

THE USE OF TREATMENT WETLANDS FOR PETROLEUM INDUSTRY EFFLUENTS

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4672
OCTOBER 1998



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The Use of Treatment Wetlands for Petroleum Industry Effluents

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4672

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OCTOBER 1998

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Executive Summary

Treatment wetlands are becoming widely used for cleansing some classes of wastewater effluents. Although the use of treatment wetlands is well established for wastewater categories such as municipal waste, stormwater, agricultural wastewater, and acid mine drainage water, their use in treating a variety of industrial wastewaters is less well developed. Constructed treatment wetlands hold considerable promise for managing some wastewaters generated by the petroleum industry. 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 report summarizes current information about the use of treatment wetlands for managing petroleum industry wastewaters and also presents background information on the general performance, design, and operation of treatment wetlands based on experience with a variety of wastewater types.

Performance

Simplistic models of pollutant reductions based on first-order disappearance kinetics provide a reasonable first approximation of overall wetland behavior. These first-order processes are unlike many conventional treatment-tank processes in that they are highly dependent on wetland area rather than wetland water volume. Moreover, they are limited to non-zero residual pollutant levels for many parameters because of natural water quality background properties of wetlands. A first-order, two-parameter, area-based model with a background concentration (k - C^* model) is used in this report and in reviewed literature to compare the performance of a variety of treatment wetlands.

This report reviews in detail treatment wetland performance for the following parameters:

- Chemical oxygen demand
- Biochemical oxygen demand
- Trace organics
- Metals
- Total suspended solids
- Forms of nitrogen
- Phosphorus

All of these parameters can be reliably removed from wastewater and returned to background levels 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 treatment wetlands to provide conservative estimates for treatment wetland sizing.

Reduction of whole effluent toxicity is an important issue for the petroleum industry and has been studied in a relatively small number of treatment wetlands. Current results indicate consistent reductions in whole effluent toxicity in treatment wetlands. These reductions are thought to be pollutant-specific, and the magnitude of reduction is dependent on the same factors that control reduction efficiencies for other pollutants.

Design Considerations

Treatment wetland systems are land intensive and their design focuses on three primary factors:

- Determining the appropriate level of pretreatment
- Selecting adequate wetland area
- Establishing effective effluent flow distribution over that area

Water depths in treatment wetlands are typically about 30 centimeters or less, except in transverse deep zones used for flow redistribution, solids retention, and wildlife habitat. Flow control structures, embankment design, lining, and use of subsurface flow substrates are all important issues during treatment wetland design. Plant selection and plant species diversity are typically dependent on project goals other than treatment performance.

Operation and Maintenance

Wetland operation and maintenance efforts can be reduced through conservative design. Treatment wetlands have few controls and respond relatively slowly to operational changes. Routine monitoring is essential for detecting changes in system performance quickly enough to respond with effective operational changes. Compared with other treatment technologies, treatment wetlands require little operation and maintenance and have low energy requirements.

Case Histories

Treatment wetland case histories from projects in the petroleum industry provide a convenient summary of experience that can be used when considering new projects. Case histories are

presented at the end of this report for six pilot-scale and four full-scale treatment wetlands receiving petroleum industry wastewaters. These studies include wastes from oil sands mining and extraction, oil and gas wells, handling and transferring facilities, refineries, and tank farms. Treatment wetland types that have been studied in the petroleum industry include surface flow and subsurface flow constructed marshes, a pond/marsh combination, and one floating aquatic plant system.

SECTION 1

Introduction

Wetlands have been engineered for water quality treatment in the United States since the early 1970s (Table 1-1). 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 individuals interested in applying this technology for water quality treatment.

Several efforts have assessed the effectiveness of treatment wetlands and summarized information from diverse data sources into coherent and predictive descriptions of performance. One of the most comprehensive summarization efforts to date was the development of the North American Treatment Wetland Database (NADB) funded by the U.S. Environmental Protection Agency (EPA) (Knight *et al.*, 1993a; NADB, 1993).

A comprehensive book that builds on the NADB and hundreds of published papers to describe the performance and design of treatment wetland has been published (Kadlec and Knight, 1996). Another ongoing compilation effort is a review of wetlands treating concentrated livestock wastewaters (CH2M HILL and Payne Engineering, 1997). This has resulted in an electronic database of design and performance information known as the Livestock Wastewater Wetland Database (LWDB). An earlier effort reviewed design and operational data from wetlands receiving wastewaters from the pulp and paper industry (CH2M HILL, 1994a).

This report continues this synthesis by providing the first review of treatment wetland research and full-scale projects in the petroleum industry worldwide. 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 water quality benefits when properly designed and maintained. However, published data have been scarce and unavailable for broad review within or outside of the industry.

In 1995, the Biomonitoring Task Force of the American Petroleum Institute (API) funded a review and summary of available (published and company confidential) treatment wetland data from the petroleum industry. The summary was intended to present the information in the much broader context of the role of wetlands for treating wastewaters from other sources. This report presents the results of this review and technology assessment.

TABLE 1-1
Timeline of Selected Events in Treatment Wetland Technology

Date	Location	Description
Selected Research Efforts		
1952-late 1970s	Plön, Germany	Removal of phenols and treatment of dairy wastewater with bulrush plants
1967-1972	Morehead City, North Carolina	Constructed estuarine ponds and natural salt marsh for municipal effluent recycling
1971-1975	Woods Hole, Massachusetts	Potential of natural salt marshes to remove nutrients, heavy metals, and organics
1972-1977	Houghton Lake, Michigan	Natural wetland treatment of municipal wastewater
1973-1974	Dulac, Louisiana	Discharge of fish processing waste to a freshwater marsh
1973-1975	Seymour, Wisconsin	Pollutant removal in constructed marshes planted with bulrush
1973-1976	Brookhaven, New York	Meadow/marsh/pond systems
1973-1977	Gainesville, Florida	Cypress wetlands for recycling of municipal wastewaters
1974-1975	Brillion, Wisconsin	Phosphorus removal in constructed and natural marsh wetlands
1974-1988	NSTL Station, Mississippi	Gravel-based, subsurface flow wetlands tested for recycling municipal wastewaters and priority pollutants
1975-1977	Trenton, New Jersey	Irrigation of small enclosures in the Hamilton Marshes (freshwater tidal) with treated sewage
1976-1979	Eagle Lake, Iowa	Assimilation of agricultural drainage and municipal wastewater nutrients in a natural marsh wetland
1976-1982	Southeast Florida	Nutrient removal in natural marsh wetlands receiving agricultural drainage waters
1979-1982	Humboldt, Saskatchewan	Batch treatment of raw municipal sewage in lagoons and wetland trenches
1979-1982	Arcata, California	Pilot wetland treatment system for municipal wastewater treatment
1980-1984	Listowel, Ontario	Testing of constructed marsh wetlands for treatment of municipal wastewater under a variety of design and operating conditions
1981-1984	Santee, California	Testing of subsurface flow wetlands for treatment of municipal wastewaters
1985-1990	Columbus, Mississippi	Testing of subsurface flow marshes for treatment of pulp mill effluent
1989-1995	Leaf River, Mississippi	Testing of surface flow marshes for treatment of pulp mill effluent
1992-1994	Hemet, California	Testing of surface flow marshes for treatment of reuse wastewater and reject brine

TABLE 1-1 (CONTINUED)
Timeline of Selected Events in Treatment Wetland Technology

Date	Location	Description
Selected Full-Scale Projects		
1972	Bellaire, Michigan	Natural forested wetland receiving municipal wastewaters
1973	Mt. View, California	Constructed wetlands for municipal wastewater treatment
1974	Othfresen, West Germany	Full-scale reed marsh facility treating municipal wastewater in an old quarry
1975	Mandan, North Dakota	Constructed ponds and marshes to treat runoff and pretreated process wastewater from an oil refinery
1977	Lake Buena Vista, Florida	Use of a natural forested wetland for year-round advanced treatment and disposal of up to 27,700 m ³ /d of municipal wastewater
1978	Houghton Lake, Michigan	Natural peatland receiving summer flows of municipal wastewater
1979	Drummond, Wisconsin	Sphagnum bog receiving summer flows from a facultative lagoon
1979	Show Low, Arizona	Constructed wetland ponds for municipal wastewater treatment and wildlife enhancement
1984	Incline Village, Nevada	Constructed wetlands for total assimilation (zero discharge) of municipal effluent
1986	Arcata, California	Constructed marsh wetlands for municipal wastewater treatment
1987	Orlando and Lakeland, Florida	Two large (> 480 ha) constructed wetlands for municipal treatment
1987	Myrtle Beach, South Carolina	Natural Carolina bay wetlands for municipal wastewater treatment
1987-1988	Benton, Hardin, and Pembroke, Kentucky	Constructed wetlands for municipal wastewater treatment designed by the Tennessee Valley Authority
1988	Orange County, Florida	Hybrid treatment system combining constructed and natural wetland units
1989	Richmond, California	Full-scale treatment marshes for petroleum refinery wastewater and stormwater treatment
1991	Columbus, Mississippi	First full-scale constructed wetland for advanced treatment of pulp and paper mill wastewater
1991	Minot, North Dakota	Northern surface flow wetland system (51.2 ha) for municipal treatment during a 180-day discharge season
1993	Everglades, Florida	Treatment of phosphorus in agricultural runoff in a 1,380 ha constructed filtering marsh
1993	Beaumont, Texas	Large (263 ha) constructed marsh for municipal wastewater polishing and public use

m³/d cubic meters per day

ha hectare

NSTL National Space Testing Laboratory

Source: Adapted from Kadlec and Knight, 1996.

This section provides a general overview of constructed treatment wetlands and their possible importance to the petroleum industry and summarizes the NADB and other relevant databases. The contents of the rest of the document are summarized as follows:

- Section 2 provides methods for estimating the water quality enhancement capability of treatment wetlands receiving petroleum industry contaminants. Specific wetland sizing methods are provided for the major pollutants commonly treated in constructed wetlands. When possible, these methods are based on data from petroleum industry wetland systems.
- Section 3 describes the other important aspects of treatment wetland design, including site selection, pretreatment, system sizing, hydraulic design, and vegetation selection.
- Section 4 describes current information important in operating treatment wetlands. It focuses on minimizing operational requirements and using monitoring to anticipate operational changes.
- Section 5 discusses treatment wetland design considerations related to providing secondary benefits for wildlife enhancement and for public use. It also examines the potential for bioaccumulation of toxics and how nuisance conditions can be avoided in treatment wetlands.
- Section 6 provides bibliographic citations for technical publications referenced in preparing this report.

The appendices, which appear at the end of this document, include a glossary of important technical terms relating to treatment wetlands and petroleum industry case histories for six pilot and four full-scale projects.

Overview of Constructed Treatment Wetlands

Wetlands are ecosystems in areas 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 (Cowardin *et al.*, 1979; Mitsch and Gosselink, 1993). 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.

Three general types of shallow vegetated ecosystems are being used for water quality treatment: (1) free water surface (surface flow), (2) subsurface flow (vegetated submerged bed), and (3) floating aquatic plant treatment systems (Figure 1-1). All three of these vegetated system types are used in the United States for engineered water quality improvement. EPA has prepared a design manual summarizing early performance information for all three system types (EPA, 1988a), as well as a subsurface flow technology assessment (EPA, 1993a). A technology assessment report focusing only on the free water surface treatment wetland technology is currently in preparation for EPA (CH2M HILL, in preparation).

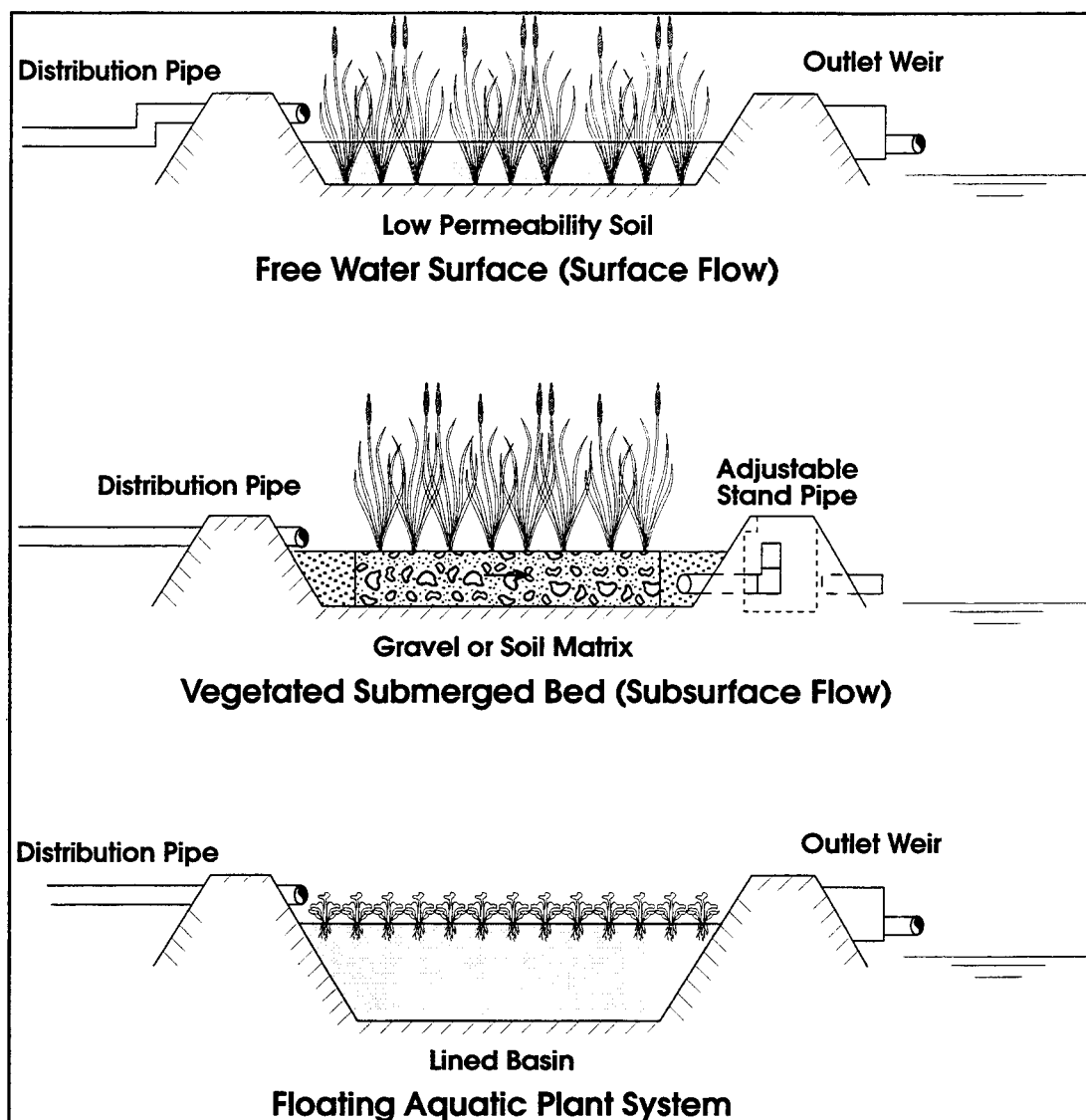


FIGURE 1-1
 Schematic of Wetland and Floating Aquatic Plant Treatment Systems
 Source: Adapted from Kadlec and Knight, 1996.

Treatment wetland technology started when natural wetlands were incorporated as components of wastewater treatment systems (Ewel and Odum, 1984; Kadlec and Tilton, 1979). Constructed free water surface treatment wetlands mimic the hydrologic regime of natural wetlands. In surface flow 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, wastewater flows through a constructed media bed planted with wetland plants which eliminates the potential for direct

exposure of humans or wildlife to the wastewater. Floating aquatic plant systems are analagous to ponds and are not treated in this review.

The analysis of performance data from natural and constructed free water surface wetlands indicates that these systems are similar in overall function in many cases. The principal differences between natural and constructed treatment wetlands are structural. Mature natural wetlands are more likely to have a forested plant community than constructed wetlands and are more likely to include a well-developed organic soil component. They are also more likely to have variable water depths and stagnant water areas outside the flow path that reduce treatment efficiency. This reduced efficiency for some parameters may be reflected in lower pollutant removal rate constants in some natural treatment wetlands. Thus, constructed wetlands offer greater opportunity to optimize hydraulic efficiency and to achieve maximum treatment within a fixed wetland area.

Natural wetlands are considered to be waters of the United States and can be permitted only as receiving waters, not as part of treatment systems. While a number of natural wetlands have been permitted to receive secondary or high-quality municipal wastewater effluents, their widespread use for treatment of industrial wastewaters is unlikely. Consequently, this report does not discuss the design and performance of natural treatment wetlands in relation to petroleum industry wastewater. However, since much of the existing performance data for municipal treatment wetlands are from natural wetlands, those data have been included in the general performance summaries that follow.

Treatment wetlands function as land-intensive biological treatment systems (Figure 1-2). In these systems, inflow water containing particulate and dissolved pollutants slows and spreads through a large area of shallow water and emergent vegetation. Particulates (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 soils 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.

Treatment wetlands have some properties in common with facultative lagoons and also have some important structural and functional differences. Water column processes in deeper water zones within surface flow treatment wetlands are nearly identical to ponds that have a surface autotrophic zone dominated by planktonic or filamentous algae, or by floating or submerged aquatic macrophytes. In the absence of light, the bottom portion of deeper zones in both treatment wetlands and facultative lagoons tends to be dominated by anaerobic microbial processes. However, shallow emergent macrophyte zones

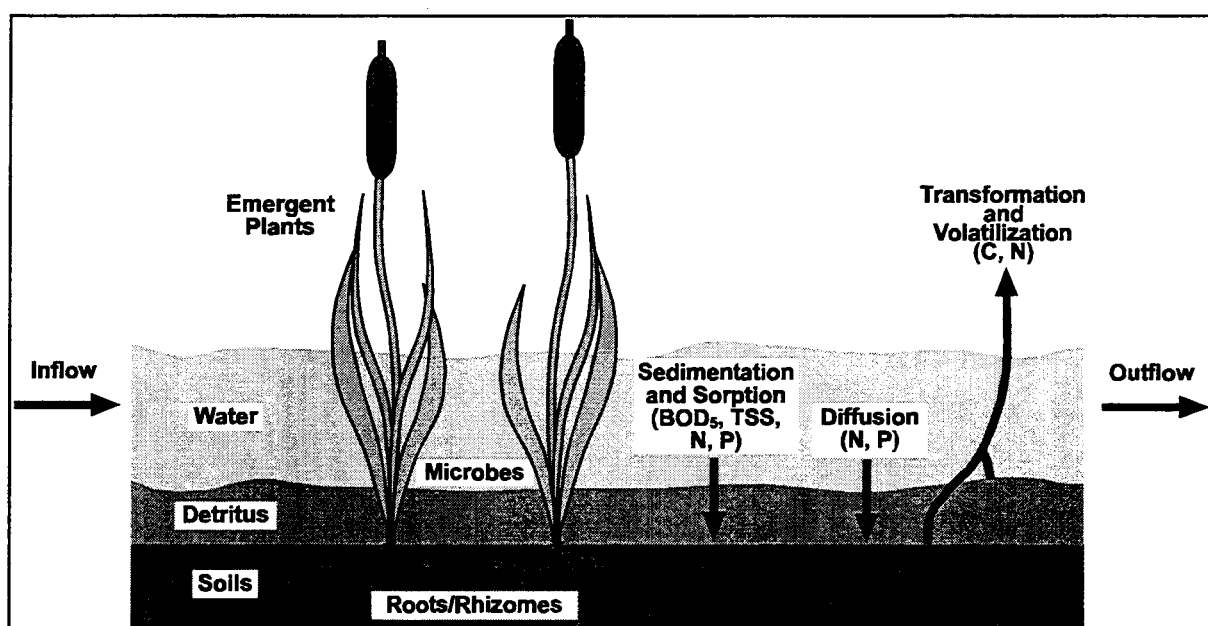


FIGURE 1-2

Wetland Processes Include Sedimentation, Chemical Sorption, and Microbial Transformations of Wastewater Source Pollutants: Adapted from ADEQ, 1995.

in treatment wetlands and aerobic lagoons can be quite dissimilar. Emergent wetland plants tend to cool and shade the water surface, reducing algae growth and concurrently reducing dissolved oxygen. Net carbon production in emergent wetlands tends to be high compared with facultative ponds, resulting in accumulation of structural carbon in the oxygen-deficient water column. This high carbon availability and the short diffusional gradients in shallow wetlands result in differences in biogeochemical cycling compared with ponds and lagoons.

During the process of elemental cycling within the wetland, chemical free energy is extracted by the heterotrophic biota, and fixed carbon and nitrogen are lost to the atmosphere. 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; in some cases for some parameters, outflow pollutant concentrations may exceed inflow concentrations. (See Section 2 of this report for information on the magnitude of these background constituent concentrations.)

Summary of Existing Data Sources

The use of wetlands for wastewater treatment is an emerging technology in North America and worldwide. These 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 handbooks provide useful syntheses of existing knowledge concerning the design of new wetlands (Kadlec and Knight, 1996; Davis, 1995; Reed *et al.*, 1995; U.S. Department of Agriculture, Soil Conservation Service [USDA NRCS], 1991; Cooper and Findlater, 1990; Water Pollution Control Federation¹ [WPCF], 1990; EPA, 1988a). Although these handbooks deal with common pollutants such as BOD, TSS, TN, and TP, they also have some information on the performance of treatment wetlands for other contaminants. Data from operational wetland treatment systems are accumulating so fast that handbooks will be outdated unless new empirical results are organized in electronic databases. Efforts are in progress to summarize and assess the surface flow treatment wetland technology (CH2M HILL, 1996) and to update the 1988 EPA constructed treatment wetland design manual.

Information on the effects of wetlands on water quality and the effects of treated wastewaters on wetland biota has been collected from many operational treatment wetland systems. Until recently, this information was widely scattered in scientific journal articles, monitoring reports to agencies, consultant reports, and private databases. A framework to record and update this expanding knowledge that would make information available to engineers and scientists nationwide was necessary to eliminate duplication of effort and to continue to refine the empirical design equations now in use. This section summarizes several treatment wetland design and performance databases developed to achieve those goals.

North American Treatment Wetland Database (NADB)

The first wetland treatment system database project was initiated in 1991 and ended in 1993. The NADB has cataloged existing information from 206 natural and constructed wetland treatment systems and available operational records for major water quality parameters. The result is a consistent, unified database. Although the NADB is the most comprehensive collection of treatment wetland data available, many data gaps exist. The NADB has been widely distributed to the engineering, scientific, and regulatory communities, and summaries of the preliminary data have been reported (Knight *et al.*, 1993a and b; Kadlec and Knight, 1996).

Types of information contained in the NADB include location, climatic factors, populations served, capital and operating costs, design considerations, operating data for water quality, biota, permit conditions, existing reports and literature, and key contact people for each system. These data are cataloged into seven linked data files using dBASE IV software.

At each wetland treatment site, either a single system with an inflow and outflow or multiple, parallel systems with discrete outflow points were included. Most of the existing wetland treatment systems in

¹ Now called the Water Environment Federation (WEF).

North America meeting several general requirements were included in the NADB. Except for some pilot-scale systems, these systems include wetlands receiving municipal wastewater, industrial wastewater, and stormwater at flows generally exceeded 100,000 gallons per day (gpd) (378 m³/d).

The primary purpose of the wetland treatment database effort was to develop a summary of existing information that could be expanded to accommodate additional information. To prepare the summary, operational data for inflow and outflow rates and constituent concentrations were averaged seasonally. Table 1-2 is a summary of the average surface flow and subsurface flow treatment wetland operational performance data. Design and operational data that affect assimilation rates were summarized for each system to allow regression analysis and the refinement of existing empirical design equations. Memoranda containing data quality records, anecdotal system design information, and interpretation of performance trends were included as electronic files.

A second purpose of the wetland treatment database was to serve as an academic research tool for scientific investigations of wetland ecology. Consequently, the database provides a detailed data repository for the physical, chemical, and biological processes of treatment wetlands. This knowledge may help direct new research efforts. The database has proven useful for calibration and verification of a variety of pollutant reduction models (Kadlec and Knight, 1996).

A third goal of the wetland treatment database was to help standardize monitoring and reporting in wetland treatment systems nationwide. Currently, permits vary widely in reporting requirements for wetlands receiving wastewater, and researchers frequently omit key water quality parameters from monitoring or pilot programs.

Version 2.0 of the NADB (NADB.v.2.0) is currently in preparation and will include treatment wetland data for vegetation, wildlife, metals, organics, toxicity, human use, and livestock wastewater sources. Future expansion of the database contents and additional analysis of the data collected in this format will enhance the usefulness of this product to the engineering, scientific, and regulatory communities.

Permit writers and researchers can use the operational data in the database to gain an understanding of the normal variability of water quality in wetland treatment system discharges and an appreciation of the difficulty of interpreting data from wetlands with insufficient information. Data gaps can help to focus attention on new issues and direct monitoring efforts to ensure that key information is collected.

Use of Wetlands for Treatment of Pulp and Paper Industry Wastewaters

In 1994, the National Council of the Paper Industry for Air and Stream Improvement (NCASI) funded a review of the status of treatment wetlands in the industry. A draft review report was prepared but has not yet been published in a final form (CH2M HILL, 1994a). This review describes ten pilot- or full-scale treatment wetland projects in the pulp and paper industry in the United States. These projects include four pilot-scale free water surface constructed wetlands, three constructed subsurface flow pilot

TABLE 1-2

Summary of North American Treatment Wetland Database Operational Performance

Parameter	Type ^b	Average Concentration (mg/L)				Average Mass (kg/ha/d) ^a			
		In	Out	Eff (%)	Count (n)	Loading	Removal	Eff (%)	Count (n)
BOD ₅	SF	30.3	8.0	74	182	7.2	5.1	71	133
	SSF	27.5	8.6	69	34	29.2	18.4	63	29
	All	29.8	8.1	73	216	10.9	7.5	68	162
TSS	SF	45.6	13.5	70	198	10.4	7.0	68	139
	SSF	48.2	10.3	79	34	48.1	35.3	74	29
	All	46.0	13.0	72	232	16.8	11.9	71	168
NH ₄ -N	SF	4.88	2.23	54	220	0.93	0.35	38	141
	SSF	5.98	4.51	25	19	7.02	0.62	9	15
	All	4.97	2.41	52	239	1.46	0.38	26	156
NO ₂ + NO ₃ -N	SF	5.56	2.15	61	187	0.80	0.40	51	125
	SSF	4.40	1.35	69	13	3.10	1.89	61	13
	All	5.49	2.10	62	200	0.99	0.54	55	138
ORG-N	SF	3.45	1.85	46	118	0.90	0.51	56	76
	SSF	10.11	4.03	60	11	7.28	4.05	56	11
	All	4.01	2.03	49	129	1.71	0.95	56	87
TKN	SF	7.60	4.31	43	144	2.20	1.03	47	94
	SSF	14.21	7.16	50	12	9.30	3.25	35	12
	All	8.11	4.53	44	156	2.99	1.29	43	106
TN	SF	9.03	4.27	53	175	1.94	1.06	55	114
	SSF	18.92	8.41	56	12	13.19	5.85	44	12
	All	9.67	4.53	53	187	2.98	1.52	51	126
O-P	SF	1.75	1.11	37	148	0.29	0.12	41	112
	SSF	ND	ND	ND	—	ND	ND	ND	—
	All	1.75	1.11	37	148	0.29	0.12	41	112
TP	SF	3.78	1.62	57	191	0.50	0.17	34	134
	SSF	4.41	2.97	32	8	5.14	1.14	22	8
	All	3.80	1.68	56	199	0.73	0.22	31	142

^a kg/ha/d x 0.892 = lb/ac/d

^b BOD₅ 5-day biochemical oxygen demand
 Eff (%) efficiency of concentration reduction or mass removal
 kg/ha/d kilograms per hectare per day
 lb/ac/d pounds per acre per day
 mg/L milligrams per liter
 N count
 ND no data
 NH₄-N ammonia-nitrogen
 NO₂ + NO₃-N nitrite plus nitrate nitrogen
 O-P ortho phosphorus
 ORG-N organic nitrogen
 SF surface flow
 SSF subsurface flow
 TKN total kjeldahl nitrogen
 TN total nitrogen
 TP total phosphorus
 TSS total suspended solids

Source: Kadlec and Knight, 1996.

wetlands, one full-scale constructed free water surface treatment wetland, and two full-scale effluent discharges to natural basins.

Data from these projects were summarized by using the NADB format but with Microsoft Access software. Table 1-3 summarizes operational performance data for these systems. Wetland systems receiving pulp and paper wastewaters achieved similar pollutant removal efficiencies as the predominantly municipal wastewater wetlands in the NADB. New information for a few additional pollutants of importance for the pulp and paper industry is included in the NCASI review. These parameters include COD, color, conductivity, and total dissolved solids (TDS). According to this database, treatment wetlands were not able to significantly reduce concentrations of color or TDS.

TABLE 1-3
Summary of Operational Performance Data for Treatment Wetlands Receiving Pulp and Paper Industry Effluents

Parameter	Average HLR (cm/d)	Average Concentration (mg/L)				Average Mass (kg/ha/d)			
		In	Out	Eff (%)	Count (n)	Loading	Removal	Eff (%)	Count (n)
BOD ₅	19.9	26.1	13.6	48	30	28.6	8.3	29	19
TSS	19.9	42.5	12.5	71	30	41.6	28.5	68	19
NH ₄ -N	20.6	4.7	3.0	36	22	3.6	0.5	14	11
NO ₂ +NO ₃ -N	5.2	1.4	0.14	90	6	0.49	0.42	86	6
TKN	5.2	7.8	3.5	55	6	3.6	1.1	31	6
TN	9.4	12.6	6.6	48	9	4.2	1.6	38	6
TP	21.1	2.3	1.7	26	20	1.0	0.3	30	9
Color	10.7	1617	1581	2	23	2541	-115	-4	17

cm/d centimeters per day

Source: CH2M HILL, 1994a.

Livestock Wastewater Treatment Wetland Database

In 1995, the GMP Nutrient Enrichment Committee funded a review of the use of wetlands for treatment of concentrated wastes from livestock feeding operations (CH2M HILL and Payne Engineering, 1997). A total of 69 pilot- and full-scale treatment wetlands receiving wastes from dairy, cattle feeding, swine, poultry, and aquaculture operations were located in the United States and Canada. Most of these systems are small (< 1 ha) and relatively new (constructed since 1991).

Table 1-4 summarizes operational performance data from these systems. Inflow pollutant concentrations and mass loadings to these systems are significantly higher than those for municipal and industrial treatment wetlands reviewed previously. Treatment efficiencies are somewhat lower at these very high loadings.

TABLE 1-4

Average Treatment Wetland Performance for Removal of BOD₅, TSS, NH₄-N, and TN in the Livestock Wastewater Treatment Wetland Database

Parameter Wastewater Type	Count (n)	Average Inflow Concentration (mg/L)	Average Outflow Concentration (mg/L)	Average Concentration Reduction (%)
BOD₅				
Cattle feeding	14	137	24	83
Dairy	374	442	141	68
Poultry	80	153	115	25
Swine	183	104	44	58
TSS				
Cattle feeding	12	291	55	81
Dairy	361	1111	592	47
Swine	180	128	62	52
NH₄-N				
Cattle feeding	12	5.1	2.2	57
Dairy	351	105	42	60
Poultry	80	74	59	20
Swine	183	366	221	40
TN				
Dairy	32	103	51	51
Poultry	80	89	70	22
Swine	164	407	248	39

Source: CH2M HILL and Payne Engineering, 1997.

The database format used for the GMP constructed wetland project is patterned after that of the NADB, with slight modifications to reflect the applicability of the database to the agriculture industry. These data will be added to the NADB.v.2.0. Additional fields that were developed to input data include types of livestock; numbers of animals; agricultural category (dairy, cattle, swine, poultry, and aquaculture); and additional monitoring and mass balance parameters, including conductivity, TDS, volatile suspended solids, COD, temperature, and pH (see Section 4 for details).

Specific Needs of the Petroleum Industry

Differing wastewater sources generate different types and concentrations of pollutants. These diverse pollutants might result in varying needs for pretreatment and treatment wetland design. For example, municipal wastewaters typically contain elevated levels of particulate and dissolved degradable organic

matter and nutrients. Stormwaters generally are characterized by high suspended solids (both mineral and organic), metals, and oil and grease. Pulp and paper mill wastewaters are dominated by pollutants characterized by COD, particulate materials (lignins), and salts resulting from pulping processes. Untreated petroleum industry wastewaters share many of these same pollutants and will also contain oil and grease, various hydrocarbons, and other associated compounds and metals.

Table 1-5 characterizes the major pollutants of importance for the petroleum industry. The relative dominance and concentration of these substances varies considerably among industrial sites. In all cases, some conventional treatment practices are in use before these wastewaters are delivered to a constructed wetland for further treatment or polishing. Specific pollutants that remain in pretreated petroleum industry wastewaters include COD, oil and grease, phenolics, trace metals, sulfides, and a range of organic compounds. Toxicity is also of concern to the petroleum industry. Thus, biological assays or toxicity tests are also used to quantify the overall acute or chronic toxic effect of these wastewaters.

This report 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. This report also describes relevant constructed wetland design and operation issues of importance to the petroleum industry.

TABLE 1-5
Typical Pollutant Concentrations in Untreated Petroleum Refinery Wastewaters

Constituent	Units	Concentration
BOD ₅	mg/L	10-800
COD	mg/L	50-600
TSS	mg/L	10-300
TDS	mg/L	1,500-3,000
NH ₄ -N	mg/L	0.05-300
TP	mg/L	1-10
PH	Standard Units	8.5-9.5
Sulfate/sulfide	mg/L	ND-400
Total Organic Carbon (TOC)	mg/L	10-500
Chromium	mg/L	ND-3
Oil and grease	mg/L	10-700
Phenols	mg/L	0.5-100
ND	not detected	

Sources: Adams *et al.*, 1981; ANL, 1990.

Water Quality Improvement Performance in Treatment Wetlands

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

Arguably, the most 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 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. The art of this innovative design process is to be free from violations without being excessively conservative.

This section provides a review of state-of-the-art methods to summarize wetland treatment performance using simple first-order mass balance models, and reviews current knowledge about wetland performance for many of the pollutants of primary importance to the petroleum industry. These constituents of interest include BOD₅, COD, specific organic pollutants, metals, whole effluent toxicity, TSS, various forms of nitrogen, and TP. When available, the reader is provided general treatment wetland performance information for each pollutant and petroleum industry data.

Modeling Treatment Wetland Water Quality Changes

Like other water quality treatment processes, treatment wetlands perform within definable limits. These limits must be summarized so the designer can size a treatment wetland to consistently reduce pollutant concentrations from some inflow value to some desired outflow concentration. Regression equations and relatively simple first-order models are used most commonly to summarize wetland performance because data to support more complex deterministic models are insufficient. The designer has the ability to determine the actual treatment efficiency to some extent by using general knowledge of performance expectations for internal design features such as wetland area, water depth, cell configuration, and plant selection.

Because treatment wetlands are living, autotrophic ecosystems, the designer should also consider certain constraints associated with natural systems. The natural processes that occur in surface flow wetlands result in background concentrations of various chemicals that may, at higher concentrations, be the same constituents requiring treatment. Knowledge of these background concentrations is important to avoid overly optimistic expectations for treatment wetlands. Also, a certain amount of statistical variability is inherent in wetland outflow constituent concentrations, some of which is due to environmental factors (such

as seasonal temperature changes) outside the control of the wetland designer and operator. The inevitability of this “chatter” should be factored into the design to avoid permit violations.

Wetland Performance Equations

A vast quantity of operational performance data have been gathered from treatment wetlands. These data were collected over wide ranges of inlet concentrations, mass loadings, flow and hydraulic loading rates, hydraulic residence times, water depths, vegetation types, and water temperatures. 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 these diverse 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. Each of these methods of summarizing performance are briefly described below.

The fundamental descriptors of wetland performance are inlet (C_i) and outlet (C_o) concentrations, volumetric flow rate (Q), wetland area (A), and water depth (h). Wetland water volume is defined as wetland area times depth times porosity (M):

$$V = Ah\epsilon \quad (2-1)$$

One measure of relative flow rate is the nominal wetland detention time, τ :

$$\tau = \frac{Ah\epsilon}{Q} = \frac{h\epsilon}{q} \quad (2-2)$$

where $q = Q/A$ is the hydraulic loading rate.

Detention time is also equal to the free water depth, Mh , divided by the flow rate per unit surface area, q . Nominal detention to an interior point in the wetland is the overall travel time (τ) multiplied by the fractional distance through the wetland (y).

Loading Rates and Efficiencies

The pollutant loading rate (LR) at the wetland inlet is defined as:

$$LR_i = qC_i \quad (2-3)$$

The percent concentration reduction efficiency is:

$$EFF = 100 \frac{C_i - C_o}{C_i} \quad (2-4)$$

The mass removal efficiency is:

$$RED = 100 \frac{LR_i - LR_o}{LR_i} \quad (2-5)$$

RED embodies the overall water mass balance and explains the fate of the mass of entering pollutant. When inlet concentrations and loadings are close to zero, both EFF and RED can be misleading and result in high positive (or negative) percentages. Both are sensitive to wetland background concentrations as well as the speed of reduction processes. These variables may be used in either regression equations or mass balance equations to describe a performance data set.

Regression Equations

Regression equations (linear or log-linear equations) are the most convenient choice to represent intersystem data sets. They must be accompanied by the ranges of the variables because regressions are unreliable outside the range of data that produced them. The correlation coefficient is another useful adjunct because it reveals the fraction of variability that is described by the regression equation. Regression equations do not directly account for factors in the water mass balance or the pollutant mass balance.

Mass Balance Equations for Plug Flow

Many pollutants decline exponentially to a background concentration (C^*) on passage through a wetland. At the same time, some substances are returned to the wetland water column through the complex chemical processes occurring in wetland soils, decomposing litter, and living plants and wildlife. Most removal and return processes involve solid surfaces, such as roots, litter, and algal mats. The simplest removal equation that embodies a steep curved decline is first-order; the simplest return rate equation that embodies a nonzero background concentration is zero order.

For first-order pollutant uptake (J_U):

$$J_U = kC \quad (2-6)$$

For zero-order pollutant return (J_R) from the ecosystem to the water column:

$$J_R = \text{constant} = kC^* \quad (2-7)$$

The net pollutant reduction rate (J) is the difference:

$$J = k(C - C^*) \quad (2-8)$$

When $C = C^*$, no net removal of the pollutant occurs, although both destruction and production processes continue. The net pollutant reduction rate (J) is the mass removal per unit wetland surface area (grams per square meter per year [$\text{g}/\text{m}^2/\text{yr}$]). Therefore, the global rate constant (k) is proportional to the amount of active area (biofilms, plants, algae, etc.) per unit wetland area.

In many treatment wetland cases, infiltration is prevented and no significant atmospheric deposition or precipitation (P) occurs. Under this special set of conditions, $Q = \text{constant}$ along the length of the wetland (y) and:

$$-Q \frac{dC}{dy} = JA = kA(C - C^*) \quad (2-9)$$

For a specified inlet concentration (C_i), this integrates to:

$$\frac{(C_o - C^*)}{(C_i - C^*)} = \exp\left(-\frac{kA}{Q}\right) = \exp\left(-\frac{k}{q}\right) \quad (2-10)$$

Equation 2-10 is the historically well known first-order plug flow concentration profile for the case of a nonzero background concentration. It relates concentrations within the wetland, including C_o (the concentration at the outlet point), to loading rate (q).

For those pollutants that have C^* values close to zero, namely nitrate and ammonia nitrogen, Equation 2-10 reduces to:

$$\frac{C_o}{C_i} = \exp\left(-\frac{kA}{Q}\right) = \exp\left(-\frac{k}{q}\right) \quad (2-11)$$

Equation 2-10 can be rearranged to provide an estimate of the wetland surface area necessary to reduce an inflow pollutant concentration C_i to a target outflow concentration C_o :

$$A = -\frac{Q}{k} \ln\left(\frac{C_o - C^*}{C_i - C^*}\right) \quad (2-12)$$

The two calibration parameters are k and C^* ; therefore, this description is termed the k - C^* model.

Figure 2-1 illustrates a typical fit to data. Some pollutants, notably nitrogen (see the *Nitrogen* discussion under *Nutrients*), are linked by a sequential reaction pathway. In that case, the k - C^* concept is applied to each step, and production rates are included in the mass balances. For cases where seepage and atmospheric losses/gains are significant, a more complex equation is required.

The exponent in Equation 2-12 is often regrouped to define a volumetric rate constant:

$$k_v = \frac{k}{qh} \quad (2-13)$$

For the volumetric case, Equation 2-10 can be modified as:

$$\frac{C_o - C^*}{C_i - C^*} = \exp(-k_v \tau) \quad (2-14)$$

For those substances where $C^* \approx$ zero, Equation 2-14 reduces to:

$$\frac{C_o}{C_i} = \exp(-k_v \tau) \quad (2-15)$$

Temperature effects on k or k_v can be summarized by use of the modified Arrhenius equation:

$$k_T = k_{20} \theta^{(T-20)} \quad (2-16)$$

where k_T is the rate constant at temperature $(T) = T^\circ\text{C}$ and k_{20} is the rate constant at 20°C . Values of the temperature correction factor (θ) have been estimated for data sets with adequate operational temperature data (Kadlec and Knight, 1996).

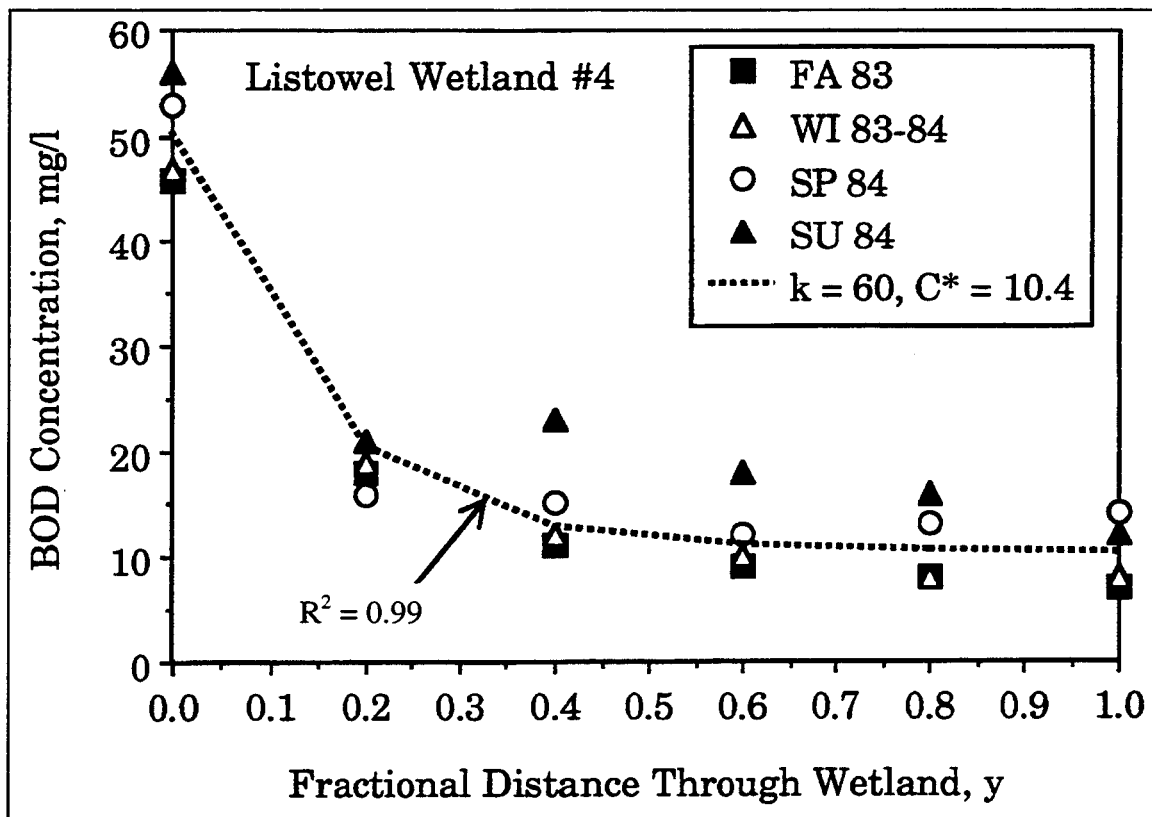


FIGURE 2-1

The k - C^* Model Fit to BOD_5 Data from the Listowel Project

This site shows little seasonal effect, despite the fact that winter operation was under ice.

Source: Based on data from Herskowitz, 1986.

The dimensions of k_v are reciprocal time, typically d^{-1} , those of k are velocity in meters per day (m/d). Because of numerical magnitudes, the units of k are typically converted to meters per year (m/yr).

As described earlier, the data from many treatment wetlands indicate nonzero values of C^* for some common pollutants (BOD_5 , TSS, organic N, TN, and TP). However, most of the existing wetland literature makes the $C^* = 0$ assumption and reports rate constants for the resulting one-parameter model (k_1 or k_{v1}). Rate constants determined under that assumption are always lower than the actual value by as much as a factor of 2 or 3 for light hydraulic loadings.

More importantly, if $C^* \neq 0$, then k_1 is not a constant and is a function of hydraulic loading rate.

Theoretically, k_1 is proportional to q for low hydraulic loading rates. This relationship is also the observed

trend of the data from a large number of free water surface wetlands. The values of k_{v1} are also nearly proportional to hydraulic loading, or inversely proportional to the detention time, for low hydraulic loadings. Because both k_1 and k_{v1} depend on hydraulic loading rate when $C^* \neq 0$, they should not be used in designing for certain pollutants.

Either k or k_v can be used to represent a data set or can be used in design. However, the use of k_v requires the accompanying information on water depth (h) because of the depth dependence indicated in Equation 2-13 (Figure 2-2). This depth dependence also means that more detention time created by deeper water is counteracted by a decrease in the volumetric rate constant. The hydraulic loading rate is not depth dependent, and data indicate that k is nearly independent of depth. Data analysis and design using volumetric coefficients require knowledge of the water depth. The use of areal coefficients does not require depth corrections. For many surface flow wetlands, especially large ones, depth is not known to a reasonable degree of accuracy. For these reasons, the parameters k , C^* , and θ are used to summarize treatment wetland operational performance data for the remainder of this section.

In general, literature values of rate constants have not been corrected for water losses and gains. In some instances, water budget information was not collected; in other cases, atmospheric losses and gains were not significant. Therefore, water mass balance effects are the cause of some fraction of the variability in rate constant data.

In some instances, a supply of a limiting reactant is required; oxygen, carbon, and alkalinity are three of the most common in treatment wetlands. In this assessment, any limitations of these essential reactants are implicit in the variability of system performance.

Wetland Background Concentrations

Wetland ecosystems typically include diverse autotrophic (primary producers such as plants) and heterotrophic (consumers such as microbes and animals) components. Most wetlands are more autotrophic than heterotrophic, resulting in a net surplus of fixed carbonaceous material that is buried as peat or is exported downstream to the next system (Mitsch and Gosselink, 1993). This net production results in an internal release of particulate and dissolved biomass to the wetland water column, which is measured as BOD_5 , TSS, TN, and TP. These wetland background concentrations are denoted by C^* . Enriched wetland ecosystems are likely to produce higher background concentrations than pristine wetlands because of the larger biogeochemical cycles that result from the addition of nutrients and organic carbon. Surface water concentrations in closed wetland basins with inflows dominated by precipitation represent the lowest wetland effluent concentrations observed.

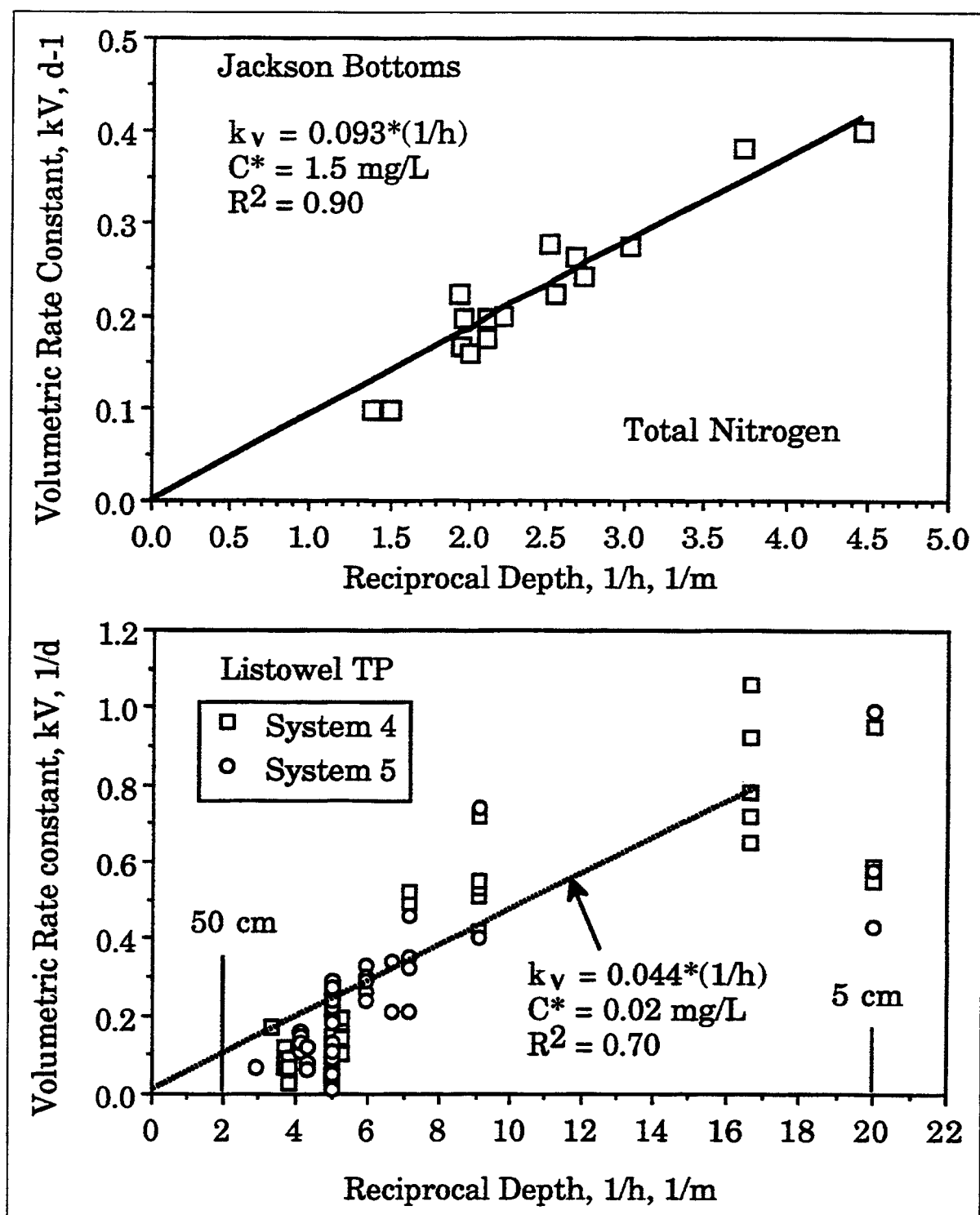


FIGURE 2-2

First-order Volumetric Rate Constants for TN and TP in Relation to Water Depth

The deeper the water, the smaller the rate constant. At very shallow depths, the rate constant again decreases as patches of the wetland are no longer immersed.

Source: Data for Jackson Bottoms from SRI, 1991; for Listowel from Herskowitz, 1986.

Wetland systems typically have background concentrations within these ranges:

- | | |
|------------------------------|----------------------------------|
| • BOD ₅ | 1 - 10 mg/L |
| • TSS | 1 - 6 mg/L |
| • Organic and total nitrogen | 1 - 3 mg/L |
| • Fecal coliforms (FC) | 50 - 500 FC/100 milliliters (mL) |
| • Ammonium N | < 0.1 mg/L |
| • Nitrate N | < 0.1 mg/L |
| • TP | < 0.1 mg/L |

Wetland Stochastic Variability

Treatment wetlands demonstrate the same water quality variability typical of other complex biological treatment processes. While inlet concentration pulses are frequently dampened through the long hydraulic and solids residence times of the treatment wetland, there remains significant spatial and temporal variability in wetland surface water pollutant concentrations.

The stochastic character of rainfall and the periodicity and seasonal fluctuation in evapotranspiration (ET) are also responsible for a portion of the variability in effluent quality in wetlands. One index of this variability is the ratio between long-term average conditions and maximum conditions observed over shorter time intervals. Data for an analysis of average ratios between the maximum month and average annual concentrations for BOD₅, TSS, TN, and TP were available from 22 sites with a total of 53 different wetland cells in the NADB. Average ratios were 2.0 for BOD₅, 2.1 for TSS, 1.6 for TN, and 1.9 for TP. Similar ratios have not yet been summarized for discharges from wetlands treating petroleum industry wastewaters.

Carbon Processing

Biomass: Growth, Death, and Decomposition

A strong correlation exists between biomass and carbon cycling within a wetland. The proportion among the nutrient elements in the biomass is often represented as a molar proportion of C:N:P = 106:16:1, or 41:7:1 on a mass basis (the Redfield ratio). This proportion translates to a carbon content of roughly 15 percent dry weight (dw) in plant tissues.

The wetland cycle of growth, death, and partial decomposition uses atmospheric carbon, and produces gases, dissolved organics, and solids. Decomposition involves the sugars, starches, and low molecular weight celluloses in the dead plant material. Gaseous products include methane and regenerated carbon dioxide. A spectrum of soluble large organic molecules, collectively termed humic substances, are released into the water. The solid residual of plant decomposition is peat or organic sediment, which originated as celluloses and lignins in the plants. These wetland soil organics are broadly classified as fulvic material,

humic material, or humin on the basis of their acid soluble, base soluble, or insoluble properties (Peat Testing Manual, 1979).

The internal wetland carbon cycle is large. Consideration of annual growth and decomposition patterns can provide a general idea of the magnitudes of the various carbon transfers in a northern treatment marsh. A eutrophic treatment marsh grows about 5,000 g/m² of above- and below-ground biomass each year, with a carbon content of about 15 percent. This translates to a requirement of 750 g/m²/yr of carbon. Decomposition of the resultant litter returns a significant portion of that carbon to the wetland ecosystem, but residuals may accrete at rates up to 150 g/m²/yr.

Carbon Processing in Wetland Soils

Decomposition "reactions," which can be generally described according to the following equations (Mitsch and Gosselink, 1993; Burgoon, 1993), occur in different horizons in the wetland, as shown in Figure 2-3.

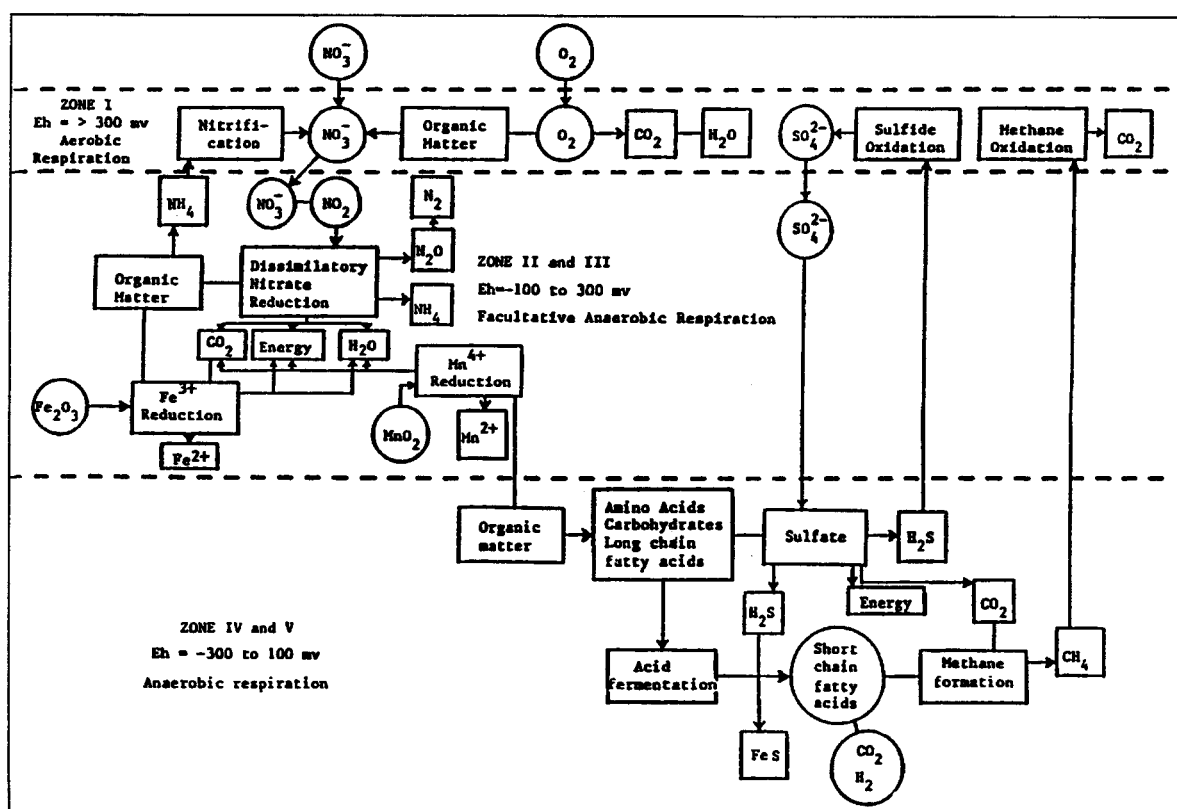


FIGURE 2-3

Pathways of Organic Carbon Decomposition in Wetland Soils

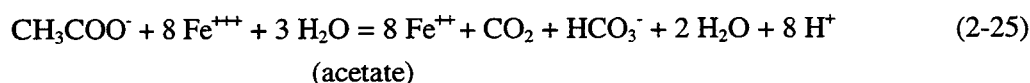
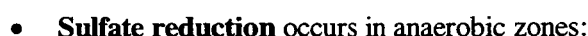
Aerobic, facultative anaerobic, and obligate anaerobic processes are typically all present at different depths in the soil.

Source: Reprinted with permission from Reddy and Graetz, 1988.

- **Fermentation** occurs in anaerobic zones:



- **Methanogenesis** occurs in anaerobic zones:



Burgoon (1993) investigated the relative percentages of these reactions in controlled subsurface flow wetland microcosms by using acetate as the carbon source. His results demonstrate that all routes can be important, depending on physical and chemical conditions (Table 2-1).

Clearly, the wetland provides a spectrum of potential pathways for the use of organic carbon compounds. Information is insufficient to quantify both the complex chemistry and the spatial distribution of chemical compounds. Therefore, the interactions must be described by correlations and rate equations that are supportable by wetland performance data.

TABLE 2-1

Percent Acetate Oxidized via Various Pathways by *Scirpus validus* Planted in Plastic Media

Reaction	High Carbon Loading		Low Carbon Loading	
	Plants	No Plants	Plants	No Plants
Nitrate-rich environment:				
Oxidation	23.2	25.6	36.1	32.8
Nitrate reduction	70.6	69.3	51.7	56
Sulfate reduction	3.0	3.1	2.3	2.3
Ferric iron reduction	0.1	0.0	0.1	0.1
Methane formation	0.0	0.0	0	0
Bacterial biomass formation	3.1	2.0	9.8	8.8
Total	100.0	100.0	100.0	100.0
Sulfate-rich environment:				
Oxidation	40.7	31.7	44.5	13.5
Nitrate reduction	0	0	0	0
Sulfate reduction	37.8	34.1	50.6	82.7
Ferric iron reduction	0.1	0.1	0.2	0.2
Methane formation	19.6	32.1	0	0
Bacterial biomass formation	1.8	2	4.7	3.6
Total	100.0	100.0	100.0	100.0

Source: Burgoon, 1993.

Biochemical Oxygen Demand Removal Performance

The wetland carbon cycle is rapid and large. Atmospheric and dissolved carbon are fixed into new biomass during photosynthesis; leaching and decomposition return a major fraction back to the water. Therefore, natural wetland waters are rich in humic substances and other forms of carbon, which add color to the water. Some of these naturally occurring compounds are detected by the widely accepted, but imperfect, BOD₅ test.

Treatment wetlands often receive loads of BOD₅ from industrial wastewater sources. Some of these carbon compounds are dissolved; others are associated with incoming particulates. Particulate settling is one removal mechanism that would typically occur in the inlet region of the wetland (Figure 2-4). Particulate removal processes in wetlands are discussed later under *Total Suspended Solids*. Soluble, biodegradable carbon compounds are processed by microbial communities associated with solid surfaces such as floating mats, litter, and plant stems. The decomposition of litter and sediments produces a return flux of BOD₅ to the water column. The balance between removal and return processes creates the wetland background concentration.

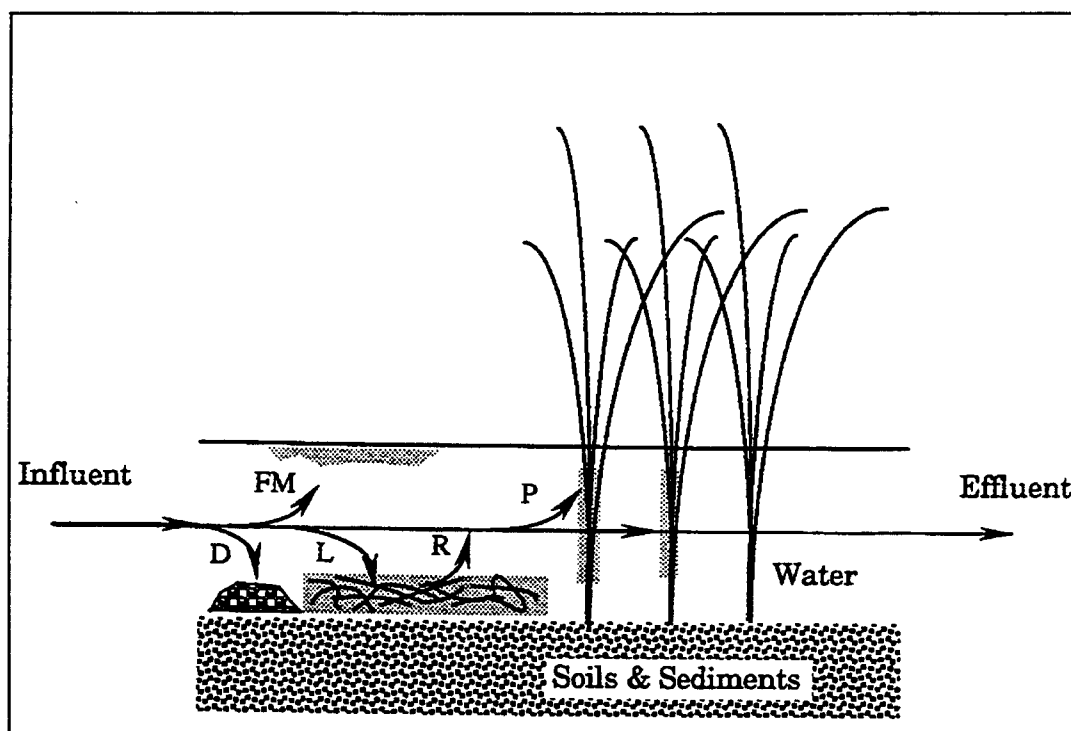


FIGURE 2-4

Simplified Portrayal of Wetland Carbon Processing

Incoming BOD₅ is reduced by deposition of particulate forms (D) and by microbial processing in floating (FM), epiphytic (P), and benthic litter (L) layers. Decomposition processes create a return flux R.

Microbial removal processes include oxidation in the aerobic 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 BOD₅ is also associated with the microorganisms attached to the submerged solids.

As a result of these combined processes, BOD₅ declines along the flow path from inlet to outlet, down to the background level (Figure 2-5). 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 percent of the intrasystem variability ($R^2 \approx 0.9$). The central tendency of rate constants from a variety of municipal wastewater treatment wetlands is $k = 34$ m/yr (Table 2-2). Seventy-three Danish soil-based wetlands receiving domestic wastewaters had values of $k = 47.5$ m/yr and $C^* = 3.0$ mg/L (Brix, 1994). A review of performance data from subsurface flow treatment wetlands yielded average values of $k = 180$ m/yr and $C^* = 3.5 + 0.053 C_i$ mg/L (Kadlec and Knight, 1996).

No published petroleum wastewater datasets are currently available to fully calibrate the k-C* model for BOD₅ reduction. However, petroleum industry operating data collected for this report indicate that k_i is typically between 11 and 75 m/yr (Table 2-3). Reductions in BOD₅ are significant for high incoming

concentrations, but less when the inlet concentration is near background. The k_1 rate constant does not reflect the wetland background value C^* and, therefore, is lower than the value for k .

BOD_5 rate constants can also be expressed with units d^{-1} ; however, wetland volumetric rate constants (k_{v1}) are known to vary directly with mass loading (Reed *et al.*, 1995) and inversely with depth (see table 2-4 and Kadlec and Knight, 1996).

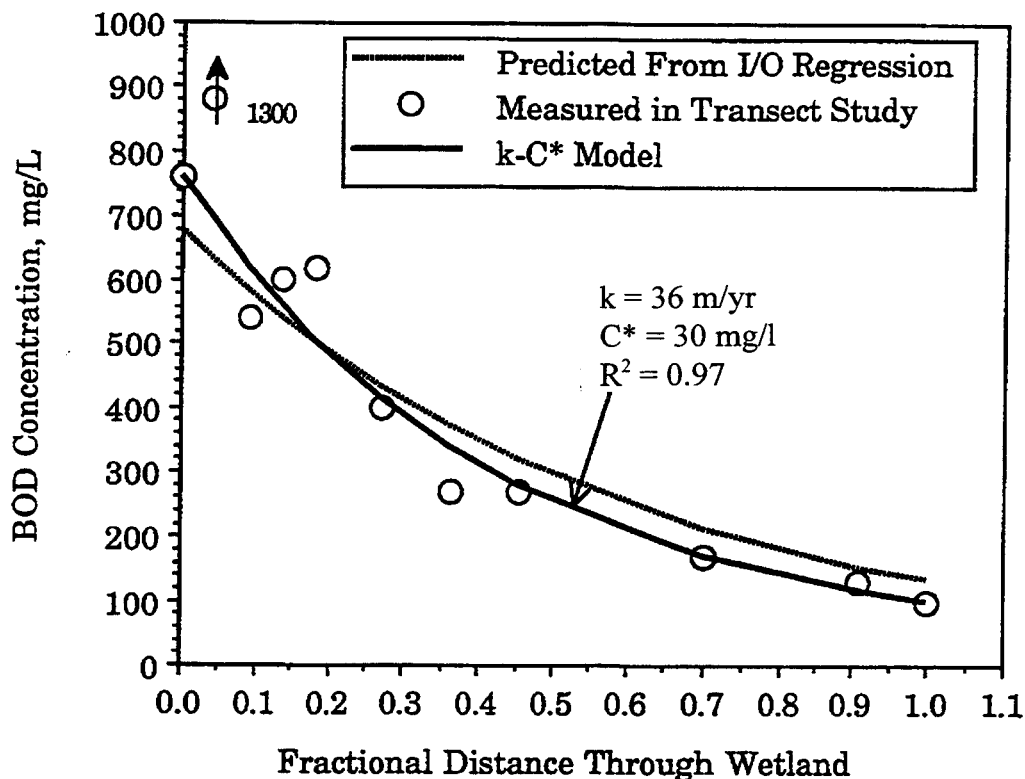


FIGURE 2-5

Transect Data for Gustine Wetland Treatment System 1D

The k - C^* model (solid line) explains the decline in BOD_5 . The outlier at 1,300 mg/L was excluded from regression. Input-output data for seven test wetlands at the site, including 1D, were also regressed to the k - C^* model (dashed line). The input/output data were fit with $k = 27 \text{ m/yr}$ and $C^* = 30 \text{ mg/L}$ and provide a reasonable description of the 1D transect data.

The decrease in BOD_5 is slower than the decline in TSS along transects or in batch mesocosm tests. Soluble BOD_5 decreases at the same value of the rate constant, as evidenced by the fit (Kadlec and Knight, 1996) of data from a sugar refinery (Gambrell *et al.*, 1987). Other individual hydrocarbons follow a similar pattern (Kadlec and Knight, 1996). No evidence exists of the instantaneous drop in BOD_5 at the wetland inlet described by some literature models (Reed *et al.*, 1995).

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 growth and, hence, accentuate the

return flux and increase the resultant background concentration. Therefore, C^* is elevated for strong influents. The possibility of irreducible components in the incoming BOD_5 also exists. The incoming BOD_5 concentration can be used as a surrogate for incoming nutrient load in many cases and is also reflective of possible residuals. Recognizing this strength dependence, the background concentration can be approximated as a function of inlet BOD_5 (Kadlec and Knight, 1996):

$$C^* = 3.5 + 0.03C_i \quad (2-26)$$

$$R^2 = 0.67$$

$$0 < C_i < 200 \text{ mg/L}$$

TABLE 2-2

Rate Constants for BOD_5 Reduction for Some Surface Flow Wetland Systems

Site	System	k Value (m/yr)	Background C^* (mg/L)
Listowel, Ontario	System 1	14	4.3
	System 2	7	3.3
	System 3	12	4.6
	System 4	37	10.4
	System 5	43	13.9
Gustine, California	Marsh 1A	18	11.6
	Marsh 1B	14	6.4
	Marsh 1C	9	13.0
	Marsh 1D	29	5.9
	Marsh 2A	22	7.8
	Marsh 2B	42	5.5
	Marsh 6A	33	3.5
	Pilot Marsh	22	4.7
Cobalt, Ontario	Marsh	54	4.7
Iron Bridge, Florida	Marsh	23	2.1
Benton, Kentucky	Marsh 1	94	5.4
	Marsh 2	60	7.9
Pembroke, Kentucky	Marsh	51	3.3
West Jackson County, Mississippi	Marsh	54	4.7
Lakeland, Florida	Marsh 1	48	1.1
Wetwang, United Kingdom	Marsh 2	52	3.9
	Marsh 3	51	5.2
Cannon Beach, Oregon	Forested	18	3.8
Bear Bay, South Carolina	Forested	7	1.9
Reedy Creek, Florida	Forested	34	1.7
Average		34	5.6
Standard Deviation		21	3.4

Source: NADB, 1993.

TABLE 2-3
Petroleum Industry Treatment Wetland Operating Data for BOD₅

Site	Size	Type	Inlet BOD ₅ (mg/L)	Outlet BOD ₅ (mg/L)	Reduction (%)	k ₁ (m/yr)	Reference
Amoco, Mandan, North Dakota	16.6 ha	FWS	79.4	12.4	84	11	Litchfield and Schatz, 1989
Texaco A	400 m ²	FWS	103.7	2.1	98	71	Hall, 1996
Texaco B	400 m ²	FWS	1.9	1.8	5	1	Hall, 1996
Chevron, Richmond 1989-91	36 ha	FWS	12.5	7.6	39	5	Duda, 1992
	1992-95	36 ha	FWS	11.3	5.1	55	Chevron, 1996
Non-USA Oil Terminal	600 m ²	SSF	75	15	80		Farmer, 1996
Mobil/DGMK Germany		SSF	700	20	97	71	Altmann <i>et al.</i> , 1989
Tisza Petrochemical, Hungary		FWS			30		Kiss and Lakatos, 1996
Nyirbogdany Petrochemical, Hungary		FWS			25		Kiss and Lakatos, 1996
Yanshan Pond/Wetland, P.R. China	25 ha	FWS	38	15.3	60	75	Dong and Lin, 1994
FWS	free water surface (surface flow)						
SSF	subsurface free flow system						

TABLE 2-4
BOD₅ Rate "Constants" vs. Depth and Loading at the Arcata, California, Treatment Wetlands

Flow (m ³ /d)	Depth (m)	Increase in HRT (%)	BOD ₅ Rate Constant (1/d)	Decrease in kv (%)
93	0.40		0.29	
94	0.55	37	0.17	42
86	0.36		0.25	
83	0.61	76	0.13	49
45	0.30		0.28	
49	0.49	49	0.14	48
29	0.33		0.14	
29	0.53	78	0.08	40
23	0.35		0.14	
24	0.50	39	0.09	36

Source: Gearheart and Higley, 1993

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 (Figure 2-6). The format used in Figure 2-6 and other figures in this report illustrates the relationship between mass loading (the product of inlet concentration and hydraulic loading) and outlet concentration. Use of Figure 2-6 allows estimation of wetland outflow BOD₅ concentration based on any design loading rate. Input-output behavior is strongly influenced by background and inlet concentrations, which are masked in simple graphical representations. However, the k-C* model spans the intersystem scatter in input/output data.

Temperature apparently plays a minor role in the net removal of BOD₅ in treatment wetlands. Temperature coefficients are close to, but slightly less than, unity. For 10 wetlands analyzed by Kadlec (1996 [unpublished data]), $\theta = 0.974 \pm 0.029$. However, the use of a temperature correction for the rate constant is not warranted, since only about 6 percent of the variability is explained by temperature ($R^2 \approx 0.066$ for 9 of the 10 systems).

If the BOD₅ in the incoming water is above wetland background, reduction occurs, and the wetland effluent is at a lower concentration. Stochastic processes cause periods of better and poorer performance than the long-term average. Temporary spikes and valleys are the result of many factors; some are related to inflow concentration and flow rate, whereas others are related to wetland events such as animal activity. The maximum monthly outlet BOD₅ concentration is typically 2.0 times higher than the long-term mean (Kadlec and Knight, 1996).

The regression of input and output data provides a simple performance description, but at the price of a relatively low correlation coefficient (Kadlec and Knight, 1996):

$$C_o = 0.173C_i + 4.70 \quad (2-27)$$

$$R^2 = 0.62, N = 440$$

$$\text{Standard Error in } C_o = 13.6$$

$$0.27 < \text{HLR} < 25.4 \text{ cm/d}$$

$$10 < C_i < 680 \text{ mg/L}$$

$$0.5 < C_o < 227 \text{ mg/L}$$

A similar relationship was found for seventy-three Danish wetlands (Brix, 1994). This regression equation does not contain the hydraulic loading rate, and the R^2 is not improved if it is added. The cause is related to the fact that many wetlands achieve near-background BOD₅. Consequently, Equation 2-27 cannot be used to size treatment wetlands.

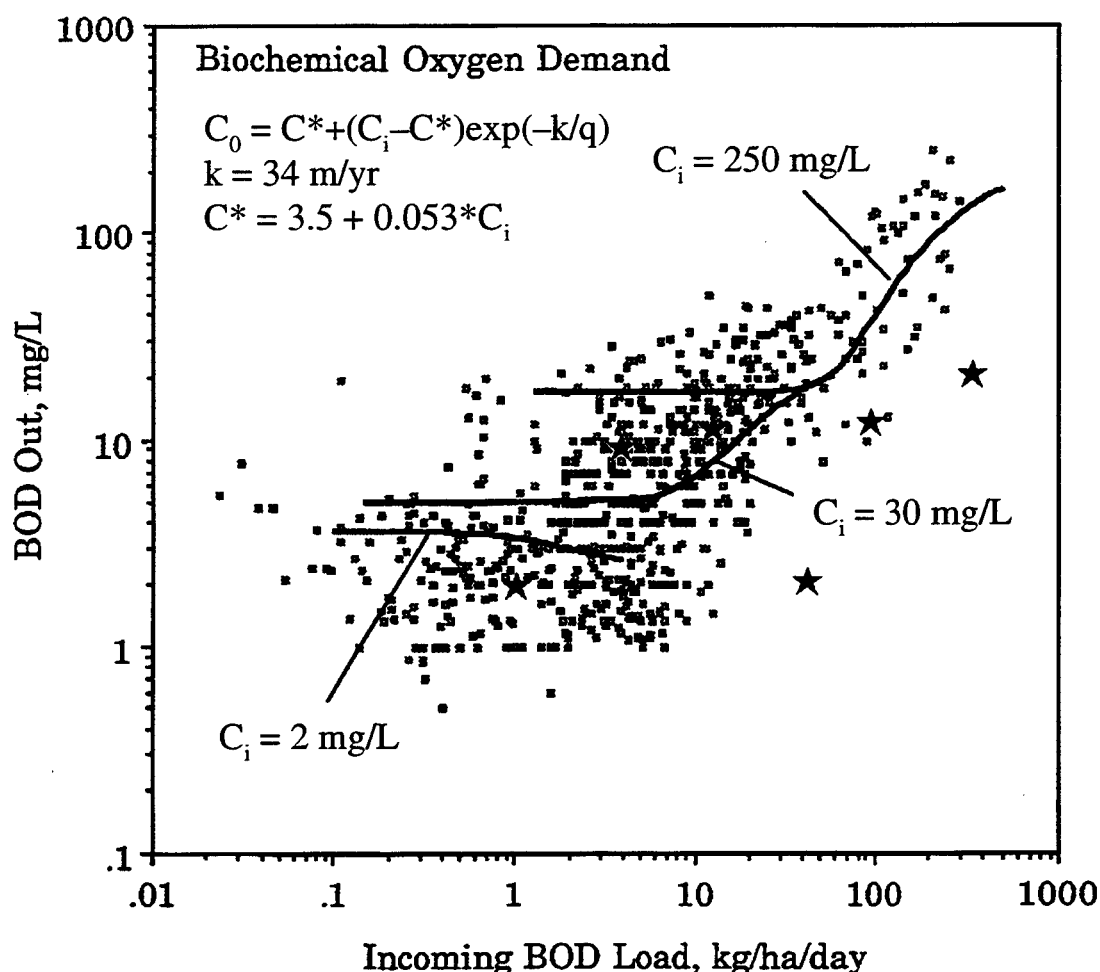


FIGURE 2-6

Intersystem Performance for BOD₅ Reduction

Data points are from 48 wetland cells at 22 sites. Petroleum industry data are highlighted (★). The k - C^* model is shown for different inlet concentrations. It spans the data set and accounts for increasing BOD₅ in lightly loaded wetlands with very low inlet concentrations, as depicted by the $C_i = 2 \text{ mg/L}$ curve.

COD Reduction in Treatment Wetlands

BOD₅ represents the class of organic compounds that are susceptible to biological oxidation; 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 BOD₅ because more organic compounds can be chemically oxidized than are degraded biologically. Often BOD₅ and COD are highly correlated for a specific wastewater.

In the wetland environment, the presence of humic materials leads to COD values that are much higher than BOD₅ values. In Northern peatlands, the BOD₅ : COD (mg/L) ratio is approximately 5 : 100 (Kadlec, unpublished data). In untreated municipal wastewaters, the ratio is 0.4 : 0.8 (Metcalf and Eddy, 1991).

Natural wetland waters contain significant COD, often in the range of 30 to 100 mg/L. When wastewater with lower than background COD is added to a natural wetland, the COD concentration increases to the background COD value as the wastewater passes through the wetland. For example, lagoon water of 30 mg/L COD was added to the Houghton Lake peatland and left the treatment area with 100 mg/L COD (Kadlec and Tilton, 1979). Similarly, when low-COD wastewater is added to a constructed wetland, the COD concentration will increase as the wastewater passes through the system. For example, in 1990, the water entering the Jackson Bottoms wetlands was at 40 mg/L COD; the water leaving the 17 parallel cells averaged 51 ± 7 mg/L COD (SRI, 1990).

No treatment wetland project has yielded COD data that can be used to calibrate the k - C^* model. Either transect data or data over variable loading rates are required to determine the value of k and C^* , and such data are lacking. Accordingly, only a one-parameter model can be fit to data ($C^* = 0$), with the knowledge that this model produces loading-variable k values (see Section 2). Equation 2-11 has been used to generate the k_1 values in Table 2-5, where the subscript "1" denotes the fact that the value of C^* has unavoidably been set to zero. This initial value leads to lower k values than those for the k - C^* model with nonzero C^* .

The sparse information on petroleum wastewater systems indicates that COD is reduced at rates comparable to those found for other types of wastewater (Table 2-5). The mean COD k_1 rate constant for all systems is 36 m/yr; that for BOD₅ from the NADB marsh systems is 13 m/yr. However, for paired data (COD and BOD₅ for the same wetlands), the $k_1\text{COD}:k_1\text{BOD}_5$ ratio is 0.81 ± 0.33 ; the ratio was 0.65 for the Amoco Mandan data in 1987 (Litchfield and Schatz, 1989). This information indicates that on average, COD is reduced less effectively than BOD₅ in treatment wetlands.

Temperature effects on BOD₅ reduction are typically minimal (see the previous subsection, *Biochemical Oxygen Demand Removal Performance*), and the same is true for COD rate constants, although data are sparse. Kadlec and Tilton (1979) report $\theta = 1.023$ for COD reduction in potato processing waters; data from Saurer (1994) for the Mühlen, Austria, domestic wastewater treatment wetland indicate $\theta = 1.030$ for COD. BOD₅ reduction for the Mühlen study was $\theta = 1.009$.

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.

TABLE 2-5
Reduction of COD for Various Wastewaters in a Variety of Wetland Types

Project Site	Wetland Area		Inlet COD (mg/L)	Outlet COD (mg/L)	Reduction (%)	k ₁ (m/yr)	Reference
Petroleum Industry							
Amoco, Mandan, North Dakota	16.6 ha	FWS	131	40	69	7	Litchfield and Schatz, 1989
Yanshan Pilot, P.R. China	Spring	FWS			38.9		Dong and Lin, 1994a
	Summer	FWS			47.7		
	Fall	FWS			30.9		
	Winter	FWS			32.5		
Yanshan Pond/Wetland, P.R. China	Full Scale	FWS	170	47.5	72	104	Dong and Lin, 1994b
Non-USA Oil Terminal	600 m ²	SSF	101	47	53		Farmer, 1996
Mobil/DGMK Germany		SSF	1,800	250	86	40	Altmann <i>et al.</i> , 1989
Tisza Petrochemical, Hungary		FWS			30		Kiss and Lakatos, 1996
Nyirbogyó Petrochemical, Hungary		FWS			25		Kiss and Lakatos, 1996
General Industrial							
Mixed, Stavropol, Russia Federation	3,980 m ²	SSF			65 - 85		Magmedov, 1996
Mixed, Tenth Ramadan City, Egypt	200 m ²	SSF			0 - 86		Addleton <i>et al.</i> , 1996
Leachate, Slovenia	450 m ²	SSF	1,264	404	51 - 94	6	Bulc <i>et al.</i> , 1996
Lower Saxony, Germany	69 m ²	VF	467	37	92	62	von Felde and Kunst, 1996
Lower Saxony, Germany	40 m ²	VF	275	15	95	51	Bahio and Wach, 1990
Oaklands Park, United Kingdom	20 m ²	VF	266	142	47	149	Burka and Lawrence, 1990
New Zealand (Meat)	250 m ²	FWS	1,531	330	78	25.8	Van Oostrom and Cooper, 1990
			247	124	50	14.6	
			161	112	30	7.7	
Belgium (Sewage)	19 m ²	FWS	240			23.8	Radoux and Kemp, 1990
Hermiston (Potato)	40 m ²	FWS	2,100	714	66	37	Kadlec <i>et al.</i> , 1996
Connell (Potato)	2,685 m ²	FWS/SSF	3,150	224	93	55	Kadlec <i>et al.</i> , 1996
American Crystal Sugar, North Dakota	64.8 ha	FWS	103	4	96	6	Anderson, 1996
Australia (Piggery)	36 m ²	SSF	630	246	61	13.7	Finlayson <i>et al.</i> , 1990
	36 m ²	SSF	630	347	45	8.7	
Czech Republic (Sewage)	1.1 m ²	SSF	380	64	83	37.1	Vymazal, 1990
	1,248 m ²	SSF	550	100	82	38.3	
Czech Republic (Chicken Waste)	1.1 m ²	SSF	2,420	395	84	16.8	Vymazal, 1990
Netherlands (Potato)	230 m ²	SSF	1,200	96	92	9.2	de Zeeuw <i>et al.</i> , 1990
					Mean	36	
					Maximum	149	
					Minimum	6	
m ²	square meter						
FWS	free water surface (surface flow)						
SSF	subsurface flow						
VF	vertical flow						

Organics Removal from Petroleum Wastewaters

General Results

Information on the effectiveness of constructed wetlands to remove organic compounds from wetland waters is derived from general reports on wetland processes and from preliminary reports from pilot- or full-scale wetlands associated with petroleum industry waste streams. 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 (Kadlec and Knight, 1996). 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 (Wang and Peverly, 1996). 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) (Wolverton, 1987; Wang and Peverly, 1996; Anderson and Walton, 1995). Free-floating plants, such as water hyacinth, have also been shown to reduce trace levels of organic compounds in aquatic treatment system wastewaters (Wolverton and McKnown, 1976; Wolverton and McDonald, 1981; Conn and Langworthy, 1984).

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. 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 (Srinivasan and Kadlec, 1995).

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). Compounds with more than three benzene rings are not capable of supporting microbial growth and are, therefore, much more difficult to degrade (Kadlec and Knight, 1996). Organic compounds with hydroxyl (OH) groups attached to a benzene ring are collectively referred to as phenols. The primary mechanism for phenol removal in wetlands occurs through sorption to various wetland components and subsequent degradation by microbial organisms (Zander, 1980).