanthrene, arsenic, iron, manganese, and pH. The primary constituents of concern (those significantly above target levels) are aniline, nitrobenzene, and iron. Additionally, oxidation of the iron naturally present in the groundwater has the potential to lower the pH below target levels. Monitoring results from December 2008 through April 2011 are summarized in Table 3:

Table 3. Mean influent and effluent concentrations for the Wellsville wetland system.

Parameter	Influent	Effluent	Removal Percentage
	VOCs, µg/L		
Benzene	10.2	1.3	87%
Ethylbenzene	6.9	0.9	87%
Toluene	3.5	0.8	77%
Xylene	8.6	0.9	89%
	SVOCs, µg/L		
Acenapthene	1.0	0.4	63%
Aniline	508	32	94%
2-Methylnapthalene	8.4	0.5	94%
Napthalene	1.6	0.6	64%
Nitrobenzene	2,612	189	93%
Phenanthrene	1.1	0.2	80%
	Metals, mg/L		
Arsenic	0.5	0.01	98%
Iron	33.3	0.6	98%
Manganese	5.3	1.3	75%
	pH		
pH	6.8	7.4	NA

For the two organic compounds of interest, aniline and nitrobenzene, the flow rate, wetland areas, and post-startup treatment performance can be combined to determine a first-order area-based rate coefficient (k) that can be used to design other wetland treatment systems, as summarized in Table 4:

Table 4. Mean areal (5TIS) rate coefficients for the Wellsville wetland system

Compound	*k*, m/d
Aniline	0.37
Nitrobenzene	0.33

For the organic constituents of concern at the Wellsville site, system performance has been stable after the initial startup period. Because aniline and nitrobenzene are present on only a portion of the site, influent concentrations to the wetland system vary greatly depending on which groundwater collection sumps are active at the time. Performance summaries for aniline and nitrobenzene are summarized in Figures 5 and 6, respectively:

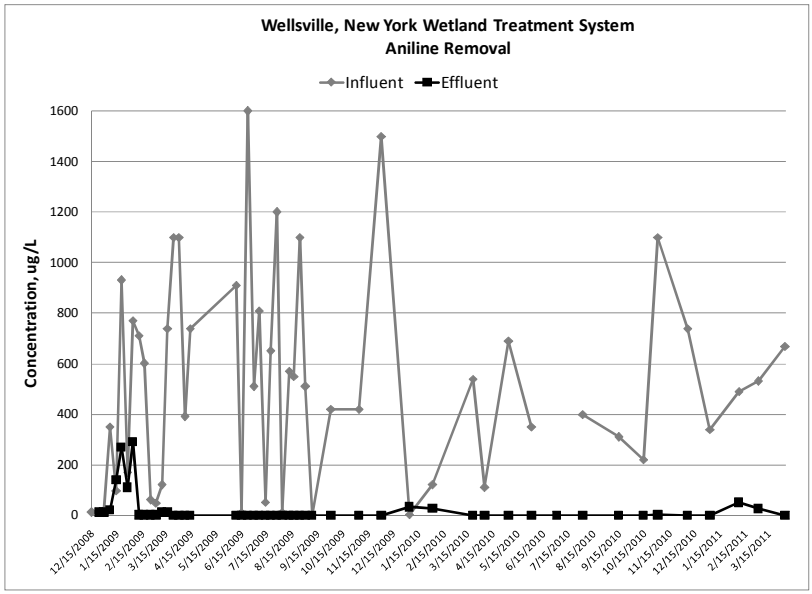

Figure 5. Aniline removal at the Wellsville wetland system

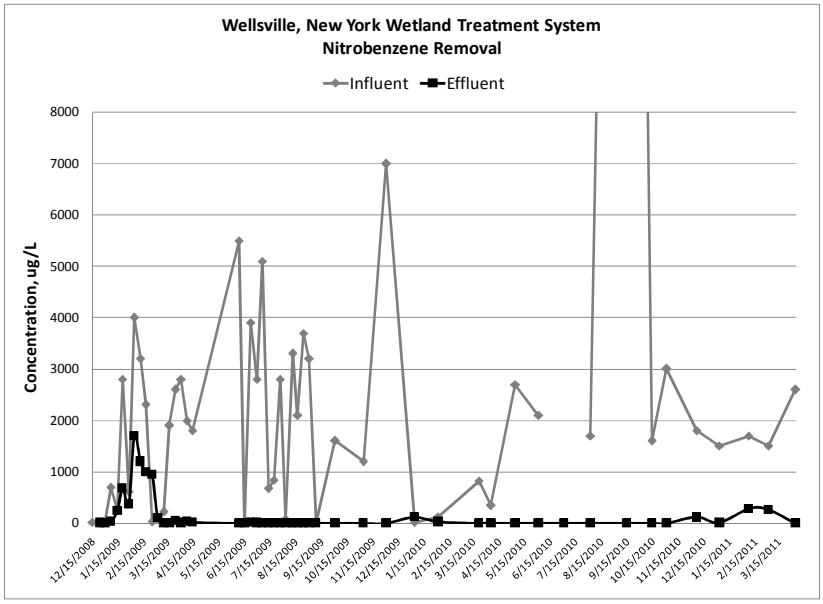

Figure 6. Nitrobenzene removal at the Wellsville wetland system

Both Figure 5 (aniline) and Figure 6 (nitrobenzene) display a seasonal trend with elevated effluent concentrations during the winter months. This trend is most prominent during the start-up period during the winter of 2008/2009, which represented a worst-case condition (complete ice cover, almost no wetland vegetation). During the 2009 construction season, an aggressive supplemental planting program was completed to accelerate plant establishment and the aeration system was activated to create ice-free zones within the surface flow wetland cells. This resulted in markedly better performance during the 2009/2010 and the 2010/2011 winter operating periods.

Iron was the remaining constituent of concern. Performance of the wetland system has been stable for iron removal as well, as illustrated in Figure 7:

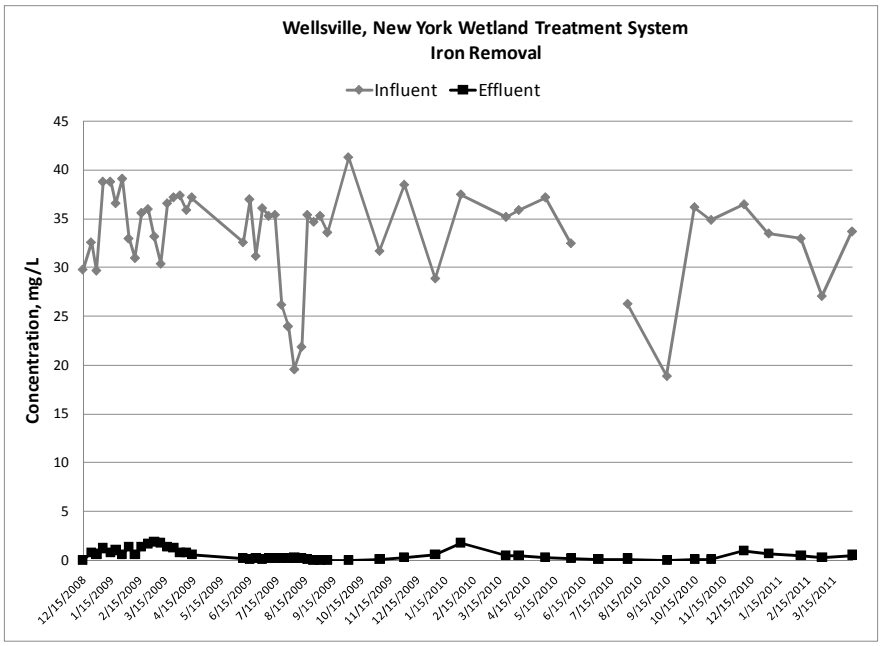

Figure 7. Iron removal at the Wellsville wetland system

Conclusions

Both the Casper, Wyoming and Wellsville, New York wetland treatment systems have demonstrated effective and stable removal of organic compounds over multi-year periods. In both cases, the low operating cost of wetland systems lead to the selection of wetland technology over mechanical alternatives.

Both treatment systems have been highly effective and have met regulatory compliance objectives. System performance can be measured by a first-order, area-based rate coefficient (k), that can be applied to future wetland design projects. For the full-scale Casper wetland, rate coefficients were measured as 0.66, 0.96, and 0.89 m/d for benzene, BTEX and gasoline-range organics, respectively. The wetland system removes essentially 100% of these constituents, with non-detect concentrations in the effluent.

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