The Use of Treatment Wetlands for Petroleum Industry Effluents

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Although the use of treatment wetlands is well established for wastewater categories such as municipal waste, stormwater, and acid mine drainage water, their use in treating a variety of industrial and agricultural wastewaters is less well developed. Several large-scale wetland projects currently exist at oil refineries, and numerous pilot studies of constructed treatment wetlands have been conducted at terminals, gas and oil extraction and pumping stations, and refineries. This paper reviews treatment wetland performance for chemical oxygen demand, biochemical oxygen demand, trace organics, metals, toxicity, total suspended solids, nitrogen, and phosphorus. All of these contaminants can be reliably removed from wastewater by treatment wetlands. Pollutant removal is highly dependent on hydraulic loading and influent concentration and to a lesser extent on internal plant communities, water depth, and hydraulic efficiency. In most cases, data from petroleum industry wetland studies indicate that treatment wetlands are equally or more effective at removing pollutants from petroleum industry wastewaters than from other types of wastewater. Until industry-specific data are more complete, this finding can be used along with published rate constants from other wastewater categories to provide conservative estimates for sizing petroleum industry treatment wetlands.

Introduction

Wetlands have been engineered for water quality treatment in Europe and in the United States since the early 1970s. Considerable information on the design and operation of these treatment wetlands has accumulated since that time. As a result, a rapidly growing body of literature is available to those interested in applying this technology for water quality treatment (*1*−*8*).

A recent report prepared for the American Petroleum Institute (API) continues this synthesis by providing the first review of treatment wetland research and full-scale projects in the petroleum industry worldwide (*9*). Over the past 10 years, journal articles and symposia proceedings have indicated the petroleum industry's interest in using constructed wetlands to manage process wastewater and stormwater at a variety of installations, including refineries, oil and gas wells, and pumping stations. These publications report that constructed wetlands provide predictable water quality benefits when properly designed and maintained. However, published data have not been given broad review within or outside of the industry.

Overview of Constructed Treatment Wetlands. Wetlands are ecosystems that occur where water conditions are intermediate between uplands and deep-water aquatic systems. Technical and regulatory definitions of wetlands focus on wetland ecosystems' dependence on shallow water conditions, which result in saturated soils, low dissolved oxygen (DO) levels or anaerobiosis in soils, and colonization by adapted plant and animal communities (*10*, *11*). The natural ability of wetland ecosystems to improve water quality has been recognized for more than 25 years. During this period, the use of engineered wetlands has evolved from a research concept to an accepted pollution control technology (*3*).

Treatment wetland technology started when natural wetlands were incorporated as components of wastewater treatment systems (*12*, *13*). Two general types of shallow vegetated ecosystems are being used for water quality treatment: (*1*) free water surface (surface flow) and (*2*) subsurface flow (vegetated submerged bed) systems (Figure 1). Free water surface treatment wetlands (Figure 1a) mimic the hydrologic regime of natural wetlands. In these wetlands, water flows over the soil surface from an inlet point to an outlet point or, in a few cases, is totally lost to evapotranspiration and infiltration within the wetland. In subsurface flow wetlands (Figure 1b), wastewater flows through a constructed media bed planted with wetland plants; this eliminates the potential for direct exposure of humans or wildlife to the wastewater.

The U.S. Environmental Protection Agency (EPA) has prepared a design manual summarizing early performance information for both system types (*14*) as well as a subsurface flow technology assessment (*15*). A technology assessment report and a design manual revision focusing only on the free water surface treatment wetland technology are currently in preparation for EPA.

Summary of Typical Performance. Treatment wetlands function as land-intensive biological treatment systems. In these systems, inflow water containing particulate and dissolved pollutants slows and spreads through a large area of shallow water and emergent vegetation. Particulates

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10.1021/es980740w CCC: $18.00
Published on Web 02/24/1999

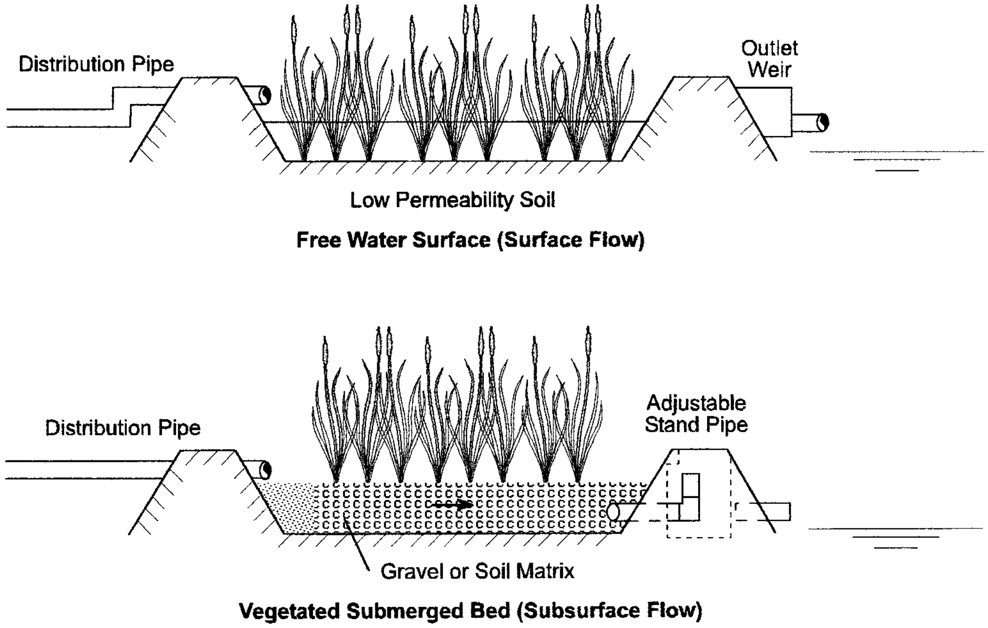

FIGURE 1. Schematic of wetland treatment systems (adapted from ref *3*).

TABLE 1. Summary of Average Performance of Treatment Wetlands: Treating Different Wastewater Types[d]

	municipal[a]				pulp and paper[b]				confined livestock[c]			
parameter	in	out	removal efficiency (%)	*n*	in	out	removal efficiency (%)	*n*	in	out	removal efficiency (%)	*n*
BOD_5	30	8.1	73	61	26	14	48	30	263	93	65	50
TSS	46	13	72	59	42	12	71	30	585	273	53	41
TN	9.7	4.5	53	28	12.6	6.6	48	9	254.1	147.5	42	13
TP	3.8	1.6	57	44	2.3	1.7	26	20	24.3	14.1	42	44

[a] References *3* and *16*. [b] Reference *17*. [c] Reference *18*. [d] All data are for average concentrations in mg/L. *n* = number of different treatment wetland systems reporting long-term data.

(typically measured as total suspended solids [TSS]) tend to settle and are trapped in the sediment due to lowered flow velocities and sheltering from wind. These particulates contain biochemical and chemical oxygen demanding (BOD and COD) components, hydrocarbons and other organics, trace metals, and fixed forms of total nitrogen (TN) and total phosphorus (TP). Particulate-based pollutants enter the biogeochemical element cycles within the water column and surface sediments of the wetland. At the same time, a fraction of the dissolved BOD, COD, organics, metals, TN, and TP are sorbed by soils and active microbial and plant populations throughout the wetland environment and become part of the mineral cycles of the wetland system. A portion of the phosphorus and other nonvolatile elements such as metals and nondegradable organics can be removed from the mineral cycle and buried in accreting sediments within the wetland.

Wetlands are autotrophic ecosystems, and the additional fixed carbon and nitrogen concentrations from the atmosphere are processed simultaneously with the pollutants introduced from the wastewater source. The net effect of these complex processes is a general reduction of pollutant concentrations between the inlet and outlet of treatment wetlands. However, because of the internal autotrophic processes of the wetland, outflow pollutant concentrations are seldom zero and, in some cases for some parameters, may exceed inflow concentrations. Treatment wetland systems have a wide variety of engineering designs, wetted areas, flow rates, inflow water qualities, plant communities, hydrologic regimes, effluent limitations, and monitoring requirements. Several databases have been assembled to collect and summarize these data (Table 1). These data comparisons indicate that treatment wetlands receiving a variety of differing wastewater types respond in a similar and predictable fashion.

Specific Needs of the Petroleum Industry. Untreated petroleum industry wastewaters contain many of the same pollutants as municipal wastewaters and also often contain oil and grease, various hydrocarbons, phenolics, sulfides, and metals. Potential toxicity of these constituents is a concern with some petrochemical wastewater discharges. This paper focuses on the effectiveness of constructed treatment wetlands for reducing the pollutants of primary concern to the petroleum industry. Other potential pollutants, including the nutrients nitrogen and phosphorus, are only discussed briefly. Existing treatment wetland performance data are synthesized and discussed with respect to current knowledge and data gaps on the use of treatment wetlands specifically for the petroleum industry. A review of the literature and direct inquiries of petroleum companies were used to identify existing full and pilot-scale treatment wetland projects used to provide water quality improvement. Table 2 briefly describes the features of the projects that were identified through this review. Each project is assigned a site number for identification throughout this paper. The reader is directed to the original references on each site to obtain additional information (see ref *9* for complete references).

Water Quality Improvement Performance in Treatment Wetlands. The primary design goal of most treatment wetlands is the improvement of wastewater effluent quality. This improvement is generally measured as a reduction in mass and concentration of one or more pollutants. The most

TABLE 2. Petroleum Industry Full-Scale and Pilot Treatment Wetlands Discussed in This Paper

site no.	site name/location	purpose	wastewater source	total wetland size (ha)	av flow (m^3/d)	refs
1	Amoco-Mandan, North Dakota, U.S.A.	process water polishing	refinery process water	16.6	5700	*19, 20*
2	Chevron-Richmond, California, U.S.A.	process water polishing	refinery process water	36.4	9500	*21*
3	Yanshan Petrochemical, Beijing, China	process water polishing	refinery process water	50	100000	*22*
4	Yanshan Petrochemical, Beijing, China	pilot facility	refinery process water	1.5		*22*
5	Jinling Petrochemical, Beijing, China	pilot facility	refinery process water	0.75		*23*
6	Suncor, Inc., Alberta, Canada	pilot facility	oil sand process water	0.08	17.3	*24*−*27*
7	BP Petroleum, Port Everglades, Florida, U.S.A.	pilot facility	contaminated groundwater at a terminal	0.007	27	*28*
8	Shell Oil-Norco, Louisiana, U.S.A.	pilot facility	refinery process water	0.02	547	*29*−*31*
9	Mobil Oil, Bremen, Germany	pilot facility	tank farm effluent		5	*32*
10	Texaco, U.S.A.	pilot facility	refinery process water	0.04		*33*
11	Australia	pilot facility	oil terminal	0.06		*34*

important step in wetland design is selecting the appropriate wetland area that will consistently achieve pollutant reduction goals. A wetland area that is too small for treatment of a specific pollutant will result in permit violations. A wetland that is larger than necessary to deal with the given design flow and mass loading variability results in unnecessary expenditure of resources.

Defining Treatment Wetland Performance. The advancement of treatment wetland technology and the ability of designers to harness wetland processes in predictable treatment systems hinges on the ability to summarize treatment wetland data sets into a small number of defining relationships. Types of descriptors that have been successfully applied to treatment wetland data include loading rates and removal efficiencies, regression equations, and first-order mass balance equations.

Rate constants for a first-order, area-based pollutant reduction model ($k-C^*$ model adapted for treatment wetlands, ref *3*) are reported in this paper to summarize performance of petroleum industry wetlands. This two-parameter model includes k, the area-based removal rate constant, and C^*, the irreducible background concentration of the pollutant in the wetland, and assumes plug flow kinetics

$$\ln[(C_2-C^*)/(C_1-C^*)] = -k/q \quad (1)$$

where C_1 is the pollutant inflow concentration (mg/L), C_2 is the outflow concentration (mg/L), k is the area based first-order rate constant (m/yr), and q is the hydraulic loading rate (m/yr).

When data are only detailed enough to calibrate for one parameter, the rate constant is reported as k_1. Volumetric based first-order rate constants (k_V) have units of time $^{-1}$ and are interchangeable with k_1 based on the relationship

$$k_1 = k_V h \quad (2)$$

where k_V is the volumetric based first-order rate constant (yr^{-1}) and h is the depth (m).

Values for k_V in treatment wetlands have been found to be inversely proportional to depth, while k has been found to be relatively constant with water depth (*3*).

Rate constants can be corrected for temperature effects by use of the equation

$$k_T = k_{20}\theta^{(T-20)} \quad (3)$$

where k_T is the area based first-order rate constant at T °C (m/yr), k_{20} is the area based first-order rate constant at 20 °C (m/yr), and θ (theta) is an empirically derived temperature correction factor.

Although simple, this model currently represents the highest level of complexity that can generally be calibrated with wetland data and provides a reasonable approximation of performance for a wide range of pollutants in wetlands. The $k-C^*$ model does not account for adaptation trends, the effects of dissolved oxygen and pH on performance, and many other factors that are known to affect the fate of petroleum industry pollutants in treatment wetlands. A more complex model incorporating the effects of plant biomass growth on phosphorus removal in treatment wetlands has been proposed and calibrated for municipal and agricultural effluents (*35*). Additional advances in providing more complete descriptions of treatment wetland behavior are dependent upon analysis of data from comprehensive research projects, including pilot studies conducted by the petroleum industry.

Carbon Processing

Biochemical Oxygen Demand Removal Performance. Microbial removal processes include oxidation in the oxic regions of the wetland and methanogenesis in the anaerobic regions. The active microorganisms are almost exclusively associated with solid surfaces such as litter, sediments, and submerged plant parts. Likewise, the generation and return of five-day BOD (BOD_5) results from the death of wetland macrophytes and microorganisms attached to the submerged solids.

As a result of these combined processes, elevated BOD_5 concentrations in treatment wetlands typically decline along the wetland flow path from inlet to outlet, down to the background level. The $k-C^*$ model provides a highly simplified description of the complex wetland carbon interactions and typically represents this progression quite well, accounting for about 90% of the intrasystem variability (*3*). The central tendency of rate constants from a variety of municipal wastewater treatment wetlands is $k = 34$ m/yr and $C^* = 6$ mg/L. Seventy Danish soil-based (intermediate between surface and subsurface flow) wetlands receiving domestic wastewaters had values of $k = 47.5$ m/yr and $C^* = 3.0$ mg/L (*36*). A review of performance data from subsurface flow treatment wetlands yielded average values of $k = 180$ m/yr and $C^* = 3.5 + 0.053C_1$ mg/L (*3*).

No published petroleum wastewater data sets are currently available to fully calibrate the $k-C^*$ model for BOD_5 reduction. However, petroleum industry operating data collected for this paper indicate that k_1 is typically between 11 and 75 m/yr (Table 3). Reductions in BOD_5 are significant for high incoming concentrations but less when the inlet concentration is near background. The k_1 rate constant does not reflect

TABLE 3. Summary of Organics Removal Data from Petroleum Industry Treatment Wetlands[b]

		five-day biochemical oxygen demand				chemical oxygen demand				oils and grease			phenols		
		av concn (mg/L)				av concn (mg/L)				av concn (mg/L)			av concn (mg/L)		
site[a]	wetland type	in	out	red. eff (%)	k_1 (m/yr)	in	out	red. eff (%)	k_1 (m/yr)	in	out	red. eff (%)	in	out	red. eff (%)
1	FWS	79.4	12.4	84	11	131	40	69	7	2.1	0.13	94	80	5	94
2	FWS	11.3	5.1	55						2.5	1.0	60	20	18	10
3	FWS	38	15.3	60	75	170	47.5	72	104				27	10	63
4	FWS							38		0.84	0.29	65			32
9	SSF	700	20	97	71	1,800	250	86	40						
10	FWS	104	2.1	98	71										
11	SSF	75	15	80		101	47	53		24	11	54			

[a] Sites are identified in Table 2. [b] Abbreviations: red. eff, reduction efficiency; av concn, average concentration; FWS, free-water surface (surface flow); and SSF, subsurface flow.

the wetland background value C^* and, therefore, is lower than the value for k.

The wetland background concentration for BOD_5 typically ranges from 3 to 15 mg/L but depends on the strength of the wetland carbon cycle. High nutrient levels stimulate plant and microbial growth and, hence, accentuate the return flux and increase the resultant background concentration. Therefore, C^* is elevated for strong influents. Intersystem performance follows the expected pattern of better performance at lower loading rates, within the constraints of the wetland carbon cycle. Data from several sites show a trend of increasing outlet concentration with increasing inlet loading rate (*3*). Temperature apparently plays a minor role in the net removal of BOD_5 in surface flow wetlands (*3*).

COD Reduction in Treatment Wetlands. COD represents the class of organic compounds that are susceptible to oxidation by a strong chemical oxidant (potassium dichromate) under acidic conditions. COD is numerically higher than BOD_5, because more organic compounds can be chemically oxidized than are degraded biologically. In the wetland environment, the presence of humic materials typically leads to COD values that are much higher than BOD_5 values (20:1 in Northern peatlands, ref *37*). In untreated municipal wastewaters, the ratio is 1.25 to 2.5 (*38*).

Limited information on petroleum wastewater treatment wetlands indicates that COD is reduced at rates comparable to wetlands treating other types of wastewater. The mean COD k_1 rate constant for municipal and industrial systems is 36 m/yr (*9*); that for BOD_5 from surface flow treatment marshes is 34 m/yr (*3*). However, for paired data (COD and BOD_5 for the same wetlands), the $k_1COD:k_1BOD_5$ ratio is 0.81 $\pm$ 0.33 (*9*); the ratio was 0.65 for the Amoco Mandan data in 1987 (*19*). This information indicates that on average, COD is reduced less effectively than BOD_5 in treatment wetlands.

Temperature effects on COD are typically minimal, although data are sparse. Kadlec et al. (*39*) report $\theta = 1.023$ for COD reduction in potato processing waters; data from Saurer (*40*) for the Mühlen, Austria, domestic wastewater treatment wetland indicate $\theta = 1.030$ for COD.

Clearly, more COD data are needed, especially for petrochemical wastewater treatment in wetlands. Internal transect data and data for varying loading rates and depths are required to quantify even the simplistic $k-C^*$ model.

Trace Organics Removal from Petroleum Wastewaters. *General Results.* Organic chemicals from waste streams that include petroleum products are potentially problematic for treatment wetlands for two reasons. First, if organic compounds are present at high concentrations, they may be potentially toxic to plants and microorganisms. Second, the various organic compounds found in the waste streams have differing susceptibilities to aerobic and anaerobic degradation processes (*3*). However, most hydrocarbons are natural products and are biodegradable. Many hydrocarbons are not toxic to organisms except at high doses, and some are used as growth enhancers at low concentrations.

Through natural processes, wetlands produce a wide range of organic compounds. Organic compounds may form complex molecules with metals (such as iron) and serve as an important mechanism to buffer redox reactions in wetlands (*41*). The roots of wetland plants contribute to the aeration of sediments, degradation of organic compounds, and the diversity of microorganisms in the root zone (rhizosphere) (*41*−*43*). Free-floating plants, such as water hyacinth, have also been shown to reduce trace levels of organic compounds in aquatic treatment system wastewaters (*45, 46*).

Many wetland soils have a high proportion of organic matter. The organic soil component has the ability to remove organics through adsorption and other binding mechanisms (*3*). Surfactant-modified smectitic clays (e.g., hectorite and montmorillonite) may also represent an inexpensive additive that could enhance the organic sorption potential of treatment wetlands (*47*).

In general, the time required to break down organic compounds is linked to the relative complexity of the molecules. The breakdown time for aliphatic hydrocarbons is longer for compounds of higher molecular weight. The breakdown time for aromatic hydrocarbons (i.e., compounds with a benzene ring) is longer when more than one benzene ring is present (referred to as polycyclic aromatic hydrocarbons or PAHs). The primary mechanism for phenol removal in wetlands occurs through sorption to various wetland components and subsequent degradation by microbial organisms (*47*). Table 3 summarizes data for organic compounds removal in treatment wetlands.

Refinery Effluents. Constructed wetlands can be used to polish secondarily treated refinery wastewaters in order to attain more stringent water quality objectives and reduce discharge permit violations (*19, 20*). Full-scale treatment wetlands are being used at a number of refineries including Chevron's Richmond, CA and Amoco's Mandan, ND facilities in the U.S.

Spills and Washings. Tenneco, Inc. used a rock-reed wetland to treat wastewaters from a natural gas pipeline compressor station. This wetland treatment system was shown to reduce oil and grease in the effluent by about 90% (*48*). TSS and COD were also reduced by over 90%. This alternative was economically attractive, both in initial capital cost and operation cost.

A subsurface flow wetland was used to treat runoff from a 0.8-ha vehicle yard in Surprise, AZ. Oil and grease was reduced between 54% and 92% by this wetland (*49*). Oil and grease removal was not observed in an unvegetated control. Dissolved oxygen decreased upon passage through the bed, and electrical conductivity increased. These preliminary

TABLE 4. Summary of Performance for Total Suspended Solids and Nutrient Removal by Petroleum Industry Treatment Wetlands

site[a]	wetland type	total suspended solids: av concn (mg/L) in	out	red. eff (%)	k_1 (m/yr)	total nitrogen: av concn (mg/L) in	out	red. eff (%)	k_1 (m/yr)	ammonia nitrogen: av concn (mg/L) in	out	red. eff (%)	k_1 (m/yr)	total phosphorus: av concn (mg/L) in	out	red. eff (%)	k_1 (m/yr)
1	FWS	106	11.7	89	13					16.9	2.6	85	11				
2	FWS	19.2	27	−41						2.1	0.0	98		28.7	18.9	34	
3	FWS	181	41	77	122	9.9	5.8	42	44	5.8	3.5	40	42	1.51	0.43	72	103
5	FWS													3.5	3.2	9	16
6	FWS					16.2	4.3	74	5	14.6	3.7	75	5	0.08	0.15	−94	
10	FWS	14.5	2.4	83	33	8.1	0.1	99	93	6.3	0.1	98	76	5.9	1.1	81	31
11	FWS	38	20	47		3.2	1.8	44									

[a] Sites are identified in Table 2. [b] Abbreviations: red. eff, reduction efficiency; concn, concentration; FWS, free-water surface (surface flow); and SSF, subsurface flow.

results indicate promise for the use of treatment wetlands for this application.

At an Australian oil terminal, a 600-m^2 constructed rock-reed wetland (primarily subsurface flow) was established in December 1992 to treat an oily water stream and a detergent-laden truckwash effluent (*34*). Preliminary results from 1993 through 1995 indicated an 80% reduction in BOD_5 and a 54% reduction in oil and grease in addition to reductions in other contaminants of interest. Phenols were also reduced, except in several cases that may have corresponded to high loading rates.

Oil Sand Processing Water. A pilot-scale wetland was constructed in 1991 to treat wastewater from an oil sand processing facility at Fort MacMurray, in Alberta, Canada. Naphthenic acids (NA), which are water soluble hydrocarbons, are considered to be the primary toxicants of concern in the waste stream. Results indicated that NA and other contaminants were reduced by the treatment wetland, as was toxicity to *Daphnia magna* and *Microtox* (bacteria luminescence test). When total extractable hydrocarbons (TEH) were used as a gross organic parameter, preliminary results showed removal efficiencies ranging from 35 to 70% under input loads of approximately 1 kg (kg)/month/100 m^2 (*50*). NA reduction was shown to be more effective in the summer than in the winter (*51*). Ammonia removal in the treatment wetlands was not limited by the presence of hydrocarbons in the treatment system (*52*).

Produced Water. The applicability of wetland treatment systems to produced waters from natural gas processing is being studied at the Argonne National Laboratory in Argonne, IL (*53*). The concept involves high evapotranspiration rates which bring water into the rhizosphere and thus promote biotreatment. Volume reduction is achieved, at the expense of increasing salt content.

A pilot-scale treatment wetland project has been conducted by the Marathon Oil Company in conjunction with the Wyoming Department of Environmental Quality (WY-DEQ). The system uses bacterial ponds followed by a riffle channel flowing into a surface flow wetlands to treat produced waters. The treatment system has been shown to reduce benzene and phenolics and can run in all seasons (*54*).

Specific Wetland Processes. A number of operative wetland processes contribute to the overall removal, conversion, or storage of hydrocarbons and other chemicals in treatment wetlands. These processes include volatilization; partitioning to sediments, biofilms, and humics; mass transfer to sorption/degradation sites; biodegradation; photodegradation; and plant and animal uptake. Detailed research is not available to support and calibrate mechanistic models for these individual processes for very many substances; nevertheless, the physical-chemical principles are well-known (*9*).

Total Suspended Solids Removal. Treatment wetlands are typically efficient in net reduction of TSS concentrations, with removal efficiencies often in the 80−90% range. As a result of the combined processes discussed above, TSS concentration declines along the flow path from inlet to outlet, down to the background level. The $k-C^*$ model provides a highly simplified description of the complex wetland solids interactions and, typically, represents the decreasing profile quite well, accounting for over 90% of the intrasystem variability (*3*).

The wetland background TSS concentration is typically in the range of 3−15 mg/L but depends on the size of the wetland carbon cycle. High nutrient levels stimulate growth and, hence, accentuate the return flux and increase the resultant background concentration. Therefore, C^* is elevated for strong influents. The incoming TSS concentration can be used as a surrogate for incoming nutrient load in some cases and it also reflects possible residuals.

Because wetland processes involve a strong stochastic component, numerous and frequent excursions occur for this water quality parameter. The outlet concentrations reflect internal wetland solids processes more than they do inlet concentrations. The character of the variability is typified by maximum monthly TSS values that average 1.9 times the annual average values (*3*). Temperature apparently plays a minor role in TSS reduction ($\theta \approx 1.00$).

The removal of suspended material has not been the principal focus of petroleum industry treatment wetland projects. The data in Table 4 indicate that reductions are possible for high entering TSS (i.e., Amoco and Yanshan) but that a clean influent may be subject to increased TSS in the outflow (*33*). This finding is commensurate with behavior in other treatment wetlands (*3*). A deep water cell near the outlet of a treatment wetland creates the potential for elevated TSS in the form of algal cells, which may have influenced the Chevron data. Performance for TSS reduction in petroleum wastewaters is generally in line with other treatment wetlands (*9*).

Metals Removal. Wetlands are capable of significant metals removal as summarized by Kadlec and Knight (*3*). A number of physical and chemical properties of soils affect metal mobilization−immobilization processes. Important soil physical properties include particle size distribution (texture) and, to some extent, the type of clay minerals present. Soil chemical properties affecting these processes include oxidation−reduction status (redox potential), pH, organic matter content, salinity, and the presence of inorganic components such as sulfides and carbonates (*55*).

Cation exchange capacity (CEC) of wetland soils and sediments tends to increase as texture becomes finer because more negatively charged binding sites are available. Silicate clay mineralogy will also affect CEC because the relative number of binding sites varies between clays with different types of crystal lattice structures. Surfactant-treated smectitic clays were shown to strongly adsorb metal ions and may represent an option to enhance sorption potential of treatment wetlands (*47*).

Organic matter behaves similarly to mineral clays because it also has a relatively high proportion of negatively charged binding sites. Salinity and pH can influence the effectiveness of CEC in soils or sediment because the negatively charged binding sites and pore water will be occupied by a high number of sodium or hydrogen cations. Sulfides and carbonates may combine with metals to form relatively insoluble compounds.

Metals removal from wetland waters by plant roots has been demonstrated in a number of studies (*41, 56*−*60*). In particular, iron root plaque formation and emergent plant roots are important factors in biogeochemical processes in wetlands because (*1*) iron, with organic compounds, composes the most important redox buffer system in wetlands, and (*2*) emergent plant roots contribute to the aeration of sediment, adsorption of heavy metals, oxidation of methane, and the diversity of microorganisms in the rhizosphere (*41*). Their study indicates that iron plaques are not only composed entirely of oxidized iron (Fe^{3+}) compounds as commonly believed but also contain a substantial proportion (33%) of compounds with the reduced iron form (Fe^{2+}). The positive effect of plant rhizospheres on microbial populations was also noted in terrestrial environments (*43*).

Increasing acidity in waters of constructed wetlands was not shown to significantly affect mobilization of metals into surface waters (*61*, *62*). Increased metals uptake by aquatic plants and invertebrates was noted in acidified wetlands as compared with nonacidified constructed wetlands (*62*). Carbon or organic matter supplementation appears to have only limited effect on increasing metals retention (*47, 61*).

Metal removal efficiencies of treatment wetlands are highly correlated with influent concentrations and mass loading rates (*3, 61*). For this reason, it is important to consider reported removal efficiencies in light of these two factors. Bishay et al. (*50*) observed that heavy metals in oil sands processing wastewaters were generally reduced by treatment wetlands but that the removal efficiency varied greatly depending on the metal and treatment water.

Wetland Effects on Effluent Toxicity. In studies of a pilot-scale subsurface flow and surface flow treatment wetlands at a U.S. refinery (*34*), reductions in chronic toxicity to fathead minnows, *Pimephales promelas,* were found to be positively related to hydraulic retention time (HRT). More than 50% of the toxicity was removed using a 12-h HRT, with increasing but smaller incremental reductions using 24-, 36-, and 48-h HRTs. Nearly all toxicity to fathead minnows was removed with the 48-h HRT. The oil refinery wastewater did not appear to affect survival of *Ceriodaphnia dubia* in a single, 7-day chronic toxicity test; however, the reproduction test showed a slight improvement in IC_{25}.

At an Australian oil terminal, toxicity tests of the influent and of the treatment wetlands effluent (at 100% concentration) using the *Microtox* (bacteria luminescence) test organism showed reduction of toxicity (reflected by EC_{50} values) by 98% (*34*).

A full-scale surface flow constructed wetlands at the Chevron refinery in Richmond, CA, has consistently shown no mortality, using rainbow trout to assess effluent toxicity (*63*).

Seven-day toxicity tests were conducted on laboratory-scale wetlands by using zinc-amended water to simulate wastewater from an oil refinery near Norco, LA (*30*). This study indicated that zinc removal (average of 80%) from the water resulted in a decrease in toxicity to *Ceriodaphnia dubia* from the influent to the effluent. With an average influent zinc concentration of 1.70 mg/L, the 7-day LC_{50} increased from 0.155 mg/L to 0.189 mg/L due to wetland treatment. Toxicity responses were determined to be similar for static-renewal and flow-through laboratory tests. The 7-day static renewal tests indicated that at influent zinc concentrations of 1.7, 0.85, and 0.43 mg/L, *Ceriodaphnia dubia* survival in wetland influent samples was zero, while survival in the wetland effluent samples was approximately 23%, 38%, and 88%, respectively. At a zinc concentration of 0.22 mg/L, influent and effluent survival rates were approximately 10% and 98%, respectively. When the influent zinc concentration was 0.11 mg/L, influent and effluent survival was around 88% and 100%, respectively.

A pilot-scale wetland has been used to treat wastewater from an oil sand processing facility at Fort MacMurray, in Alberta, Canada. Studies indicate that the treatment wetlands have reduced toxicity to the aquatic invertebrate *Dapnia magna* (*50*−*51, 64*) as well as the luminescent bacteria *Microtox (50*).

Low levels of various hydrocarbons in wastewaters have not caused stress in cattails (*Typha* spp.) or bulrushes (*Schoenoplectus* spp.) (*33, 64*). However, very strong effluents (average influent COD = 1800 mg/L with peaks > 14 000 mg/L) have caused acute toxicity to *Typha* and *Schoenoplectus* and especially to *Phragmites australis* (*32*).

In summary, treatment wetlands have been found to reduce acute and chronic toxicity to both cladocerans and fathead minnows in almost every case studied (*9*). The magnitude of toxicity reduction is typically inversely related to the wastewater loading rate and directly related to the effectiveness of mixing (water flow distribution) within the treatment wetland. These general observations suggest that toxicity reductions in treatment wetlands are likely a secondary benefit of the myriad of pollutant removal processes in these complex biological systems. Additional research is needed on the specific mechanisms of toxicity reduction in treatment wetlands.

Nutrient Removal. *Nitrogen*. Nitrogen (N) is a key element in biogeochemical cycles. Nitrogen occurs in a number of different oxidation states in wastewaters and in treatment wetlands, and numerous biological and physio-chemical processes can transform N between these different forms. Atmospheric pathways are also available for volatilization of some of these N forms and permanent loss from the wetland water column. Because of the complex transformations affecting N forms in wetlands, a sequence of reactions must be considered to adequately describe treatment performance, even on the most elementary level (*3*).

Nearly all treatment wetland studies have reported reductions in total N (TN) and organic N. Because of the potential for interconversion of N forms, wetland outflow concentrations of ammonium or nitrate N may be higher than inflow concentrations under some conditions. Mass balance equations for inter-related reactions relating to plug flow hydraulics in treatment wetlands have been published (*3*).

Petroleum industry data for N forms are summarized in Table 4. Because flow data or data for variable operational conditions are limited, they cannot be used to calibrate the full sequential $k-C^*$ model. Nitrogen removal rate constant values for these wetlands are comparable to or higher than values for other treatment wetlands (*9*).

Treatment wetland removal of all major N forms is sensitive to temperature. Theta value estimates range from about 1.04 for ammonium, to 1.09 for nitrate N (*3*). Because N is a major plant growth element, plant uptake is an important component of this element's biogeochemical cycle. During a period of rapid plant biomass increase, ammonium and nitrate removal rate constants may be significantly higher than steady-state values.

Phosphorus. Constructed and natural wetlands are capable of absorbing new phosphorus (P) loadings and, in appropriate circumstances, can provide a low cost alternative to chemical and biological treatment. Phosphorus interacts strongly with wetland soils and biota, which provide both short-term and sustainable long-term storage of this nutrient.

Soil sorption can provide initial removal, but this partly reversible storage eventually becomes saturated. For some antecedent soil conditions, an initial release of P could occur. A new source of P acts to fertilize the wetland, and some P is used to establish a larger standing crop of vegetation.

The sustainable removal processes involve accretion of new wetland sediments. Uptake by small organisms, including bacteria, algae, and duckweed, forms a rapid-action, partly reversible removal mechanism. Cycling through growth, death, and decomposition returns most of the microbiotic uptake via leaching, but an important residual contributes to long-term accretion in newly formed sediments and soils. Macrophytes, such as cattails and bulrushes, follow a similar cycle but on a slower time scale of months or years. The detrital residual from the macrophyte cycle also contributes to the long-term storage in accreted solids. Direct settling and trapping of particulate P may contribute to the accretion process. Biological enhancement of mineralogical processes, such as iron and aluminum uptake and subsequent P binding in detritus and the algae-driven precipitation of P with calcium, can also occur.

Surface flow wetlands provide sustainable removal of P but at relatively slow rates. The internal progression of removal causes concentrations to decrease exponentially to a background value, along the water flow path. The first-order areal mass balance model is currently the most supportable level of detail for describing long-term sustainable performance (*3*). It typically explains about 80% of the variability in transect data and explains internal profiles as well as input/output data for individual wetlands. This model must be applied over more than three to five detention times to avoid transit time effects.

The background concentration C^* for total P (TP) is in the range of 10−50 μg/L based on information from large natural and constructed wetlands. Therefore, it does not exert a strong influence on model predictions until outlet concentrations reach this low range. The first-order rate constants for a number of nonforested treatment wetlands show a central tendency of $k \approx 10$ m/yr (*3*).

TP performance data from petroleum industry treatment wetlands are summarized in Table 4. Reductions in TP are significant. Loadings are high compared to other treatment wetlands. Rate constants, k_1, are also relatively high, and performance is generally better than for other wastewater categories. Insufficient nutrient data currently exist from petroleum industry treatment wetlands to fully calibrate the $k-C^*$ model.

Acknowledgments

The work summarized in this paper was supported by the Biomonitoring Task Force of the American Petroleum Institute (API). API's project manager was Alexis Steen. Jan Farmer with British Petroleum provided a review of the manuscript. The helpful comments of three anonymous reviewers are also acknowledged and appreciated.

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Received for review July 21, 1998. Revised manuscript received January 6, 1999. Accepted December 11, 1998.

ES980740W