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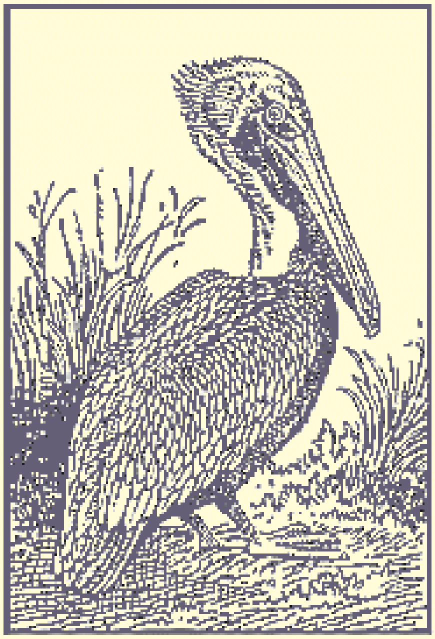
Wetlands Research Program Technical Report WRP-CP-9

Screening-Level Model for Estimating Pollutant Removal by Wetlands

by Mark S. Dortch, Jeffrey A. Gerald



October 1995 – Final Report

The following two letters used as part of the number designating technical reports of research published under the Wetlands Research Program identify the area under which the report was prepared:

	Task		Task
CP	Critical Processes	RE	Restoration & Establishment
DE	Delineation & Evaluation	SM	Stewardship & Management

Wetlands Research Program

Technical Report WRP-CP-9
October 1995

Screening-Level Model for Estimating Pollutant Removal by Wetlands

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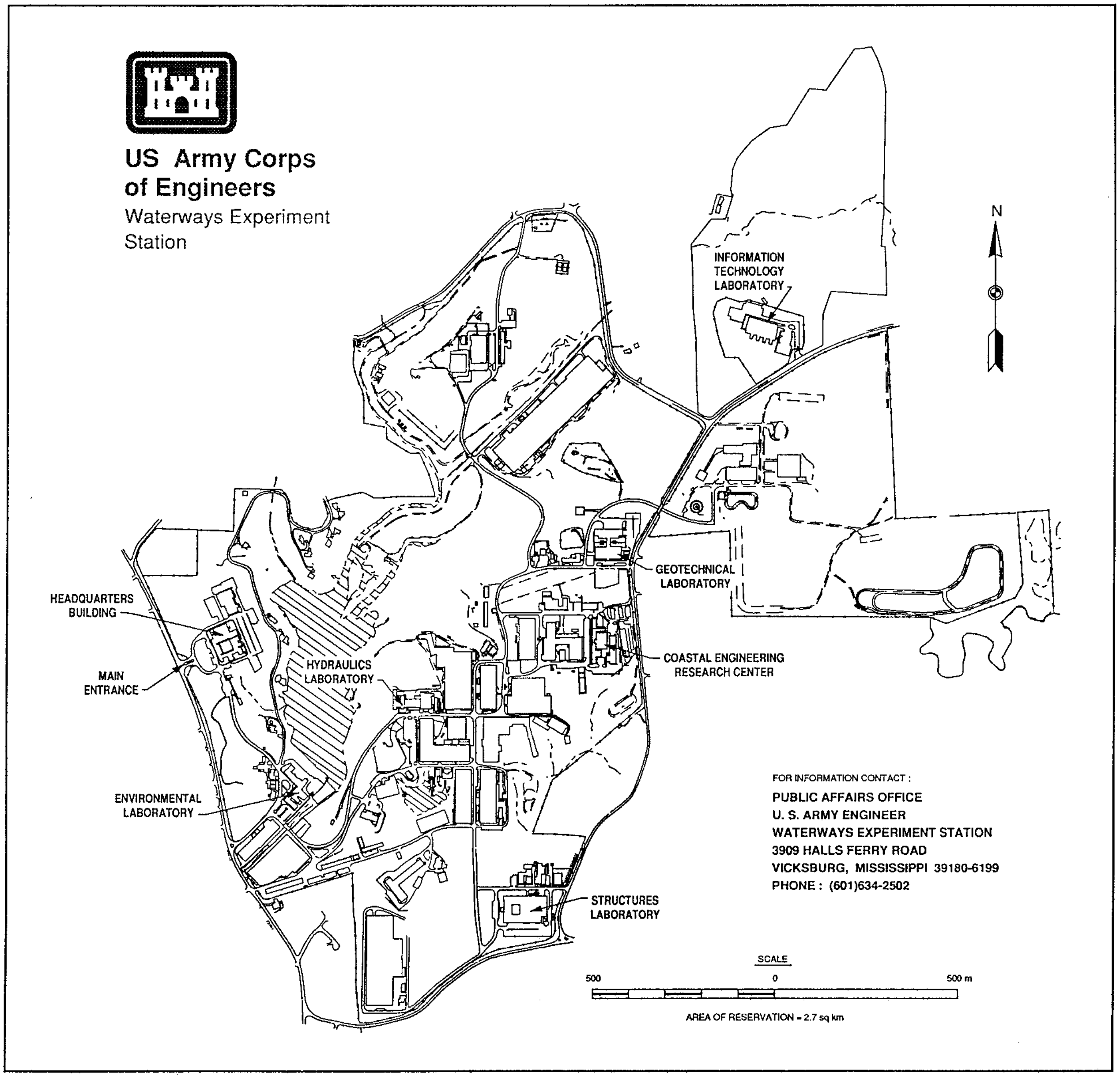

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Corps of Engineers Research Report Summary, October 1995

Wetlands and Water Quality

Screening-Level Model for Estimating Pollutant Removal by Wetlands (TR WRP-CP-9)

ISSUE:

Wetlands can effectively remove pollutants from wastewaters and runoff, thus improving water quality. Methods are needed for estimating the amount of pollutant removal and water quality improvement provided by wetlands. A screening-level, analytical model is needed for rapid assessment of this wetland function.

RESEARCH:

A screening-level, analytical model was developed that can be rapidly applied with minimal input data for estimating the amount of water quality improvement provided by wetlands. Given basic characteristics about the wetland, pollutant removal efficiency (RE) can be computed for total suspended solids, total coliform bacteria, biochemical oxygen demand, total nitrogen, total phosphorus, and contaminants (e.g., organic chemicals and trace metals). The RE depends on the wetland detention time and the removal rate, K (day^{-1}), for the constituent. The removal rates depend on a number of processes, such as microbial metabolism, adsorption, volatilization, denitrification, settling, etc., and ambient conditions, such as water temperature. The model was focused on the dominant long-term removal mechanisms, making use of literature values of mathematical formulations for those mechanisms when possible.

SUMMARY:

This report presents analytical model formulations for predicting pollutant RE provided by wetlands. These formulations have been programmed into an interactive, user-friendly, PC-based computer program, which is also described in the report. Comparisons of predicted versus observed REs for the Cache River wetland, Arkansas, are made for total suspended solids, total nitrogen, and total phosphorus.

AVAILABILITY OF REPORT:

The report is available on Interlibrary Loan Service from the U.S. Army Engineer Waterways Experiment Station (WES) Library, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199, telephone (601) 634-2355.

To purchase a copy, call the National Technical Information Service (NTIS) at (703) 487-4650. For help in identifying a title for sale, call (703) 487-4780.

NTIS report numbers may also be requested from the WES librarians.

About the Authors:

The model formulations were developed by Dr. Mark S. Dortch, who is a Research Civil Engineer at WES. The model software was developed by Mr. Jeffrey A. Gerald, who is an engineer with AScI, Inc. Point of contact at WES is Dr. Dortch at (601) 634-3517.

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Preface

The work described in this report was authorized by Headquarters, U.S. Army Corps of Engineers (HQUSACE), as part of the Critical Processes Task Area of the Wetlands Research Program (WRP). The work was performed under the Work Unit 32753, "Water Quality," for which Dr. Mark S. Dortch was Principal Investigator. Mr. Dick DiBuono (CECW-EH-W) was the WRP Technical Monitor for this work.

Mr. Dave Mathis (CERD-C) was the WRP Coordinator at the Directorate of Research and Development, HQUSACE; Dr. William L. Klesch (CECW-PO) served as the WRP Technical Monitors' Representative; Dr. Russell F. Theriot, U.S. Army Engineer Waterways Experiment Station (WES), was the Wetlands Program Manager. Mr. Jack Davis, WES, was the Task Area Manager.

The methods presented in this report were developed by Dr. Dortch, Environmental Processes and Effects Division (EPED), Environmental Laboratory (EL), WES. Mr. Jeffrey Gerald, AScI, Inc., developed the model software. This report was prepared by Dr. Dortch and Mr. Gerald under the general supervision of Mr. Donald L. Robey, Chief, EPED. Dr. Edwin A. Theriot was Assistant Director and Dr. John W. Keeley was Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Bruce K. Howard, EN.

This report should be cited as follows:

> Dortch, M. S., and Gerald, J. A. (1995). "Screening-level model for estimating pollutant removal by wetlands," Technical Report WRP-CP-9, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

1 Introduction

Background

Water quality improvement is potentially an important function of wetlands. Quantitative techniques are needed to assess this function. Specifically, methods are needed to assess the role of wetlands for water quality enhancement for permitting and planning activities, and predictive techniques are required when designing constructed wetlands for use in water quality improvement of receiving water.

Ideally, a predictive model should maximize the amount of information provided while minimizing the amount of effort to obtain the information. In other words, rather simplistic modeling approaches that yield useful information are highly desirable. A screening-level model refers to the use of simplified, quantitative, predictive methods that minimize time and effort for implementation. Simplification is achieved by making assumptions that reduce complexity of the predictive mathematical formulations and input data requirements. The intent here was to develop a screening-level model that can be rapidly applied with minimal input data for estimating the amount of water quality improvement provided by wetlands. A screening-level approach may not be appropriate when more definitive predictions or estimates are required, which may be the case for costly construction projects or high-profile projects under litigation.

Objective

The objective of this report is to develop the theoretical basis for an analytical, screening-level mathematical model for estimating the amount of pollutant removal provided by wetlands with a standing (free) water surface. These techniques have been programmed into an interactive, user-friendly, PC-based computer program, which is also described herein. At the time of this publication, the model software was undergoing final development and testing to improve ease-of-use. The formulations outlined in this report can still be used to calculate removal efficiency without the software. However, the software will greatly reduce the time and effort required to make these calculations. Symbols used in this report are described in Appendix A.

2 Approach

Removal Efficiency

The amount of pollution removed from receiving water can be quantitatively expressed in terms of the removal efficiency (RE), where RE is a percentage between 0 and 100 percent. RE is defined as

$$RE = 100 \times \frac{W_L - QC}{W_L} \qquad (1)$$

where

W_L = total loading of pollutant entering wetland, i.e., $\sum Q_i C_i$

Q = total water flow rate exiting wetland

C = pollutant concentration of flow exiting wetland

Q_i = water flow rate entering wetland at point i

C_i = pollutant concentration of flow entering at point i

Thus, RE = 100 percent denotes total removal of a pollutant. Figure 1 is a schematic for two pollutant loadings entering a wetland, where one loading is due to a stream and the other arises from a discharger (i.e., a point source). Thus, Equation 1 is applicable to both point and nonpoint source loadings since $W_L = \sum Q_i C_i$, i.e., the total load (mass/time) entering can be considered. If the outflow from the wetland occurs at more than one location, then QC would also be summed for all outflow points since RE should be a measure of the total pollutant removal efficiency achieved by the wetland. The main focus of this model is to compute RE.

The primary assumption made with this model to achieve simplicity is that the wetland is at steady-state (i.e., flow and concentrations are constant in time). Although wetlands may not be at steady-state, steady-state analyses are useful for evaluating long-term, average values. Mean annual input conditions (e.g., flows and depth) are consistent with this assumption.

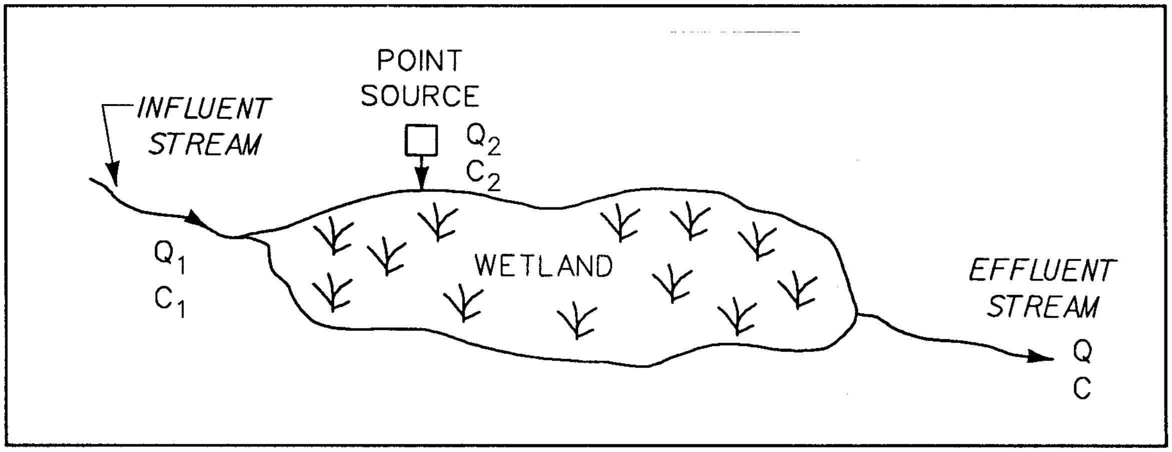

Figure 1. Schematic of two pollutant loads (i.e., stream and point source) entering a wetland

Either of two conditions are assumed for spatial gradients in concentration: (a) fully mixed (i.e., no gradients); and (b) gradients along the main flow axis (i.e., longitudinal gradients, but well mixed laterally and vertically, or plug flow). These two conditions are shown schematically in Figure 2. Notice that for the fully mixed condition, concentration within the wetland is constant and equal to that exiting the wetland. For the longitudinal gradient condition, concentration decays exponentially within the wetland.

The mass balance equation for the first spatial assumption is stated as

$$\frac{d(VC)}{dt} = W_L - QC - KVC \tag{2}$$

where

V = volume of wetland

C = pollutant concentration in wetland and flowing out of wetland for fully mixed assumption

t = time

K = bulk loss or removal rate of pollutant because of physical, chemical, or biological processes

For the steady-state assumption, Equation 2 reduces to

$$QC = \frac{W_L}{1 + K\tau} \tag{3}$$

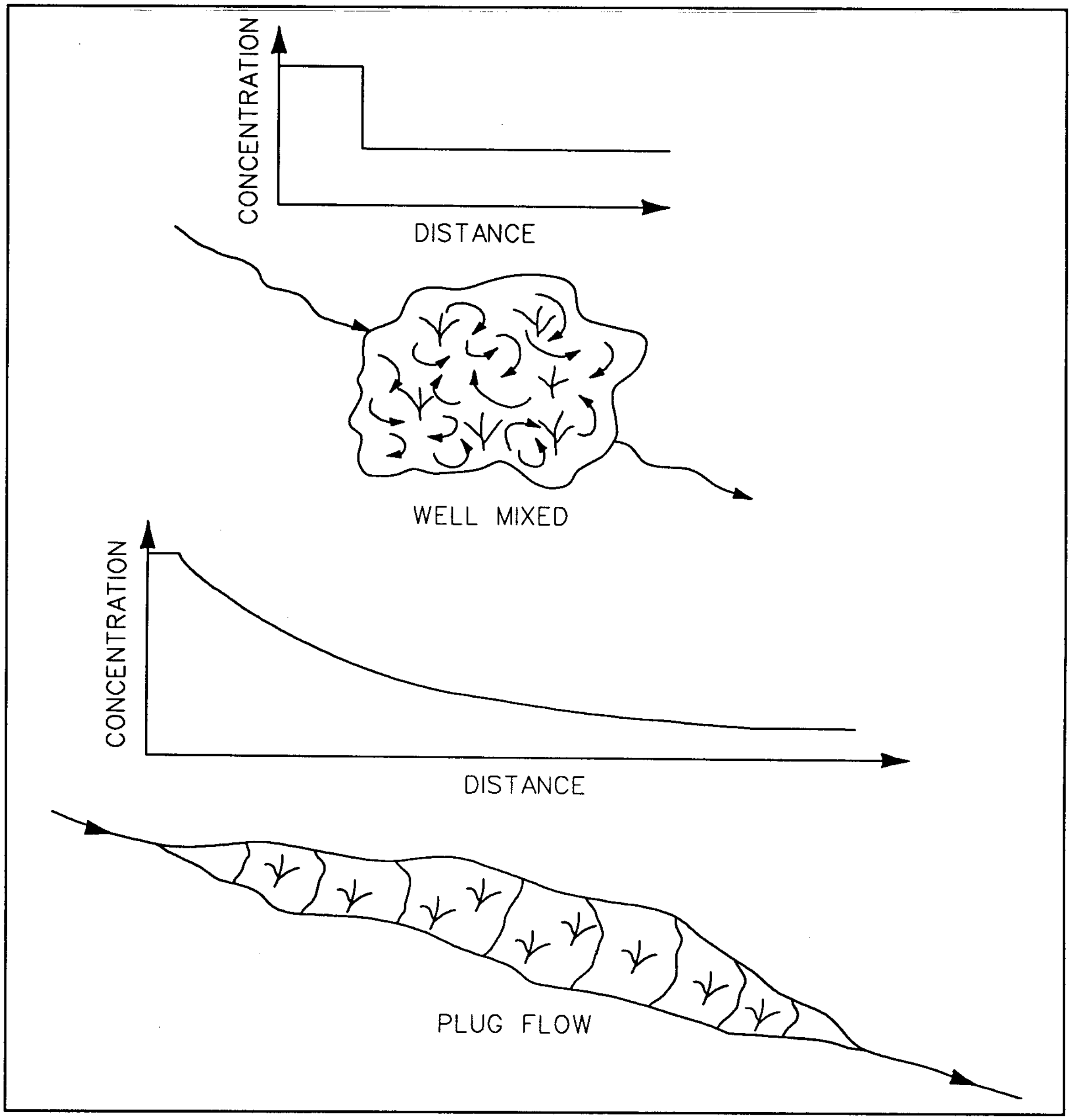

Figure 2. Two wetland mixing assumptions used for model, well mixed and plug flow

where τ is the hydraulic residence time, V/Q. Rearranging Equation 3 and substituting Equation 1 results in

$$RE = \left(\frac{K\tau}{1 + K\tau} \right) \times 100 \tag{4}$$

The relationship for RE with the second spatial assumption (i.e., existence of longitudinal gradients or plug flow) and steady-state conditions is derived from the one-dimensional mass transport equation (neglecting dispersion) as shown in WRP Technical Note WQ-EV-2.1 and is stated as

$$RE = (1 - e^{-K\tau}) \times 100 \qquad (5)$$

RE can now be estimated from either Equation 4 (fully mixed) or Equation 5 (plug flow) given K and τ.

The choice of Equation 4 or 5 depends on wetland mixing characteristics. A bowl-shaped wetland with little sheltering from the wind would be expected to exhibit relatively uniform concentrations; thus, Equation 4 should be used. Well-mixed conditions also tend to be associated with wetlands having small hydraulic residence times (V/Q) and small length-to-width ratios (e.g., $L/W \approx 1.0$). A long, narrow wetland would tend to exhibit longitudinal gradients, requiring the use of Equation 5. The plug flow assumption is reasonable for large L/W ratios (e.g., $L/W > 10.0$) and large detention times. In most cases, Equation 5 should be used.

Values for K depend upon the pollutant of concern and wetland characteristics as discussed later. The determination of K values is critical to the application of this model, and the values have a profound impact on the results. The major emphasis of this report is to provide the details for estimating K values. Values used for τ also have a very significant impact on results from Equation 4 or 5. Methods for estimating τ are discussed in the next section.

Hydraulic Parameters

Hydraulic residence time (HRT) is defined as the theoretical maximum detention time, V/Q, where V and Q are mean annual values for wetland volume and flow, respectively. However, the true detention time (τ) of water parcels can be less than V/Q because of dominant flow paths that result in dead zones and short-circuiting. Additionally, the location where the pollutant is introduced in the wetland (e.g., a point source load) affects the detention time. The detention time, τ (days), as affected by L/W, can be estimated from (Thackston, Shields, and Schroeder 1987)

$$\tau = 0.84 \frac{V}{Q} \left(1 - e^{-0.59\frac{L}{W}} \right) \qquad (6)$$

where L/W is the ratio of wetland length to width. As L/W increases, τ approaches 0.84 V/Q. For large L/W, τ should eventually reach HRT (i.e., V/Q). If a wetland is considered to be well mixed, then Equation 4 should be used, and τ should be approximated as V/Q. For plug flow conditions, Equation 5 is recommended, and τ should be either estimated from Equation 6 or set equal to V/Q for large L/W (i.e., $L/W > 10$).

It is possible to measure τ through dye studies. However, detention time is affected by flow, and flow can be variable. Thus, for a wetland affected by natural hydrology, the flow available during a dye study may not be representative of the flow conditions of interest, such as long-term average flows. Dye studies may be suitable for wetlands fed by controlled discharges.

Some of the formulations for estimating removal rates (K values) depend on hydraulic parameters, such as flow velocity, hydraulic depth, and the water surface area. The wetland hydraulic depth, H (m), is defined as V/A, where A (m^2) is the water surface area, and V has units of m^3. Thus, with an estimate of two of the three variables (V, A, and H), the third variable can be computed. The mean velocity of the flow, U, is either specified by the user or estimated from L/τ or Q/WH.

A numerical hydrodynamic and water quality model study of the Cache River was conducted by Dortch, Gerald, and Bunch (in preparation). The numerical model was used to quantify detention time and other hydrologic variables required by the analytical model to compute removal efficiency of wetland influent material.

The numerical model variable, *age*, was used to calculate detention time of water within each computational cell throughout the 1987-1990 simulation. Age was computed by adding a source term of unity to the advection-diffusion equation. Thus, the dependent variable age is transported and incremented with each model time step. Age was set to zero at the inflow boundary. The age exiting the system represents the detention time of the entire wetland. The computed average detention time for the 1987-1990 study period was 5.02 days. This compares closely with the average hydraulic retention time of 5.15 days, which was calculated from HRT = AH/Q. Simulation average values of $A = 19.9 \times 10^6\ m^2$, $H = 0.95$ m, and $Q = 42.45\ m^3/sec$ were obtained from the numerical model for the period 1987-1990, yielding $\tau = 5.15$ days.

Water Quality Constituents

The model contains algorithms for the following water quality constituents:

a. Total suspended solids (TSS), or total inorganic suspended solids (ISS).

b. Total coliform bacteria (TCB).

c. Biochemical oxygen demand (BOD).

d. Total nitrogen (TN).

e. Total phosphorus (TP).

f. Contaminants (e.g., organic chemicals and trace metals).

The RE computed from Equation 4 or 5 for each constituent depends on the removal rate, K, for the constituent. The removal rates depend on a number of processes, such as microbial metabolism, adsorption, volatilization, denitrification, settling, etc. Additionally, these processes are dependent on ambient conditions, such as water temperature, pH, etc., so obtaining a representative K value can be problematic. The approach here is to focus on the dominant long-term removal mechanisms, making use of literature values or mathematical formulations for those mechanisms when possible. Methods for estimating K values are discussed in the next chapter for each water quality constituent. Examples of literature estimates and comparisons to Cache River results are also provided.

Cache River Wetland Comparisons

Observations from the Cache River wetland, the primary field study site during the WRP, are used to demonstrate the utility of the predictive techniques for suspended solids, total nitrogen, and total phosphorus. Data measured from the Cache River during 1987-1992 were provided by B. A. Kleiss.[1] Observations collected at the upstream and downstream boundaries of the Cache (i.e., Patterson and Cotton Plant gauges, respectively) were used to compute RE values for ISS, TN, and TP. Daily discharge, ISS, and TP measurements taken between April 1987 and September 1990 and TN measured at 2-week intervals between June 1987 and August 1990 were used for the RE analyses. Mass fluxes (i.e., QC) entering at the Patterson gauge and exiting at the Cotton Plant gauge were summed over the study period to compute observed RE values using Equation 1.

Unfortunately, the Patterson gauge did not represent all flows and constituent loads entering the Cache River wetland. Daily flows at Patterson and Cotton Plant summed over the study period showed that 23 percent more water exited the system than entered during 1987-1990. Plots of cumulative flow at Patterson and Cotton Plant showed that most of the extra flow entered during and immediately following high flow periods. It is likely that additional storm flow entered below the Patterson gauge due to runoff from the local watershed, which is about 10 percent of the Cache River watershed above the Patterson gauge. Temporary gauges for Miller Branch and Moore Creek, which enter the Cache River between Patterson and Cotton Plant, indicated that as much as 7 percent of the Patterson flow enters through these two tributaries during large storms. There were several large storms during the period 1987-1990, thus, potentially contributing the 23 percent additional water. It is not clear how much of the local runoff entered the Cache River wetland as free surface streamflow or subsurface seepage.

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[1] Personal Communication, 1994, B. A. Kleiss, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

For the analyses presented here, it was assumed that the ungauged local flows entered as a free surface streamflow and carried constituent concentrations similar to those observed at the Patterson gauge. Therefore, the total mass load entering the system was corrected for ungauged loadings by multiplying the Patterson mass input by 1.23.

3 Removal Rates

Total Suspended Solids

Total suspended solids include both inorganic and organic solids. The approach taken here is generally applicable to both types. However, total solids is the variable of interest since water quality is often judged by the total suspended solids concentration without distinction to the type. Additionally, a total solids balance is necessary to perform analyses for other water quality constituents, such as phosphorus and contaminants. However, the approach taken here is also valid to ISS.

The steady-state assumption implies that wetland conditions are in equilibrium, when actually, wetland sedimentation is rarely in equilibrium. For example, a wetland must accrete to continue to effectively trap any material other than carbon, nitrogen, and sulfur (which can be removed through microbial action). Accretion can not occur indefinitely without an equal amount of subsidence. The ultimate behavior of a riverine wetland is to trap sediments until the wetland grows out of the depression, and the river abandons the site (Gosselink and Gosselink 1985). The assumption here is that accretion can continue indefinitely. Thus, this analysis does not attempt to determine when the wetland will become filled with sediment.

For a steady-state analysis, inflowing TSS are removed by net settling, which depends on particle settling, sediment resuspension and burial, or sedimentation (Thomann and Mueller 1987). The TSS removal rate, K_S, is the net settling rate, V_n, divided by the mean water depth of the wetland. The task is to estimate V_n. From a coupled steady-state solids balance in the water column and sediment bed or from a sediment mass balance around the surficial and active sediment segments, V_n can be estimated from (Thomann and Mueller 1987)

$$V_n = \frac{V_s V_b}{V_r + V_b} = \frac{\rho_b V_b}{S} = \frac{\rho_a V_a}{S} \qquad (7)$$

where

V_s = settling velocity, m/day

V_b = active sediment layer burial velocity, m/day

V_r = active sediment layer resuspension velocity, m/day

ρ_b = active sediment layer bulk density, $\rho_b = \rho_s (1-\phi_b)$, g/L

S = suspended solids concentration, g/L

ρ_a = surficial sediment bulk density, $\rho_a = \rho_s (1-\phi_a)$, g/L

V_a = surficial sediment accretion rate, m/day

ρ_s = dry sediment density, g/L

ϕ_b = active sediment layer porosity or water content

ϕ_a = surficial sediment porosity or water content, $\phi_a \approx 0.9$

The variables in Equation 7 are shown schematically in Figure 3. The active sediment layer is the top 5 to 15 cm of sediment where resuspension takes place, and pore water exchanges more readily than for deeper sediments that are more compacted. The surficial sediment layer is the upper few centimeters of the bed where recently deposited sediment has not consolidated.

Properties (such as porosity) are assumed to be constant within the active layer, but, in reality, properties are not constant over depth. V_b decreases and ρ_b increases with depth into the sediment (Chapra and Reckhow 1983) because of decreasing porosity resulting from compaction. However, for this screening-level model, sediment density, porosity, and burial velocity are assumed to be constant for the active layer; thus, representative average values should be used. Sediment dating methods, such as the cesium atmospheric fallout method (Kleiss 1993), can be used to measure V_b. With measurements for the bulk density of the active layer (ρ_b) and the average suspended solids concentration, V_n can be calculated (see Equation 7).

Net deposition rates (i.e., sediment accretion rates, V_a) can be rather easily measured at the sediment-water interface to estimate V_n (see Equation 7). The feldspar clay marker horizon method (Kleiss 1993) is a relatively simple, inexpensive, and accurate method of measuring recent (e.g., past several years) surficial sediment accretion. Sediment accretion rates (V_a) are typically 0.1 to 1.0 cm/year; values of 0.18 and 0.66 cm/year were cited by Pardue et al. (1993) for a bottomland hardwood site and a freshwater marsh, respectively. Sediment accretion rates measured in the Cache River wetland averaged 0.82 cm/year.

Sediment bulk density (i.e., sediment solids concentration), which can be measured, can range by more than an order of magnitude from less than 100

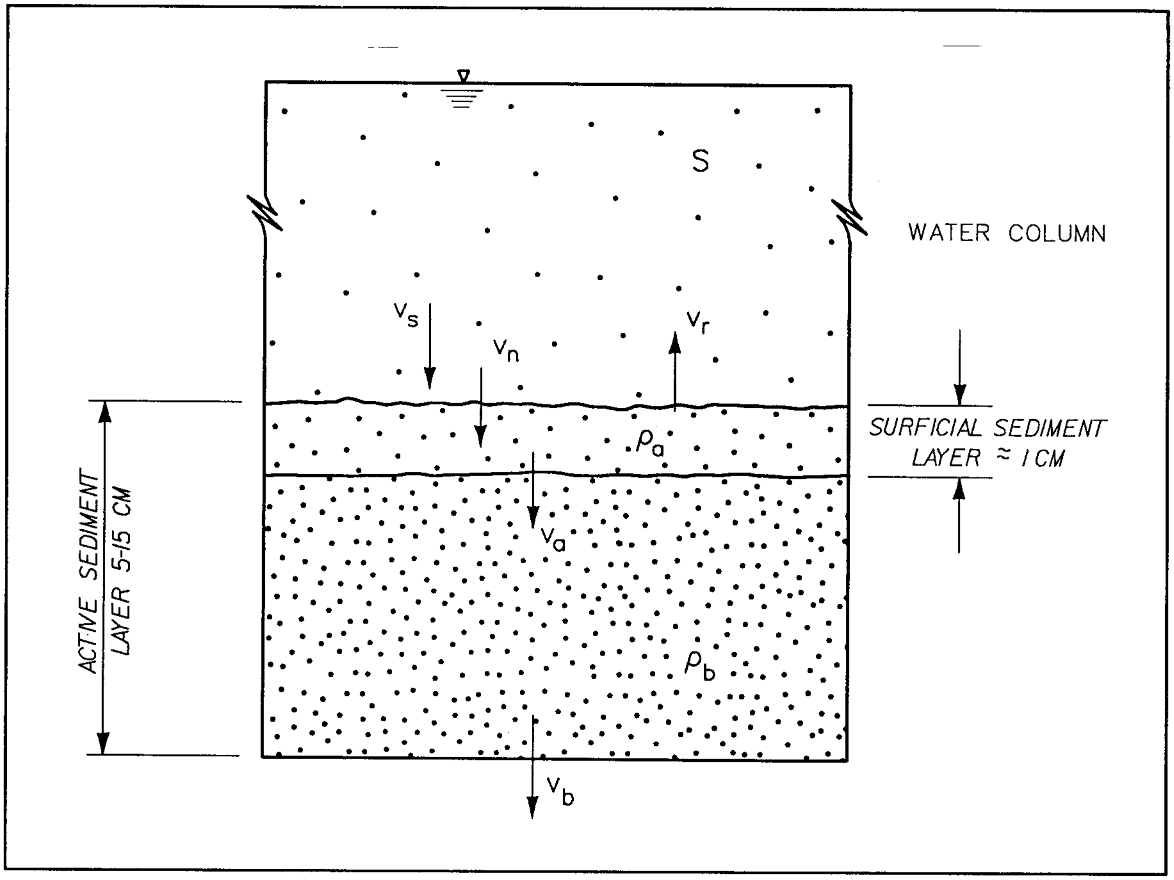

Figure 3. Schematic of model representation of water column and bed interactions for sediment

for peat to more than 1,600 g/L (or kg/m^3) for sands. Bulk density depends on dry sediment density which is inversely correlated to percent organic carbon content. However, for waterborne sediments, ρ_s typically has a value of about 2,650 g/L. Porosity of the surficial sediment is usually high (e.g., $\phi_a \approx 0.90$), thus, ρ_a is usually quite small (e.g., 265 g/L).

Although suspended solids can vary substantially, concentrations are generally less than 500 mg/L and are typically less than 100 mg/L. Measured TSS entering and leaving the Cache River averaged about 93 mg/L. With estimates of S, V_a, and ρ_a, V_n can be calculated from Equation 7.

If resuspension is negligible compared with burial, then V_n is approximately V_s, which can depend on water density and viscosity and particle density, size, shape, and roughness. V_s varies widely with particle size. However, for water quality analysis, the removal of small particles (i.e., silts and clays) is the primary interest. Ignoring flocculation, the settling velocity of these small particles can be approximated by Stokes law (Simons and Senturk 1977), which is stated as

$$V_s = \frac{g\,D^2\,(S_g - 1)}{18\,\nu} \qquad (8)$$

where

V_s = settling velocity, m/sec

g = gravitational acceleration, 9.82 m/sec^2

D = particle diameter, m

S_g = specific gravity of the particles

ν = kinematic viscosity of water at temperature T, m^2/sec

Waterborne sediments are mainly quartz and felsparthic minerals with a specific gravity of approximately 2.65. However, this value must be assumed with caution since specific gravity can range as low as 1.35 for pumice and as high as 7.6 for galena (Simons and Senturk 1977). The amount of organic matter can also decrease the specific gravity. Kinematic viscosity can be computed from

$$\nu = \frac{1.79 \times 10^{-6}}{1.0 + 0.03368\,T + 0.000221\,T^2} \qquad (9)$$

where T is in °C. The settling velocity can range from about 270 m/day for coarse silt (62 μm) to about 0.004 m/day for very fine clay (0.24 μm) and is about 0.1 m/day for medium clay (1.5 μm).

Net settling rates were computed using observed RE values for TSS, depth, and detention time data reported by the Water Pollution Control Federation (WPCF) (1990) and the U.S. Environmental Protection Agency (USEPA) (1988) for 27 data sets (including various types of constructed and natural wetlands). The hydraulic parameters observed for these wetlands are summarized in Table 1. Observed RE values and computed net settling rates (V_n) are listed in Table 2. Computed net removal rates were calculated from Equation 5 using observed RE and detention time data. Net settling rate is the removal rate times the depth. This analysis yielded an average V_n of 0.09 m/day with a standard deviation of 0.10; the range of these data was 0.008 to 0.47 m/day.

The above approach for estimating suspended solids removal is demonstrated with data from the Cache River wetland. The steps for the suspended solids example calculation are outlined below.

Table 1
Hydraulic Parameters for Wetland Studies Reported in Literature

Site	Type	HRT, days	Area, ha	Q, m^3/day	H, cm	L/W
Emittsburg	CW VSB	2.9	0.069	110	46	8.37
Hawkesbury	CW VSB	18.9	0.04	10.56	50	25
Santee BR	CW VSB	16.3	0.006	3.04	76	5.3
Santee CT	CW VSB	16.3	0.006	3.04	76	5.3
Santee RE	CW VSB	16.3	0.006	3.04	76	5.3
Arcata High	CW FWS	1.9	0.036	87.2	47	10
Arcata Low	CW FWS	7.8	0.036	21.8	47	10
Arcata Med	CW FWS	3.9	0.036	4.36	47	10
Lk Coral 83-84	CW FWS	153.6	21	1,477	108	
Listowel 3	CW FWS	23.3	0.132	17	30	83.5
Listowel 4	CW FWS	23.3	0.132	17	30	83.5
Boggy Gut 85	NW MAR	53.7	20	1,136	30.5	3.75
Boggy Gut 85-86	NW MAR	26.2	20	2,328	30.5	3.75
Boggy Gut 86	NW MAR	17.5	20	3,486	30.5	3.75
Boggy Gut 87	NW MAR	22	20	2,778	30.5	3.75
Boney Marsh NF	NW MAR	197.3	93.1	2,171	46	
Brillon	NW MAR	780	156	1,000	50	
Houghton 76	NW MAR	6.2	1	321	20	0.25
Houghton 77	NW MAR	7.6	1	264	20	
Houghton 78	NW MAR	4.2	10	4,800	20	
Houghton 79	NW MAR	5.7	18	6,281	20	
Houghton 80	NW MAR	14.1	25	3,539	20	
Houghton 81	NW MAR	12.8	32	5,000	20	
Houghton 82	NW MAR	18.9	39	4,122	20	
Houghton 83	NW MAR	17.5	45	5,142	20	
Houghton 84	NW MAR	18.9	51	5,383	20	
Houghton 85	NW MAR	23.8	57	4,797	20	
Houghton 86	NW MAR	30.2	61	4,043	20	

(Continued)

Note: HRT = Hydraulic residence time ≈ detention time, τ; CW VSB = constructed wetland, vegetated submerged bed; CW FWS = constructed wetland, free water surface; NW MAR = natural wetland, marsh; NW FOR = natural wetland, forested. Data taken from WPCF (1990) and USEPA (1988).

Table 1 (Concluded)

Site	Type	HRT, days	Area, ha	Q, m^3/day	H, cm	L/W
Houghton 87	NW MAR	44.5	66	2,966	20	
Bellaire 76	NW FOR	17.4	18.2	2,087	12	2
Bellaire 77	NW FOR	12	18.2	3,032	12	2
Bellaire 78	NW FOR	14.5	18.2	2,511	12	2
Bellaire 79	NW FOR	17.4	18.2	2,087	12	2
Bellaire 80	NW FOR	17.6	18.2	2,065	12	2
Bellaire 81	NW FOR	16.4	18.2	2,226	12	2
Reedy Cr 78	NW FOR	13	35	6,135	18	5
Reedy Cr 79	NW FOR	5	35	6,726	18	5
Reedy Cr 80	NW FOR	5	35	9,296	18	5
Reedy Cr 81	NW FOR	12	35	9,924	18	5
Reedy Cr 82	NW FOR	7	35	8,895	18	5
Reedy Cr 83	NW FOR	3	35	14,758	18	5
Reedy Cr 84	NW FOR	4	35	14,235	18	5
Reedy Cr 85	NW FOR	4	35	14,133	18	5
Biloxi, MS	CW FWS	21			240	
Collins, MS	CW FWS	7			40	
Sleep Eye, MN	CW FWS	70			150	
NSTL, MS	CW FWS	8			40	

ρ_a : Measurements indicate that about 82 percent of the solids are inorganic. Using ρ_s = 2,650 g/L for inorganic solids, $\rho_s \approx$ 1,040 g/L for organic solids, a weighted-average sediment dry density of 2,360 g/L is computed. With an assumed surficial sediment porosity of 0.9 and a dry sediment density of 2,360 g/L, the bulk density of the surficial sediment (ρ_a) is estimated to be 236 g/L.

V_n : Sediment accretion rates (V_a) measured in the Cache River wetland averaged 0.82 cm/year. Using ρ_a = 236 g/L, a sediment accretion rate of 0.82 cm/year, and an average measured suspended solids (S) value of 93 mg/L, a net settling value (V_n) of 0.057 m/day is computed from Equation 7.

A value of V_n = 0.057 m/day compares favorably with medium-size clay settling rates of 0.10 m/day. Approximately 95 percent of the particles are smaller than 2.0 μm (i.e., medium-size clay) for the Cache River. The

Table 2
Observed RE Values and Computed *K* Rates for Wetland Studies Reported in Literature

Site	BOD RE	K_r, day^{-1}	TSS RE	V_n m/day	TN RE	K_{TN} day^{-1}	TP RE	HK_{TP} m/day
Emittsburg	71	0.43	73	0.208				
Hawkesbury	86	0.10	92	0.067			32	0.0102
Santee BR	99	0.28	98	0.182	93	0.16		
Santee CT	74	0.08	90	0.107				
Santee RE	81	0.10	86	0.092				
Arcata High	51	0.38	85	0.469				
Arcata Low	59	0.11	84	0.110				
Arcata Med	49	0.17	85	0.229				
Lk Coral 83-84	81	0.01	80	0.011	93	0.02	31	0.0026
Listowel 3	59	0.04	61	0.012	43	0.02	46	0.0079
Listowel 4	82	0.07	93	0.034	48	0.03	79	0.0201
Boggy Gut 85	87	0.04	76	0.008	97	0.07	84	0.0104
Boggy Gut 85-86	73	0.05	89	0.026	89	0.08	65	0.0122
Boggy Gut 86	78	0.09	84	0.032	78	0.09	58	0.0151
Boggy Gut 87	80	0.07	88	0.029	85	0.09	51	0.0099
Boney Marsh NF					81	0.01	94	0.0066
Brillon							32	0.0002
Houghton 76					98	0.63	95	0.0966
Houghton 77					82	0.23	67	0.0292
Houghton 78							97	0.1670
Houghton 79							98	0.1373
Houghton 80							97	0.0497
Houghton 81							96	0.0503
Houghton 82							98	0.0414
Houghton 83							97	0.0401
Houghton 84							97	0.0371
Houghton 85							97	0.0295
Houghton 86							99	0.0305

(Continued)

Note: Data taken from WPCF (1990) and USEPA (1988) (the last four entries in the table).

Table 2 (Concluded)

Site	BOD RE	K_r, day^{-1}	TSS RE	V_n m/day	TN RE	K_{TN}, day^{-1}	TP RE	HK_{TP} m/day
Houghton 87							97	0.0158
Bellaire 76					75	0.08	91	0.0166
Bellaire 77					80	0.13	88	0.0212
Bellaire 78					80	0.11	72	0.0105
Bellaire 79					77	0.08	64	0.0070
Bellaire 80					75	0.08	65	0.0072
Bellaire 81					81	0.10	-27	
Reedy Cr 78	84	0.14	84	0.025	93	0.20	-5	
Reedy Cr 79	77	0.29	83	0.064	71	0.25	-103	
Reedy Cr 80	80	0.32	86	0.071	84	0.37	-79	
Reedy Cr 81	79	0.13	87	0.031	95	0.25	23	0.0039
Reedy Cr 82	81	0.24	85	0.049	87	0.29	-52	
Reedy Cr 83	83	0.59	76	0.086	77	0.49	-171	
Reedy Cr 84	31	0.09	53	0.034	76	0.36	-30	
Reedy Cr 85	28	0.08	28	0.015	77	0.37	-28	
Biloxi, MS	50	0.03	92	0.289				
Collins, MS	61	0.13	64	0.058				
Sleep Eye, MN	96	0.05	91	0.052				
NSTL, MS	92	0.32	76	0.071				
	Statistics							
	Average	0.165		0.091		0.183		0.0316
	Stand. Dev.	0.140		0.102		0.156		0.0391
	Maximum	0.591		0.469		0.631		0.1670
	Minimum	0.011		0.008		0.008		0.0002

calculated net settling rate also compares well with the average V_n for the 27 literature wetlands, i.e., $V_n = 0.09$ m/day.

Using the average depth of 0.95 m, the calculated net removal rate for TSS in the Cache River is 0.06 day^{-1} (from V_n/H). With an estimated average detention time of 5 days (Dortch, Gerald, and Bunch, in preparation) and $K_s = 0.06$, RE = 25.9 percent from Equation 5. The computed RE agrees fairly closely with the observed ISS RE of 29.5 percent.

Total Coliform Bacteria

TCB are a large group of bacteria that have been widely used as a measure of health hazard. A first-order decay rate is usually used to describe the net loss of TCB because of death, predation, and settling (Thomann and Mueller 1987). Typical values for the TCB decay rate, K_B, are about 0.8 day^{-1} for freshwater and about 1.4 day^{-1} for seawater (Thomann and Mueller 1987). Bavor et al. (1989) reported K_B values that range from 0.46 day^{-1} for open water to 1.31 day^{-1} for mixed wetland systems (i.e., plants, gravel, and water). A median rate of 0.96 day^{-1} is reported by Bowie et al. (1985) for 30 in situ studies.

The death rate is affected by water temperature, solar radiation in the water column, and salinity, but only the effect of temperature is considered in this simplistic analysis. Solar radiation can increase the death rate by more than tenfold, but the effect of solar radiation is offset by vegetative shading and light attenuation in the water column. The effect of temperature is taken into account as follows (Thomann and Mueller 1987)

$$K_B = (K_B)_{20}\,\theta^{T-20} \tag{10}$$

where

$(K_B)_{20}$ = decay rate at 20 °C

T = water temperature °C

θ = temperature correction factor, which has a recommended value of 1.07 for TCB (Thomann and Mueller 1987)

The form of Equation 10 is also used for temperature correction of other constituents, but the value θ varies for each constituent. An average annual value is suggested for water temperature considering the purpose of this model.

Biochemical Oxygen Demand

BOD is actually composed of carbonaceous and nitrogenous BOD, but for this analysis only total BOD is considered and is assumed to be mostly carbonaceous. BOD removal occurs through water column microbial degradation, settling of the particulate fraction of BOD from the water column to the sediments, and adsorption to benthic biota. These removal pathways are combined into an overall first-order removal rate, K_r (day^{-1}). Observed K_r values vary by nearly two orders of magnitude (i.e., from about 0.08 to 5.0) and depend on several factors including the nature of the BOD source (e.g., labile or refractory) and hydraulic conditions, e.g., depth.

Hydraulic residence time data (Table 1) and RE values for BOD (Table 2) from the WPCF (1990) and USEPA (1988), which were reported for 27 data sets (including various types of constructed and natural wetlands) were used to compute K_r values. This analysis yielded an average K_r of 0.17 day^{-1} with a standard deviation of 0.14.

Reed, Middlebrooks, and Crites (1988) recommend $K_r = 0.28$ day^{-1} for waste stabilization ponds and $K_r \approx 0.45$ for constructed wetlands with a standing, free-water surface. The latter value was obtained from a predictive equation for K_r using recommended parameter default values.

The USEPA (1983) (cited in Bowie et al. 1985), using data of Hydroscience (1971) and Wright and McDonnell (1979), showed that the removal rate decreases with increasing depth, but is relatively constant at small and large depths. The removal rates fell within a band that spanned about an order of magnitude. This relationship is mathematically stated as follows:

Shallow water: $0.8 \leq K_r \leq 5.0$ for $0.0 \leq H \leq 1.0$

Deep water: $0.08 \leq K_r \leq 0.5$ for $H \geq 5.0$

Between deep and shallow:

$$K_r = 2.3\ H^{-1.52} \tag{11}$$

for $1.0 < H < 5.0$

where H is in feet and K_r is in units of day^{-1}. For the shallow water and deepwater cases, the midrange values of K_r are about 2.3 and 0.2, respectively. Equation 11 represents midrange values, where removal rates vary by approximately one order of magnitude. For example, if H is 3.0 ft, K_r is 0.43 from Equation 11; but the observed K_r values range from about 0.14 to 1.4 for $H = 3.0$. The midrange values for shallow and deep water and Equation 11 are used for defaults in the model. The recommended value for the temperature correction factor for BOD (i.e., θ in Equation 10) is 1.047 (Thomann and Mueller 1987 and Bowie et al. 1985).

Total Nitrogen

Nitrogen is composed of various forms that can exist in water, such as particulate and dissolved organic N, ammonium, nitrite, and nitrate. These various forms can transform and serve as sources or end products for each other within the nitrogen cycle. For this reason, only TN is considered. Although the nitrogen components can be affected by various processes (e.g., settling, mineralization, hydrolysis, uptake and release by biota, nitrification, and denitrification), denitrification is the only major net, long-term removal process for TN (Howard-Williams 1985; WPCF 1990; Graetz et al. 1980; Gale, Reddy, and Graetz 1993). Some N is also lost by burial in the sediments, but this effect is small compared with denitrification. Denitrification in wetlands takes place primarily in the anaerobic bottom sediments where nitrate is reduced during organic matter decomposition to gaseous N_2, which is released to the atmosphere. Nitrate is supplied to the sediments by the deposition and mineralization of organic nitrogen, nitrification, and diffusion of nitrate from the water column.

A nitrate balance can not be used to compute the loss of TN because nitrate also may be gained through nitrification as water moves through a wetland. However, the loss of nitrate through denitrification can be used to estimate TN loss. The first-order loss model for TN is expressed mathematically as

$$\frac{d\,TN}{dt} = -K_{TN}\,TN = -K_{dn}\,NO_3 \tag{12}$$

where

K_{TN} = first-order removal rate for TN

K_{dn} = denitrification rate

NO_3 = concentration of NO_3-N

From Equation 12,

$$K_{TN} = \frac{NO_3}{TN}\,K_{dn} \tag{13}$$

With an estimate K_{dn} and the ratio of nitrate to TN, K_{TN} can be determined from Equation 13 and used in Equation 4 or 5 to compute RE for TN.

An example calculation for TN RE is provided for the Cache River. A two-dimensional, depth-averaged, numerical water quality model was applied to the Cache River for the period October 1987 through September 1991 (Dortch, Gerald, and Bunch, In preparation). The numerical model was calibrated for various forms of carbon, nitrogen, and phosphorus. Sediment denitrification is one of the modeled mechanisms affecting nitrogen. The numerical model calibration value for K_{dn} was 0.2 day^{-1}. The numerical model showed that the average detention time of the wetland for the 4-year study period was about 5 days. Using the calibrated K_{dn} value and the observed nitrate to TN ratio of about 0.2, $K_{TN} = 0.04$ day^{-1} from Equation 13. With this value of K_{TN} and $\tau = 5$ days, the predicted RE for TN in the Cache River (from Equation 5) is 18.1 percent, which compares fairly well with the observed RE for TN of 21.4 percent.

Graetz et al. (1980) found that K_{dn} varied from 0.04 to 0.192 day^{-1} for 15 Florida wetland soils. K_{TN} values were computed from Equation 5 using observed TN RE and detention time data (See Tables 1 and 2) reported by the WPCF (1990) for 25 data sets (including various types of constructed and natural wetlands). This analysis yielded a range of K_{TN} between 0.008 and 0.63 day^{-1} with an average K_{TN} of 0.18 day^{-1} and with a standard deviation of 0.16.

Unfortunately, there are no definitive formulae for estimating K values for nitrogen as there are for some of the other water quality constituents, such as TSS. Several publications (Kadlec 1987; Hammer and Kadlec 1983) indicate that the rate of N removal is affected primarily by the rate of nitrate mass transfer into the anaerobic bed. Although some limited analyses tend to support this theory, there are not yet any widely accepted formulae. Nitrate must diffuse through the laminar diffusive sublayer of the water column and through the aerobic sediment layer before reaching the denitrifying sediments. Predicting the thickness of the aerobic sediment layer complicates a mass transfer approach. For now, a range of $0.05 \leq K_{TN} \leq 0.30$ and a default value of $K_{TN} = 0.15\ \text{day}^{-1}$ are suggested. A temperature correction factor, θ, of 1.045 is recommended (Bowie et al. 1985).

Total Phosphorus

Analysis for phosphorus is much more complex than for the other constituents presented above. Phosphorus (P) can exist in water in dissolved, particulate, organic, and inorganic forms, which are affected by biotransformation, sorption, settling, sedimentation, mineralization, and hydrolysis. Like nitrogen, only TP is considered for this analysis. However, unlike TN, microbial activity does not result in a net loss of TP out of the system. Vegetation can take up considerable amounts of P. However, biomass compartments become saturated; following death of biomass, P is released, so vegetation serves as only a temporary sink for P unless the biomass is harvested. Long-term peat accumulation of P is also very limited. The long-term storage of P is dependent primarily on inorganic sediment adsorption and accretion (Richardson 1985). Therefore, the only natural, long-term, removal mechanism is sediment burial.

Whereas TN retention is practically constant with time, TP retention decreases with time for a relatively new wetland as the sediments become saturated with P (Nichols 1980; Richardson 1985; Hammer and Kadlec 1983). Constructed wastewater wetlands experience an aging phenomena where sorption of P in the upper sediment horizons reaches equilibrium, reducing the P uptake rate over time (Kadlec 1985). After the sediments reach a saturated equilibrium, the removal rate becomes relatively constant with time and is proportional to the sediment burial rate. This is why older wetlands tend to retain little P and even appear to export P at times. New wetlands with low soil P content can affectively remove P for a while through a net loss of solids (with sorbed P) from the water column.

The objective here is to estimate RE for both new and old (i.e., at saturated equilibrium) wetlands and to estimate the effective life of a new wetland (i.e., when the sediments become saturated with P). Methods for estimating RE are presented first, followed by a procedure for estimating the effective life of a new wetland.

Removal efficiency

RE for TP can be computed from Equation 4 or 5 given a net removal rate coefficient, K_{TP} (day^{-1}). A formulation for K_{TP} can be obtained from steady-state coupled TP mass balance equations for the water column and active layer of the sediment bed, considering settling and resuspension of particulate P, burial of TP, and diffusion of dissolved P between the water column and the bed. The result for K_{TP} derived from these equations is

$$K_{TP} = \frac{V_n}{H} \frac{(V_s f_{pw} + V_d f_{dw})}{\left(V_s + V_d f_{dp} \frac{\rho_b}{S} \right)} \tag{14}$$

where

f_{pw} = fraction of particulate to total P in the water column

f_{dw} = fraction of dissolved to total P in the water column

V_d = mass transfer velocity (m/day) across the sediment-water interface resulting from diffusion of dissolved P

f_{dp} = fraction of dissolved phosphorus in the sediment pore water to total P in the bed layer

Considering that TP is made up of inorganic and organic phosphorus, where organic phosphorus is assumed to be in particulate form only, the fractions are

$$\begin{aligned} f_{pw} &= f_o + f_i F_{pw} \\ f_{dw} &= f_i F_{dw} \\ f_{dp} &= f_{i_b} F_{dp} \end{aligned} \tag{15}$$

where

f_i and f_o = fractions of total inorganic and total organic P to total P, respectively, and double subscript b on f_i refers to sediment bed

F_{dw}, F_{pw}, and F_{dp} = fractions of dissolved inorganic P to total inorganic P in water column, particulate inorganic P to total inorganic P in water column, and dissolved pore water inorganic P to total sediment inorganic P, respectively

Assuming linear, equilibrium partitioning, these fractions are computed as

$$F_{dw} = \frac{1}{1 + K_{dw} S}$$

$$F_{pw} = \frac{K_{dw} S}{1 + K_{dw} S} \tag{16}$$

$$F_{dp} = \frac{1}{\phi + K_{ds}(1-\phi)\rho_s}$$

where

K_{dw} = distribution (i.e., partitioning) coefficient for phosphorus in water column, L/g

ϕ = sediment porosity (or water content)

K_{ds} = distribution (i.e., partitioning) coefficient for phosphorus in sediment bed, L/g

ρ_s = dry sediment density, g/L

The distribution coefficients are defined as the ratio of P concentration sorbed onto solids (i.e., mass P per mass solid) to dissolved concentration in water (i.e., mass P per water volume). The quantity $(1-\phi)\rho_s$ is the bulk density, ρ_b.

Using Equation 7, Equation 14 can also be stated as

$$K_{TP} = \frac{V_b \left(V_s f_{pw} + V_d f_{dw}\right)}{H \left(V_r + V_b + V_d f_{dp}\right)} \tag{17}$$

All other variables in Equations 14-17 were defined previously above. From Equation 17, it can be observed that the P removal rate is proportional to the burial velocity. Equations 14 and 17 can also be derived from a steady-state mass balance for the water column where the only removal mechanism is burial of sediment P (i.e., AV_bC_b, where C_b is total P concentration in the bed).

The problem in applying Equation 14 or 17 for an "old" wetland (i.e., in equilibrium) is that the assumption for linear partitioning in the sediment is weak. The concentration of dissolved P in the sediment pore water (thus, f_{dp}) is not small and is a nonlinear relationship involving C_b. The equilibrium concentration for C_b depends on the water column total P concentration, C, which depends on P loading and sediment pore water concentrations. A proper solution for the f values in Equation 14 or 17 requires simultaneous solution of five equations with five unknowns as follows.

A steady-state mass balance of total P in the sediment and water column (i.e., C_b and C) yields

$$C_b = C\,\frac{V_s f_{pw} + V_d f_{dw}}{V_r + V_b + V_d f_{dp}} \tag{18}$$

and

$$C = \frac{\frac{W_L}{A}\left(V_r + V_b + V_d f_{dp}\right)}{V_b\left(V_s f_{pw} + V_d f_{dw}\right) + \left(V_r + V_b + V_d f_{dp}\right)\frac{Q}{A}} \tag{19}$$

By definition, the fractions in Equations 18 and 19 are stated as

$$\begin{aligned} f_{pw} &= f_o + \frac{C_p}{C} \\ f_{dw} &= \frac{C_d}{C} \\ f_{dp} &= \frac{C_{dp}}{C_b} \end{aligned} \tag{20}$$

where

C_d and C_p = dissolved and particulate inorganic P in the water column

C_{dp} = dissolved inorganic P in the sediment pore water

Relationships for C_d, C_p, and C_{dp} can be obtained through the nonlinear Langmuir model for partitioning, which states in general

$$\nu = \frac{m \nu_m c}{1 + mc} \tag{21}$$

where

ν = sorbed constituent mass per mass of solids, mg/g

ν_m = sorption maximum, mg/g

c = equilibrium dissolved constituent concentration, mg/L

m = constant related to the bonding energy, L/mg

For low dissolved concentration, the Langmuir model reduces to the linear model where the product m ν_m = K_d. Recognizing that

$$\begin{gathered} f_i C = C_d + C_p = C_d + \nu S \\ f_{i_b} C_b = \phi C_{dp} + \nu_b \rho_b \end{gathered} \tag{22}$$

where ν_b is the sorbed concentration in the bed, Equations 21 and 22 can be manipulated to yield

$$\begin{gathered} C_d = \frac{-\Gamma_1 + \sqrt{\Gamma_1^2 + 4 m f_i C}}{2m} \\ C_p = \frac{-\Gamma_2 - \sqrt{\Gamma_2^2 - 4 \nu_m m^2 S f_i C}}{2m} \\ C_{dp} = \frac{-\Gamma_3 + \sqrt{\Gamma_3^2 + 4 \phi m f_{i_b} C_b}}{2m\phi} \end{gathered} \tag{23}$$

where

$$\begin{gathered} \Gamma_1 = 1 + m \nu_m S - m f_i C \\ \Gamma_2 = -(1 + m \nu_m S + m f_i C) \\ \Gamma_3 = \phi + m \nu_m \rho_b - m f_{i_b} C_b \end{gathered} \tag{24}$$

Equations 18 and 19 and Equation set 23 constitute five equations with five unknowns (C, C_b, C_d, C_p, and C_{dp}) that must be solved simultaneously. C and C_b are first estimated, then the dissolved and particulate concentrations are evaluated from Equation set 23. With values for the dissolved and particulate concentrations, the fractions of Equation set 20 can be estimated and substituted into Equations 18 and 19 to update C and C_b. This iteration continues until the change in the values for C and C_b are within an accepted tolerance. After the solution has converged, the final fraction values of Equation set 20 can be used to obtain K_{TP} from either Equation 14 or 17. This procedure is more accurate than assuming linear partitioning (i.e., Equations 15 and 16).

Application of Equations 18 and 19 (and Equations 14 or 17) also requires estimation of the velocity terms. As explained under the section on total suspended solids, V_n can be estimated from data on sediment accretion rates. With an estimate of V_n, V_b can be calculated from Equation 7 with a value for ρ_b representative of the active sediment layer, where the active layer is the top 5 to 15 cm of sediment. Settling velocity for small particles, V_s, can be estimated from Equation 8 given mean particle size. By rearranging Equation 7, V_r can be estimated with estimates of V_s and V_b as follows

$$V_r = \frac{V_s S}{\rho_b} - V_b \tag{25}$$

The relationship of Schink and Guinasso (1977) is used to estimate the sediment-water mass transfer velocity, V_d,

$$V_d = \frac{u_* \left(\frac{D_m}{\nu}\right)^{2/3}}{24} \tag{26}$$

where

D_m = molecular diffusivity of dissolved chemical (approximately 1.0×10^{-9} m^2/sec for phosphate)

u_* = flow shear velocity along bed, which is approximately 10 percent of the mean velocity of flow, U

The parameters of the Langmuir model (m and ν_m) must also be estimated. The partitioning of phosphorus between dissolved and particulate phases is quite complex and dependent on a number of factors, such as the amount and type of clay, amount of Fe and Al oxides and Ca compounds, and pH (Richardson 1985). Gale, Reddy, and Graetz (1994) reported values for the Langmuir parameters for several constructed and natural wetlands in central Florida using the top 15 cm of sediment and tested under aerobic and anaerobic conditions. For their studies, m ranged from 0.014 to 0.641 L/mg and ν_m ranged from 0.032 to 1.82 mg/g. Ku, DiGiano, and Feng (1978) reported phosphate Langmuir parameters for sediments from two lakes where m ranged from 0.10 to 33.4 L/mg, and ν_m ranged from 1.13 to 2.22 mg/g. Furumai, Kondo, and Ohgaki (1989) obtained phosphorus Langmuir parameters with varying pH for sediments from a lake in Japan; m varied from 0.46 to 13.0 L/mg, and ν_m varied from 0.29 to 0.96 mg/g. Istvanovics, Herodek, and Szilagyi (1989) reported Langmuir parameters from lake sediments where m ranged from 2.6 to 88.0 L/mg and ν_m ranged from 0.079 to 1.07 mg/g. These literature values are summarized in Table 3. In conclusion, the Langmuir parameters varied considerably for these four references ($0.014 < m < 88$ L/mg, $0.032 < \nu_m < 2.22$ mg/g), which suggests that site specific measurements are advisable. Values of ν_m have been found to be as high as 5.0 mg/g (Richardson, Walbridge, and Burns 1988).

Table 3
Literature Values for Langmuir Parameters

Reference	ν_m, mg/g	m, L/mg
Gale, Reddy, and Graetz (1994)	0.032 - 1.82	0.014 - 0.641
Ku, DiGiano, and Feng (1978)	1.13 - 2.22	0.10 - 33.4
Furumai, Kondo, and Ohgaki (1989)	0.29 - 0.96	0.46 - 13.0
Istvanovics, Herodek, and Szilagyi (1989)	0.079 - 1.07	2.6 - 88.0

Phosphorus partitioning experiments were conducted with soil samples taken from the Cache River wetland.[1] Analysis of this data yielded Langmuir parameters of $\nu_m \approx 1.3$ mg/g and $m \approx 0.05$ L/mg. The problem with this analysis is it did not take into account the amount of P in the soil initially. Assuming an initial sorbed P concentration in the soil increases both parameters, but m is increased in a much greater proportion than ν_m.

RE for TP in the Cache River wetland was estimated using the methods described above. The steps of this example calculation are outlined below.

V_n: See example for computing V_n under Total Suspended Solids section; $V_n = 0.057$ m/day.

V_b: Assuming the active layer is 10 cm where the measured ρ_b averaged 1,130 g/L and the measured ϕ averaged 0.35, the burial rate is estimated to be 4.70×10^{-6} m/day from Equation 7 using $V_n = 0.057$.

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[1] Personal Communication, 1994, B. A. Kleiss, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

V_s: Approximately 95 percent of the particles common to the Cache River can be considered clay with grain sizes less than 2.0 μm; thus, a settling velocity of 0.1 m/day is appropriate (from Equation 8).

V_r: All the information for computing V_r from Equation 25 is now available, and V_r is estimated to be 3.53×10^{-6} m/day.

U_*: With an estimated travel time of 5 days over a distance of about 33 km, the shear stress of the flow is estimated to be 0.76 cm/s (i.e., 10 percent of the mean flow velocity).

V_d: From Equation 26, $V_d = 0.27$ m/day.

f_i: From P components measured in the water column, about 73 percent of TP is inorganic.

ν_m and m: From the P partitioning experiments conducted with Cache River wetland soils, m = 0.05 L/mg and $\nu_m = 1.3$ mg/g.

A: The surface area of the Cache River wetland averages about 19.9×10^6 m^2, for an average discharge of about 42.5 m^3. This value was obtained from a numerical model (Dortch, Gerald, and Bunch, In preparation) by summing the surface area for all computational cells for each time step, then computing the average total area for the entire 4-year simulation.

W_L: The observed TP loading to the Cache averaged about 1,043 kg/day. This value was obtained by averaging the product of daily observations of flow and TP concentration over the study period (April 1987 - September 1990). The average loading concentration observed was 0.24 mg/L.

With the above information, Equations 18 and 19 and Equation sets 20, 23, and 24 were solved, yielding a removal velocity (i.e., $K_{TP}H$) of 0.0004 m/day. For an average depth of 0.95 m, K_{TP} is 0.00042 day^{-1}, which from Equation 5 (with $\tau = 5$ days) results in RE = 0.21 percent. This value is an order of magnitude less than the observed RE = 3.0 percent, which is based on measured daily TP loads entering and exiting the system between April 1987 and September 1990. As mentioned above, it is not known how much P was in the soil prior to the partitioning experiments and how much this would have changed the Langmuir parameters. When values of ν_m = 1.0 mg/g and m = 1.0 L/mg are used (which are values that fall well within the range of values reported in the literature), the model yields $K_{TP}H$ = 0.0047 and RE = 2.5 percent, which is close to the observed value. For this model solution, C_b = 235 mg/L, which is considerably less than the theoretical maximum sediment P capacity of 1,130 mg/L (i.e., $\nu_m \rho_b = 1.0$ mg/g • 1,130 g/L).

Measured properties[1] for the top 5.0 cm of Cache River sediments averaged ρ_b = 630 g/L and ϕ = 0.58. All variables were recalculated using these values for the active bed layer (and with ν_m = 1.0 and m = 1.0) resulting in RE = 1.4 percent. Apparently, the model is not nearly as sensitive to the specification of the active sediment layer and its properties as it is to the Langmuir model parameters.

RE simplification for new wetlands

For sediments with low P concentrations (e.g., a new or constructed wetland), the water column and bed sediment partitioning coefficients for P can be assumed to be equal. With this assumption, it can be shown that the solid phase constituent concentration in the sediment is equal to the solid phase constituent concentration in the water column (Thomann and Mueller 1987); thus, the dissolved phase inorganic P concentrations in the water and sediment pore water are equal, and diffusion across the sediment-water interface can be neglected. For this condition, Equation 14 reduces to

$$K_{TP} = \frac{V_n}{H} f_{pw} \tag{27}$$

which states that the removal rate is proportional to the net settling rate of particulate P. V_n can be estimated from Equation 7 given estimates of the sediment accretion rate as explained above, and f_{pw} can be obtained from the linear partitioning model. It should be realized that a new wetland can remove P fairly effectively initially (i.e., according to Equation 27), but the removal rate will diminish over time as the sediment P increases.

An example application of Equation 27 follows.

V_n: Assuming estimates of V_a = 0.80 cm/year, ρ_a = 265 g/L, and S = 100 mg/L in Equation 7 results in V_n = 0.058 m/day.

f_{pw}: The fraction of TP that is inorganic (i.e., f_i) is site specific; a value of 0.73 was obtained from the Cache River data from 1992. Although P partitioning is nonlinear (e.g., Langmuir or Fruendlich models), a linear relationship (i.e., K_d) can be used for dilute concentrations. Literature values for K_d vary widely from as low as 0.001 L/g (Gale, Reddy, and Graetz 1994) to greater than 20 L/g (Ku, DiGiano, and Feng 1978). Typically, values fall in the range of 0.1 to 10 L/g. Assuming K_d = 1.0 L/g and f_i = 0.5 and using S = 100 mg/L, a value of 0.55 is computed for f_{pw} from Equations 15 and 16.

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[1] Personal Communication, 1994, B. A. Kleiss, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

With this value of f_{pw} and $V_n = 0.058$ m/day, Equation 27 yields a removal velocity for TP (i.e., $K_{TP}H$) of 0.032 m/day. This value is of the same order of magnitude of measured TP removal velocities. For example, an average value of 0.032 m/day was computed for $K_{TP}H$ (see Table 2) using Equation 5 and observed TP RE, detention time, and depth data shown in Tables 1 and 2, which were reported by the WPCF (1990) for 28 data sets (including various types of constructed and natural wetlands). It was not possible to determine the state of these wetlands for P removal (i.e., new versus old or saturated). Values for TP removal velocity of approximately 0.12 m/day and 0.10 m/day were extracted from work in a Florida wetland reported by Ammon, Huber, and Heaney (1981) and wetland buffer areas for agricultural drainage reported by Chescheir et al. (1988), respectively.

Time to reach equilibrium saturation

The effective life of a wetland for removing P can be approximated by estimating the time to reach equilibrium saturation. An aged wetland is assumed to have received substantial P loads long enough that the sediments have reached an equilibrium saturation condition with P, i.e., the sediments can not effectively hold additional P. The maximum P sorption capacity, ν_m (mg/g), can be obtained from batch adsorption equilibrium partitioning experiments or easily measured with a single batch equilibrium at a high P concentration (Gale, Reddy, and Graetz 1994). With an estimate of ν_m (g/kg, or mg/g), the maximum sediment P retention capacity, CAP (g/m^2), can be estimated from

$$CAP = \nu_m \, \rho_b \, h \tag{28}$$

where bulk density here has units of kg/m^3 (i.e., g/L), and h is the active top sediment layer thickness (m). Values for h range from about 0.05 to 0.15 m (Richardson 1985; Gale, Reddy, and Graetz 1994). With an estimate of CAP, the time to reach P saturated conditions in the sediments, t^* (years), can be estimated (Gale, Reddy, and Graetz 1994) from

$$t^* = \frac{CAP \;\; A}{W_L} \times 10^{-3} \tag{29}$$

where A is the wetland surface area (m^2), and W_L is the P load (kg/year). If the wetland age is much less than t^*, then the wetland is assumed to be new, and Equation 27 can be used. If the age is approximately equal to or greater than t^*, then Equation 14 or 17 should be used along with the supporting equations for nonlinear partitioning. It should be noted that Equation 29 is an upper bound estimate of t^* since the maximum sorption capacity is used to obtain CAP. The maximum sediment P concentration may be less than ν_m as was indicated for the Cache river where C_b was estimated to be considerably less than $\nu_m \rho_b$.

Contaminants

Contaminants (i.e., toxic substances, such as organic chemicals, heavy metals, and radionuclides) can be treated in a manner similar to phosphorus since dissolved and particulate concentrations in both the water column and sediment bed must be taken into account. However, linear partitioning may be used in most cases since contaminant concentrations are often low or in trace amounts. Additionally, for some contaminants, other loss pathways should be considered such as volatilization, biodegradation, photolysis, and hydrolysis. The net loss rate for a toxicant, K_T, is the net removal velocity, V_T, divided by H. With an estimate of K_T and τ, Equation 4 or 5 can be used to compute RE. If a steady-state analysis is not adequate, the time-varying contaminant screening-level model, RECOVERY (Boyer et al. 1994), is available for aquatic systems. RECOVERY makes the assumption of a fully mixed water column (i.e., no longitudinal gradients), but the bottom sediments are discretized into multiple vertical layers with varying properties.

Equations presented by Thomann and Mueller (1987) are used to estimate the toxicant removal velocity, V_T. These equations were derived from the steady-state mass balance equations for dissolved and particulate forms of the toxicant in the water column and sediment bed assuming equilibrium partitioning, similar to the approach used for deriving the phosphorus equations above. V_T is expressed as

$$V_T = V_{Td} + V_{Ts} \tag{30}$$

where V_{Td} is the dissolved chemical removal velocity from the water column and is expressed as

$$V_{Td} = (k_d H + k_v)\, F_{dw} \tag{31}$$

and where

k_d = decay rate of dissolved chemical in water column, day^{-1}

k_v = volatilization rate of dissolved chemical from water column, m/day

Decay is the sum of hydrolysis, photolysis, oxidation, and biodegradation decay rates. The relative importance of sorption, volatilization, biodegradation, photolysis, and hydrolysis for various organic chemicals are summarized in Table II-11 by Mills et al. (1985).

V_{Ts} is the removal velocity due to sediment interaction (i.e., sorption, settling, decay, etc.) and can be expressed as

$$V_{Ts} = V_n \left[\frac{V_s F_{pw} + V_d F_{dw}}{V_s + F_{dp} \frac{\rho_b}{S}(V_d + k_{db} h)} \right] \left(1 + \frac{\rho_b k_{db} F_{dp} h}{V_n S} \right) \tag{32}$$

where k_{db} (day^{-1}) is the decay rate of dissolved chemical in the pore water of the sediment bed. All other variables were defined previously under the sections on phosphorus and suspended solids. Note that the active sediment layer thickness, h, must be specified to account for decay, whereas h was not needed for the P calculations. Recall that F_{dw}, F_{pw}, and F_{dp} are calculated from Equation set 16, which assumes linear partitioning. Also, recall that V_n, V_s, and V_d are defined by Equations 7, 8, and 26, respectively. Note that Equation 32 reduces to the form of Equation 14 when sediment decay is set to zero. Heavy metals and long-lived radionuclides neither decay nor volatilize, thus Equation 14 would be appropriate if the F coefficients defined by Equation set 16 are exchanged for the f coefficients defined by Equation set 15. The various pathways affecting modeled contaminants are shown schematically in Figure 4.

Some chemicals are highly soluble in water, and the sediment interaction terms are insignificant. In such cases, removal is due to only decay and volatilization, and the loss rate can be rapid. The loss rate for some chemicals may be published in terms of the half-life, $\tau_{1/2}$, which is the time for the chemical to decrease to half of the original concentration. From first-order removal kinetics, the removal rate can be stated as

$$K_T = \frac{0.693}{\tau_{1/2}} \tag{33}$$

Half-lives for various chemicals are reported by Howard (1991a,b), Howard et al. (1991), and Mackay, Shiu, and Ma (1992).

If sediment interactions are important or Equation 33 is not appropriate, then Equations 30-32 must be used, and the variables in these equations must be estimated. Methods for estimating volatilization, decay, and sediment partitioning are discussed below.

Volatilization

From the two film theory, the volatilization rate is given as

$$\frac{1}{k_v} = \frac{1}{K_l} + \frac{1}{K_g H_e} \tag{34}$$

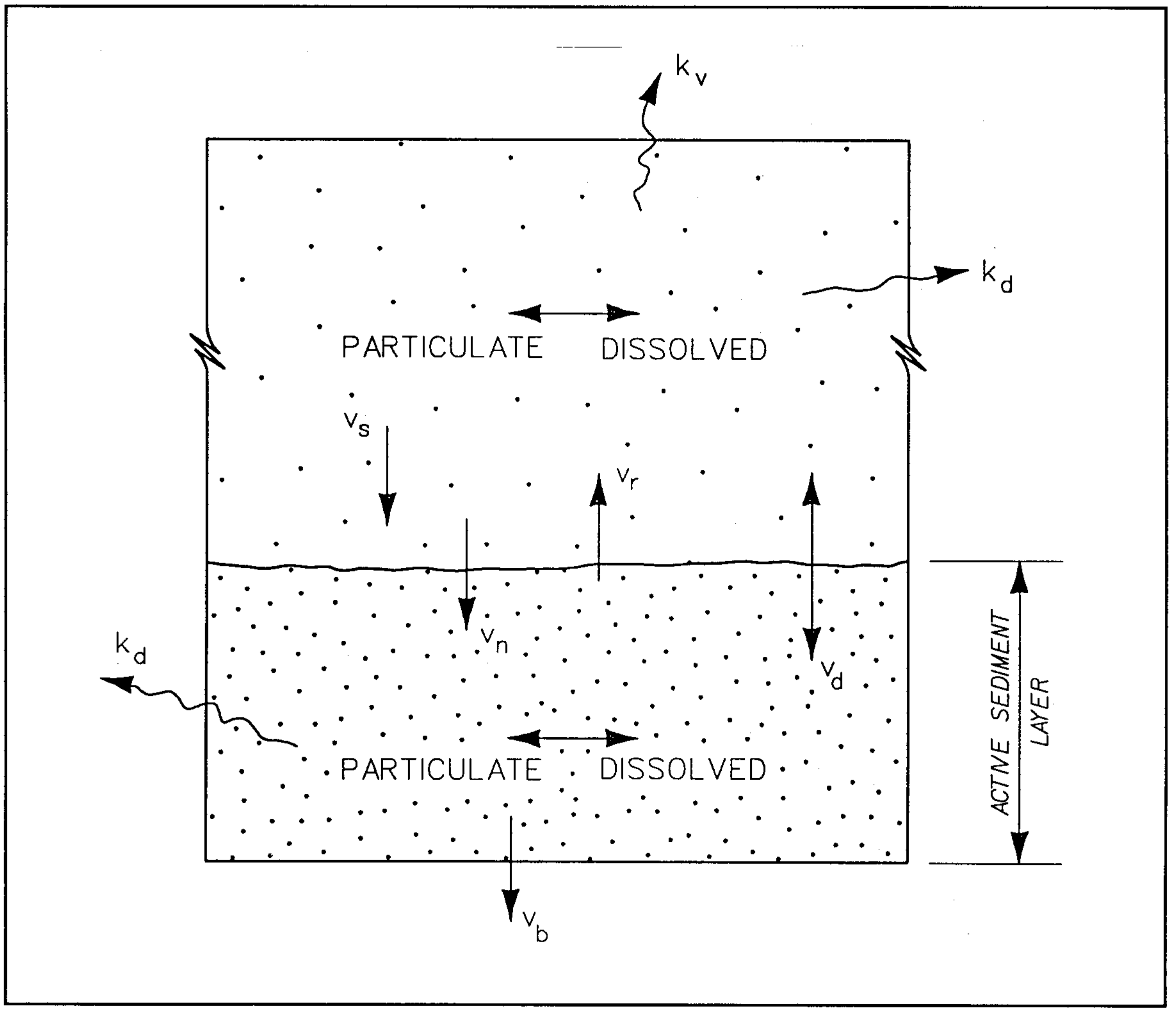

Figure 4. Schematic of pathways affecting modeled contaminants

where K_l is the liquid film coefficient, K_g is the gas film coefficient, and H_e is dimensionless Henry's constant, which is

$$H_e = \frac{H_e'}{RT} \tag{35}$$

where

H_e' = dimensional Henry's constant, atm · m^3/mole

R = universal gas constant = 8.206×10^{-5} atm · m^3/°K · mole

T = temperature, °K

Values for Henry's constant can be found in handbooks for various chemicals, such as Montgomery and Welkom (1990), Montgomery (1991), Mackay, Shiu, and Ma (1992), Schnoor et al. (1987), and Mills et al. (1985). Additionally, Henry's constant can be estimated from the chemical's molecular weight, solubility in water, and saturation vapor pressure (Mills et al. 1985).

When Henry's constant is large (relatively insoluble chemicals), transfer is liquid phase controlled, and the volatilization rate is high. When Henry's constant is small (relatively soluble chemicals), transfer is gas phase controlled, and the volatilization rate is low. A high volatilization rate does not necessarily translate into a high volatilization flux since the flux depends on the dissolved concentration.

Mills et al. (1985) provides an estimate of the liquid film coefficient as

$$K_l = \left(\frac{32}{M} \right)^{1/4} K_L \tag{36}$$

where K_L is the oxygen transfer rate (i.e., reaeration rate, m/day) at ambient water temperature, and M is the molecular weight of the chemical, which can be found in handbooks such as Montgomery and Welkon (1990). K_L can be estimated from reaeration formulae. Reaeration is caused by turbulence near the water surface because of flow and wind. Thomann and Mueller (1987) recommend the Banks and Herrera formula for wind-driven reaeration,

$$K_L = 0.728\, U_w^{1/2} - 0.317\, U_w + 0.0372\, U_w^2 \tag{37}$$

where U_w is the wind speed in m/sec at 10 m above the water surface, and the units for K_L are in m/day. This equation does not take into account the effects of sheltering because of vegetation or topographic features. The effective wind speed may be much less than measured because of sheltering by vegetation. As a first-order approach to account for this effect, the wind speed can be multiplied by the percent of open water to obtain the effective wind speed for use in Equation 37.

The O'Connor-Dobbins (1958) equation is suggested for streamflow reaeration,

$$K_L = 3.95 \left(\frac{U}{H} \right)^{1/2} \tag{38}$$

where U and H were defined previously as flow velocity (m/sec) and depth (m), respectively. The units on K_L here are also in m/day. The maximum K_L value for wind or flow is used for Equation 36.

The gas film coefficient, K_g (m/day), is given by (Mills et al. 1985)

$$K_g = 168 \left(\frac{18}{M} \right)^{1/4} U_w \tag{39}$$

where the wind speed, U_w , has units of m/sec.

Decay

The decay rate (k_d, day^{-1}) is expressed as the sum of the rates of hydrolysis (k_h), photolysis (k_p), biodegradation (k_b), and oxidation (k_o) or

$$k_d = k_h + k_p + k_b + k_o \tag{40}$$

Incorporation of mathematical expressions for estimating these four loss rates, which are provided by Mills et al. (1985) and Schnoor et al. (1987), extend beyond the scope of this screening-level model. If any of these loss terms are considered important, the user is encouraged to use these references to estimate the rates.

Water column decay rates are usually greater than sediment decay because of the opportunity for photolysis. Additionally, sediments are often anaerobic, which further reduces opportunity for biodegradation. Hydrolysis rates depend on pH and range from 10^{-1} to 10^{-7} day^{-1} (Thomann and Mueller 1987). Photolysis rates also vary widely because of the effect of light attenuation over the water depth.

Mills et al. (1985) and Schnoor et al. (1987) provide guidance on biodegradation rates for various organic chemicals. Biodegradation half-life values are provided by Howard et al. (1991) for various organic chemicals in aerobic and anaerobic water. When the half-life values are provided for a process (e.g., biodegradation), Equation 33 can be used to estimate the corresponding process decay rate. Biodegradation rates are temperature dependent with a recommended temperature correction factor (θ) of 1.072 (Mills et al. 1985). If available in sufficient concentration, oxidants (e.g., chlorine and ozone) can degrade chemicals through oxidation reactions. Schnoor et al. (1987) provide guidance on oxidation rates.

Partitioning

To apply Equation 32 (which requires Equation set 16), distribution coefficients must be estimated for prescribing partitioning of chemical between solids and water for both the water column and bed. Linear, reversible, equilibrium partitioning is assumed for this screening-level model, or

$$K_d = \frac{\nu}{c} \tag{41}$$

where

K_d = distribution coefficient, L/kg

ν = mass of chemical sorbed per mass of solid, μg/kg

c = dissolved chemical concentration per unit volume of water, μg/L

Methods for estimating K_d for the water column and sediment bed (i.e., K_{dw} and K_{ds}) are provided below for heavy metals and organic chemicals.

Metals. There is considerable evidence that the distribution coefficient for organic chemicals and metals often displays an inverse relationship to the water column concentration of solids (Di Toro 1985; O'Connor 1988; Thomann and Mueller 1987). O'Connor (1988) suggests the following relationship for describing partitioning in the water column as a function of solids concentration (S, mg/L),

$$K_{dw} = \frac{K_{d0}}{S^n} + K_{dm} \tag{42}$$

where

K_{d0} (L/kg) = maximum water column distribution coefficient (i.e., without any suspended solids)

K_{dm} (L/kg) = minimum value for distribution coefficient with high solids concentrations

The exponent n on S ranges from 0 (no solids effect) to about 1.0.

The distribution coefficient for heavy metals depends on pH, redox conditions, ionic strength, and complexing capacity. Values of K_{d0} for copper, zinc, cadmium, chromium, lead, and nickel range from about 10^4 - 10^5 L/kg (Thomann and Mueller 1987). Mills et al. (1985) report values of K_{d0} of about 10^6 for these six metals in addition to arsenic and mercury. Mills et al. (1985) also report n values for these eight heavy metals.

Thomann and Mueller (1987) recommend $K_{d0} = 2.5 \times 10^5$ and n = 1 in Equation 42 to estimate the effect of solids on metals partitioning. Although Thomann and Mueller did not specifically recommend a value for K_{dm}, they did state that the water column distribution coefficient ranges from about 10^2 - 10^5 for metals. Therefore, $K_{dm} = 10^2$ is suggested, resulting in

$$K_{dw} = \frac{2.5 \times 10^5}{S} + 10^2 \tag{43}$$

where S is in mg/L, and K_{dw} has units of L/kg. Equation 43 is used in the model for estimating K_{dw} for metals.

Di Toro et al. (1990, 1992) have shown that when the reactive pool of solid-phase sulfide (i.e., acid volatile sulfide (AVS), which is extracted from the sediment using cold hydrochloric acid) exceeds the total metal concentration (which is simultaneously extracted from the sediment), insoluble metal sulfides are formed. Anaerobic sediments for both freshwater and saltwater systems usually have enough AVS to sequester a significant quantity of metal. Wetlands usually have anaerobic sediments close to the sediment-water interface (e.g., within a few millimeters to a few centimeters). Therefore, distribution coefficients for metals in wetland sediment beds are expected to be quite large. A conservative default value of $K_{ds} = 10^6$ L/kg is used in the model, but actual values can be orders of magnitude greater.

Organic chemicals. Karickhoff, Brown, and Scott (1979) showed that for organic chemicals,

$$K_d = f_{oc} K_{oc} = 0.617 f_{oc} K_{ow} \tag{44}$$

where

f_{oc} = weight fraction of organic carbon in suspended solids (i.e., mass total organic carbon per mass of solids)

K_{oc} = organic carbon partition coefficient

K_{ow} = octanol-water partition coefficient, which measures the distribution of organic chemical between water and octanol

Values for f_{oc} typically range from 0.001 to about 0.1 (Thomann and Mueller 1987). K_{ow} can range as high as about 10^7 L/kg, such as for polychlorinated biphenals (PCBs), and is inversely proportional to solubility in water (Mills et al. 1985). Di Toro et al. (1991) indicate that $K_{oc} \approx K_{ow}$ is a good approximation for low solids concentrations.

The effect of solids concentration on organic chemical partitioning is now generally considered to result from solids-organic carbon interactions and the partitioning of chemical to dissolved organic carbon (Di Toro et al. 1991). This effect is described as follows. As the solids concentration increases, the concentration of dissolved organic carbon (i.e., nonsettling or nonfilterable microparticles or organic macromolecules) increases. As dissolved organic carbon (DOC) increases, the organic chemical sorbed to DOC increases, thus, causing an increase in the apparent dissolved chemical concentration. From Equation 41, as the apparent dissolved chemical concentration increases, the apparent K_d decreases. Thus, K_d appears to decrease with increasing solids concentration.

Gschwend and Wu (1985) and Di Toro et al. (1991) explained mathematically and verified through experiment the DOC effect on organic chemical partitioning. The apparent distribution coefficient (K_d') for an organic chemical is stated as

$$K_d' = \frac{\nu}{C_w + C_{DOC}} \tag{45}$$

where

C_w = concentration of chemical dissolved in water

C_{DOC} = mass of chemical sorbed onto DOC per unit volume of water

Defining K_{DOC} (L/kg) as the coefficient for partitioning the chemical between DOC and water, i.e.,

$$K_{DOC} = \frac{C_{DOC}}{DOC \cdot C_w \cdot 10^{-6}} \tag{46}$$

where DOC is the dissolved organic carbon concentration (mg/L), rearranging Equation 45, and making use of Equations 46 and 41 results in

$$K_d' = \frac{K_d}{1 + K_{DOC}\ DOC\ 10^{-6}} \tag{47}$$

Using Equation 44 and setting $K_{DOC} = K_{oc}$, which data tend to support (Di Toro et al. 1991), Equation 47 can also be written as

$$K_d' = \frac{f_{oc}\ K_{oc}}{1 + K_{oc}\ DOC\ 10^{-6}} \tag{48}$$

Equation 48 is used in the model to compute the partitioning coefficient for organic chemicals in the water column and in the bed. From Equation 44, $K_{oc} = 0.617\ K_{ow}$. Values of f_{oc} and DOC representative of water column and bed conditions should be used in Equation 48 when computing apparent values for K_{dw} and K_{ds}. Water column values for DOC are typically on the order of about 5 mg/L. Concentrations of DOC in bed pore water are at least as large as the water column DOC concentration (e.g., 5 mg/L) and can be much higher than the water column concentration (e.g., an order of magnitude higher or about 50 mg/L) because of the high solids concentration in the bed. Values for f_{oc} are typically a few percent (e.g., 0.02) for both the water column and the bed.

For large K_{oc} (or K_{ow}) values, increasing DOC has a strong effect of decreasing K_d' below K_d. However, for small K_{oc} values, increasing DOC has little or no effect of decreasing K_d' below K_d (i.e., $K_d' \approx K_d$). For large K_{oc} and large DOC, $K_d' \approx f_{oc} / (DOC\ 10^{-6})$.

Sources of information for chemical properties

Various handbooks are available for chemical properties, such as Henry's constant, molecular weight, half-lives, degradation rates, K_{ow} , solubility, vapor pressure, etc. Such references include Montgomery and Welkom (1990), Montgomery (1991), Howard et al. (1991), Howard (1991a,b), Mackay, Shiu, and Ma (1992), Lyman, Reehl, and Rosenblatt (1982), Verschueren (1983), Schnoor et al. (1987), and Mills et al. (1985).

4 Software Description and Implementation

Background

The methods described above have been coded into a user-friendly, interactive computer program operational on PCs. The program is called PREWET, which is an acronym for Pollutant Removal Estimates for Wetlands. The equations and logic are programmed in C++, and a commercially available graphical user interface (GUI) library, Zinc, which is written in C++, is utilized. PREWET uses menus for selection of variables and parameters, and default values are also provided for parameters. The model is designed to be self-explanatory, but on-line help features are available if necessary.

PREWET had undergone initial development and testing at the time this report was published. Upon final development and testing, the model will be released to the general public. At that time, information will be provided on how to obtain copies of the software.

General Description

The program is a protected-mode DOS program that requires a computer with a minimum of an 80386 central processor, with at least two megabytes of random excess memory. The files necessary for using the program are PREWET.EXE, DOS4GW.EXE, and PREWET.DAT, which must be located in the same directory. The program creates temporary files while executing; therefore, there should be sufficient hard disk space available. The output files created by the program are RE.OUT and any file specified by the user to save as an input file. The file RE.OUT is created for any run that the user has selected with the Run Model button. This file can be viewed or printed after exiting the program and contains the summary of the user's session showing input parameters and the calculated removal efficiencies.

When the user runs the PREWET model, the program will display the main screen (Figure 5) followed immediately by the about-model screen. The program then waits for the user to either press cancel to remove the

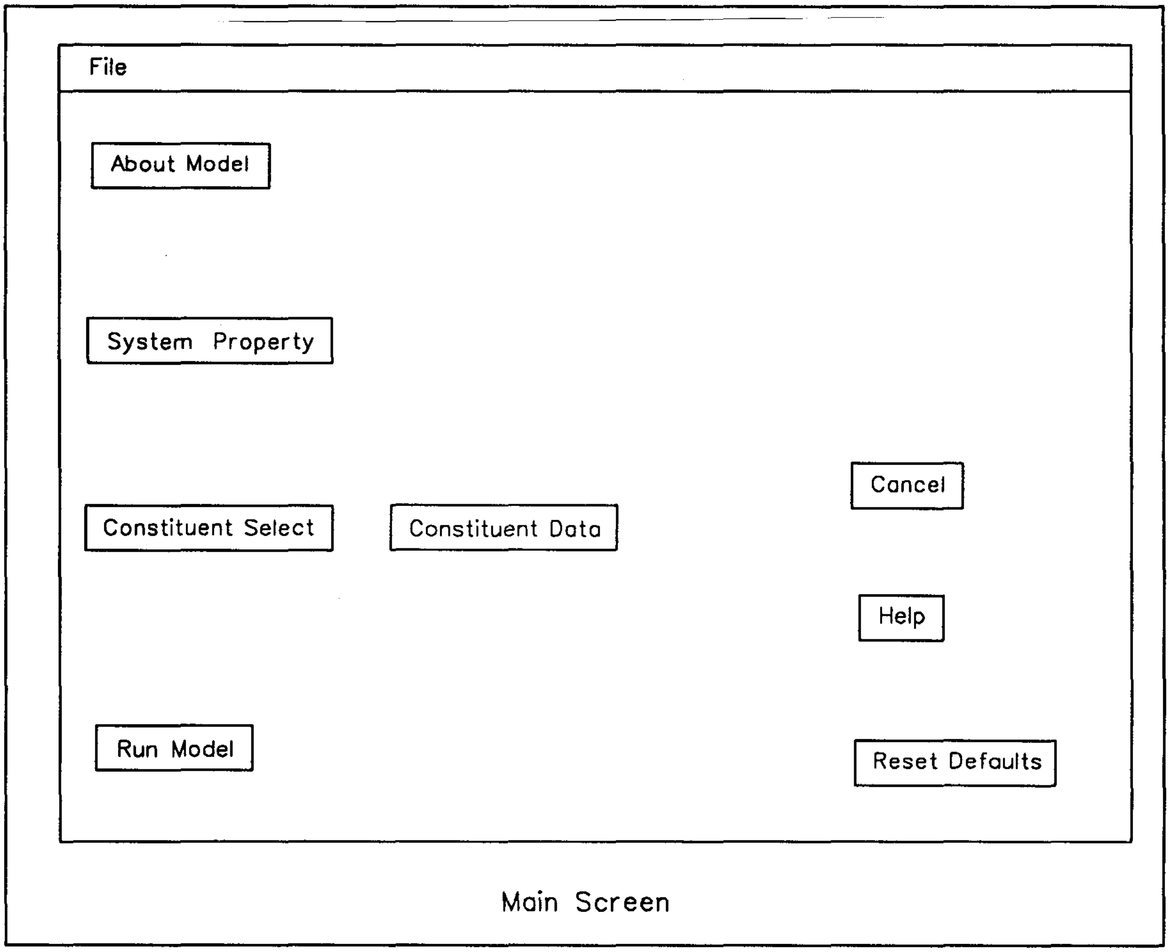

Figure 5. Features on main screen of PREWET

about-model screen or to press the detail button for further information on the development of the model. The main screen consists of: "about model," "system properties," "constituent selection," "constituent data," "run model," "reset defaults," "cancel," and "help" buttons. In addition, the main screen has a pull down menu for "file" operations.

The program uses the Newton-Raphson algorithm to solve the five simultaneous equations for total phosphorus (under the "established wetland" option). A maximum of 150 iterations are allowed in trying to solve the phosphorus equations. The iteration tolerance between successive iterated values is 1e-06.

About the Screens and Buttons

Cancel and Help buttons

The Cancel button on the main screen is used to exit the model. When this button is pressed, a confirmation window pops up and asks the user if he/she really wants to quit and provides the opportunity to return to the model or quit. The Help button is used to provide the user with information on how to use the options available from the main screen as well as commands that can be used to close help windows.

The program has Help and Cancel buttons on virtually every screen. The exception to this is the pop up windows, which are activated when some type of error occurs. These windows, in general have an OK button on them. The Help buttons provide help for the user specific to the current screen. The Cancel buttons are used to back out of the current screen and return to the previous screen. In general, pressing the Cancel button discards any changes made to the variables on the current screen, whereas pressing accept saves the changes made.

File Menu button

The File Menu button will allow the user to save a session to a file specified by the user, retrieve a previous session from a file, or delete a file. This allows the user the opportunity to save the current program input, then exit the program and later retrieve the saved information and continue with data input. Figure 6 shows the logic flow for the File Menu option.

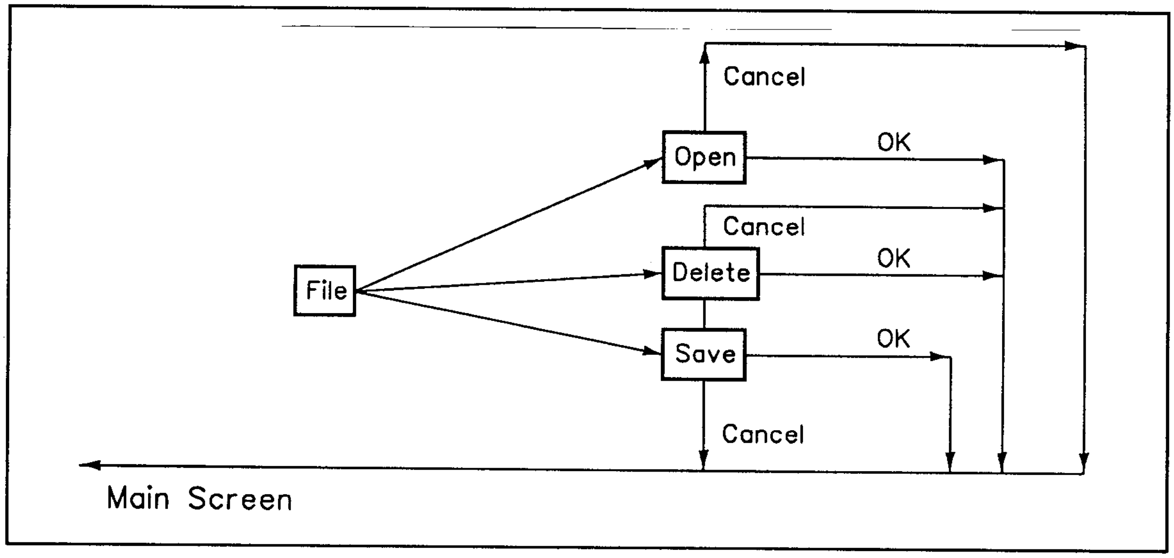

Figure 6. Logic flow for File Menu option

About Model button

The About Model button is used to show the model information screen and can be used to obtain more information about the model by pressing the Detail button on this screen. The About Model button is selected for the user each time the program is started. Figure 7 shows the logic flow for the About Model option.

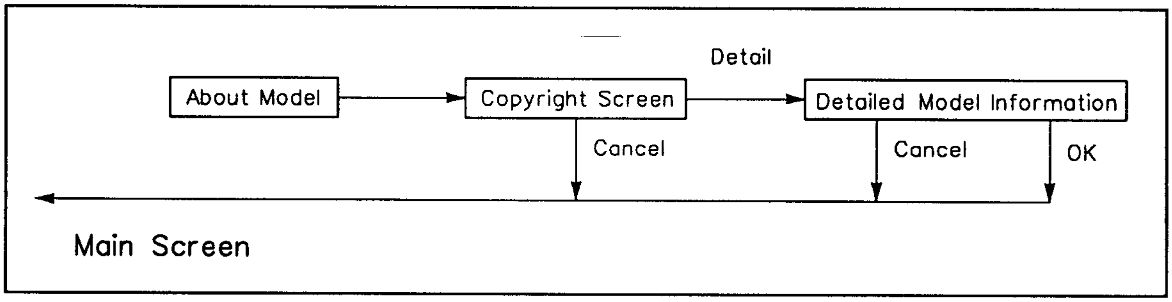

Figure 7. Logic flow for About Model option

System Property button

The System Property button requires input from the user before any of the other main screen buttons can be used (with the exception of the Cancel and Help buttons). This is because the model uses data input by the user from the System Property windows to calculate default values for the various constituents that can be modeled. If the user tries to select one of the other buttons from the main screen without selecting the System Property button first, then the program will pop up a message window stating that the user should select the System Property button first.

Once the user has pressed the System Property button, then the program will display a window with a list box for the user to select among any two of three required input parameters of wetland volume, surface area, or mean depth. Only two of the three values should be checked since the third will be calculated by the program. If the user tries selecting too many or too few, then the program will display a pop up window indicating an appropriate message to reselect. There is also a list box for the user to select either length or width of the wetland and have the other property calculated.

Once the choice for volume, area, depth, length, and width are made and the user presses accept, then the program will display an input screen for system properties, which include average wetland temperature, length, width, flow, area, volume, and depth. One of the volume, area, or depth fields will be shaded gray (depending on which two the user selected), and the user will not be able to enter this field. The program updates these fields as the user makes a change in the fields from which the parameter is determined. The same is true for the length/width field.

Once the user has pressed accept, then the program will display an additional input screen showing four calculated values and a check box for the overall solution scheme. The calculated values are as follows: the length-to-width ratio, the hydraulic residence time (V/Q), the mean velocity, and the detention time. Of these four, the user may change the mean velocity and the detention time. However, the detention time varies depending on the length-to-width ratio and the option checked in the solution scheme box. If the user desires to specify the detention time, then it should be changed after the user has selected the solution scheme since the program updates the detention time whenever the solution scheme is changed. There are two choices for solution scheme, well-mixed and longitudinal gradients. The characteristics of these two schemes are discussed in Chapter 2 of this report. Pressing accept returns the user to the main input screen. Pressing cancel backs up to the previous screen. Figure 8 shows the logic flow for the System Property screens.

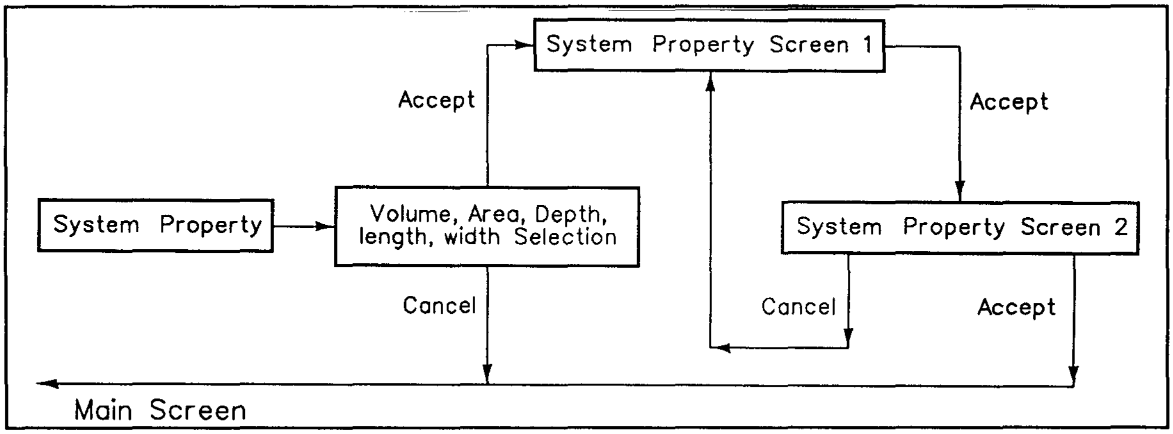

Figure 8. Logic flow for System Properties screen

Constituent Selection button

After entering the system property data, the next selection should be the Constituent Selection button. This button displays a window that contains the selection list for the available constituents for which removal efficiencies can be calculated. The user may select any or all of the available selections that include the following: Total Suspended Solid (TSS), Total Coliform Bacteria (TCB), Biochemical Oxygen Demand (BOD), Total Nitrogen (TN), Total Phosphorus (TP), and Contaminants. If the user selects to model Total Phosphorus and/or Contaminants and did not select TSS, then the program will automatically select TSS since information required by the TP and Contaminant algorithms requires information from the input of TSS parameters. Figure 9 shows the logic flow for the constituent selection button.

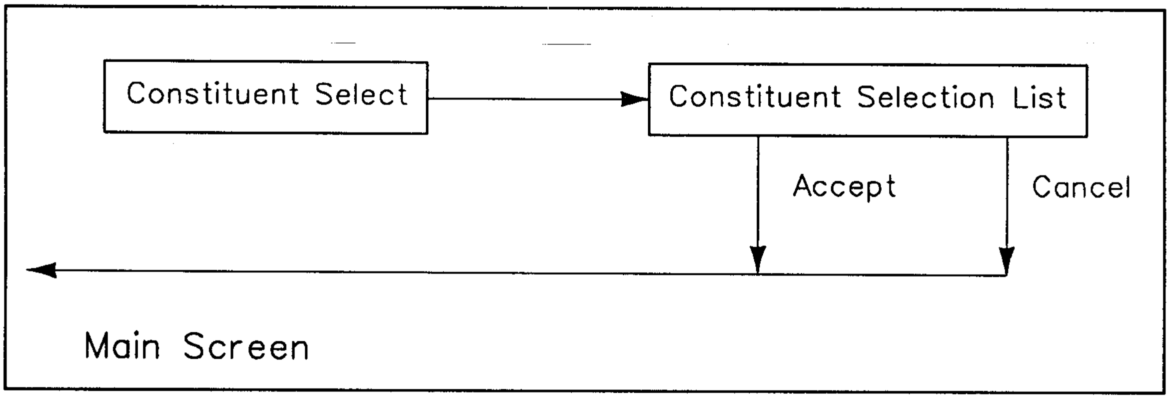

Figure 9. Logic flow for Constituent Selection button

Constituent Data button

Once the user has selected which constituents he/she wishes to analyze, then the next selection should be the Constituent Data button. This button provides the user with the data input buttons for the constituents selected from the Constituent Selection screen. The user then selects the buttons and enters the necessary information. If TP and/or Contaminants have been selected, then the user should enter TSS data first. The program will display a pop up window stating that the user should enter TSS data first if the user selects TP or Contaminants without first entering TSS data. Figure 10 shows the logic flow.

TSS Data button

When the user selects this button, the program will display a selection list that includes the following possible selections:

- Assume V_n equals particle settling rate (V_s)
- Calculate V_n based on sediment accretion rate (V_a)
- Calculate V_n based on sediment burial rate (V_b)

Once the user has made a choice from the available options and pressed accept, the program will present the user with an input screen for the parameters checked. The user then enters the parameters and presses accept to save the values and return to the Constituent Data screen where the next data button can be selected and its data entered.

TCB Data button

When the user selects this button, the program will display an input screen for the user to input the TCB decay rate at 20 °C and the associated temperature correction factor.

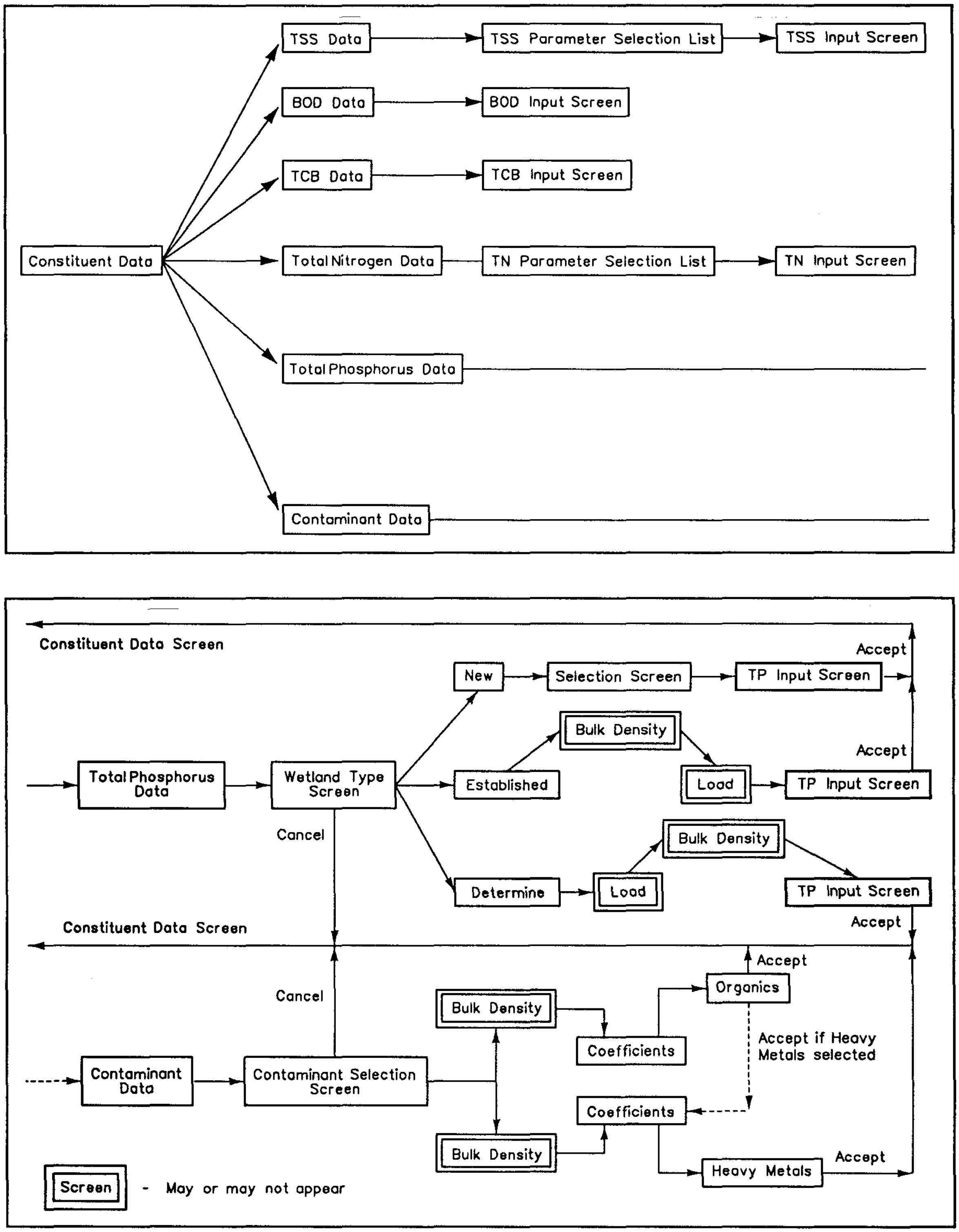

Figure 10. Logic flow for Constituent Data buttons

BOD Data button

When the user selects this button, the program will display an input screen for the user to enter the BOD first order removal rate at 20 °C and the associated temperature correction factor.

TN Data button

When the user selects this button, the program will display a selection screen for the user to select the parameters he/she wishes to input. The available choices are denitrification rate or first order removal rate for TN. Once the user selects the parameters he/she wishes to enter, the program will display an input screen for the parameters chosen with the temperature correction factor to be applied.

TP Data button

When the user selects this button, the program will display a checkbox selection screen for the user to enter the type of wetland or for the program to determine into which category the wetland falls. The type of wetland can be either New or Established.

If the user had selected Determine from the available choices, then the program will display an input screen for the user to enter the active layer thickness, the maximum phosphorus sorption capacity, and the TP loading or flow rate and concentration of entering TP load. Then the program will calculate whether the wetland is New or Established and display a pop up window stating which type was determined. The program then waits for the user to press OK to acknowledge the message and then returns the user to the Wetland Type screen with the selection being made for the wetland type. The user can then press accept, and the program will display the input screens for either the New wetland or Established wetland types.

If the wetland type is new, then the program will display a selection screen that requires the user to select one of the following:

- Fraction of total particulate phosphorus (TPP) to total phosphorus (TP), f_{pw}.
- Fraction of total dissolved phosphorus (TDP) to TP, f_{dw}.
- Fraction of total inorganic phosphorus (TIP) to TP, i.e., f_i, and fraction of particulate inorganic phosphorus (PIP) to TIP, F_{pw}.
- Fraction of TIP to TP, i.e., f_i, and fraction of dissolved inorganic phosphorus (DIP) to TIP, F_{dw}.
- Fraction of total organic phosphorus (TOP) to TP, i.e., f_o, and fraction of PIP to TIP, F_{pw}.
- Fraction of TOP to TP, i.e., f_o, and fraction of DIP to TIP, F_{dw}.

- Fraction of TIP to TP, i.e., f_i, and the phosphorus partitioning coefficient (K_{dw}) and the suspended solids concentration (S).
- Fraction of TOP to TP, i.e., f_i, and K_{dw} and S.

All of the above variables are for the water column. The selection of any one of the above input options will allow the determination of f_{pw}, which is required to estimate the phosphorus removal rate (Equation 27).

Once the user has made the selection and pressed accept, the program will display an input screen for the user to enter the selections he/she made. Once the data for the new wetland has been entered, the program will return the user to the Constituent Data screen where additional data for other parameters can be entered or OK can be pressed to return to the main screen.

If the wetland type is established, the program will prompt the user to input or calculate active sediment layer bulk density and settling velocity (provided these have not already been entered or calculated at this point). Once the user has made a selection and entered the appropriate data, the program will then display a screen asking how the user wishes to input the TP load (either as a load, i.e., mass/time, or as flow times concentration). Once the user has selected accept, the program will display an input screen for the user to input the following:

- Bonding energy constant for sorption.
- Maximum P sorption.
- Fraction total inorganic P to TP in water column.
- Fraction total inorganic P to TP in sediment.
- TP loading (if selected and not already entered).
- TP flow (if selected and not already entered).
- TP concentration (if selected and not already entered).

The program will then display the resuspension and mass transfer velocities after pressing accept. The user is given the opportunity to change the calculated mass transfer velocity and then proceed. After the data has been entered, the program will return the user to the Constituent Data screen where other data can be entered or OK can be pressed to return to the main screen.

Contaminant Data button

When the user selects this button, the program will display a window requiring the user to enter the following:

a. The number (maximum of three) of organic chemical data sets on which to perform removal efficiency calculations.

b. Whether the organic chemical REs will be computed from input half-lives or estimated from removal rates.

c. The number (maximum of three) of heavy metal/long-life radionuclides on which to calculate removal efficiencies.

Once the user has completed this entry screen and pressed accept, the program may require the user to input or calculate the active layer bulk density and active layer porosity if they have not been entered prior to this point.

If the user has selected an organic chemical data set that is to be computed by removal rate estimates, then the program will display a selection screen to the user to input or calculate water column distribution coefficients, sediment distribution coefficients, and the volatization rate of dissolved chemical from the water column. After making the appropriate selections and pressing accept, the program will display the organic chemical removal rates input screen.

If the user has selected an organic chemical data set that is to be computed by half-lives, then the program will present the user with the half-life input screen.

Once the user has entered any organic chemical data sets that he/she wishes and has selected to perform removal efficiency calculation on heavy metals, the program will then present the user with a selection screen for the user to input or calculate the water column distribution coefficient for heavy metals. After making the appropriate selections and pressing accept, the program will display the heavy metal input screen.

If the user selected to perform RE estimates for heavy metal data sets only, then the program will require that the user input or calculate active layer bulk density and active layer porosity (provided they have not been entered at this point) before inquiring about the water column distribution coefficient input selection for heavy metals.

Once the user has entered the data for the contaminants and presses accept, the program will return the user to the Constituent Data screen where other data can be entered or OK can be pressed to return to the main screen.

Run Model button

Once the user has entered all of the data for each of the constituents for which he/she wishes to estimate the removal efficiency, the user can select the Run Model button. Selecting this button will display a confirmation window providing the user with the opportunity to proceed with the estimates or to return to the main screen. Selecting to proceed will allow the program to calculate the various removal efficiencies for the constituents selected on a pop up window displaying this information. Figure 11 shows the logic flow for this option.

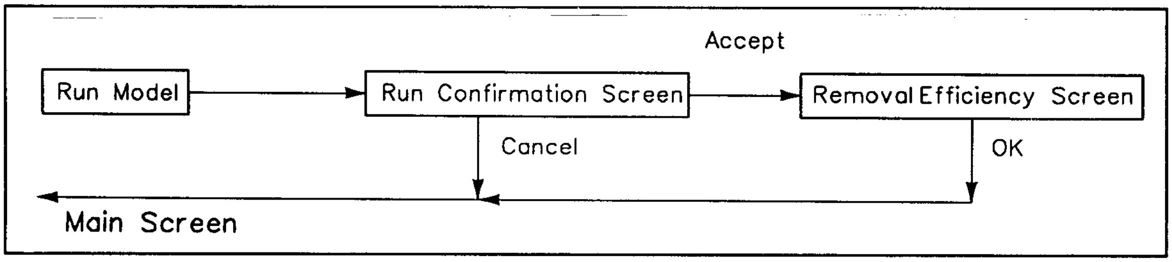

Figure 11. Logic flow for Run Model option

Reset Default Button

This button is used to reset the default values for the program. When the user selects this button, the program will reset all values to the default values, and the user is ready to input the parameters for a new wetland study. The user will have to enter the system properties first for the new study.

Default Choices

The program assumes the following default choices for the initial status of the following buttons noted in quotes:

- Solution scheme of "longitudinal gradients"
- Total phosphorus loading, "enter as loads"
- Wetland type is set to "determine"
- "Half lives" will be input for organic chemicals

Default values are also assumed for various input parameter values. These values are displayed during data entry and can be changed through user input.

5 Summary and Recommendations

An analytical, screening-level model has been developed for estimating pollutant removal efficiency for free surface wetlands. The model is applicable to TSS (or ISS), BOD, TCB, TN, TP, and contaminants. The model assumes steady-state conditions and either fully mixed conditions or one-dimensional (longitudinal) spatial gradients for the constituent mass balance equation. A first-order removal rate law is used. The removal rates for TSS, TP, and contaminants, which have sedimentary implications, are based on mechanistic concepts taken from the literature; whereas, more empiricism is employed for BOD, TCB, and TN, which are predominantly biologically mediated. The model, referred to as PREWET, has been developed for PC application.

Consistent with the steady-state assumption, the model focuses on dominant, long-term, net removal processes, such as denitrification and sediment burial. Seasonal and annual processes, such as plant growth and death are not included. Thus, this model should not be used to evaluate seasonal effects, which can be influenced significantly by plant photosynthesis, respiration, mortality, and detrital decomposition. Nutrients are cycled through plants by these processes, but at steady-state, plants do not have a net effect on nutrient removal except through detrital deposition to the sediments, which can affect sediment burial. Therefore, one potential improvement for this model is to add detrital deposition to the sediments.

The model accounts for sorption of phosphorus and contaminants to suspended solids that settle. Thus, partitioning within the water column provides a removal mechanism. However, sorption removal of dissolved water column constituents can also occur through direct contact with the sediment bed. This process may be especially important for trace metals when the suspended solids concentration is low. Incorporation of this feature should be considered during any future improvements to PREWET. The capability to allow nonlinear partitioning for metals is also identified as a potential improvement.

PREWET was tested against TP, TN, and ISS data obtained from the Cache River wetland. The model performed well for the Cache River application where RE predictions were within 15 percent of RE estimates obtained for a 3-year period of observations. Similar long-term data sets were not available for testing the other model variables (i.e., BOD, TCB, and contaminants). However, recommendations are provided for estimating rate constants needed to compute RE for each of these constituents. As with any new model, additional applications are needed to gain a better understanding of the model's strengths and limitations.

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Appendix A
Symbols

The symbols used in this report are described below.

A	water surface area, m^2
BOD	biochemical oxygen demand
C	pollutant concentration of flow exiting the wetland, mg/L or g/m^3
c	equilibrium dissolved chemical concentration, mg/L
C_{DOC}	equilibrium chemical concentration sorbed onto DOC, mg/L
C_w	equilibrium dissolved chemical concentration in water, mg/L
CAP	maximum sediment P retention capacity, g/m^2
C_b	chemical (e.g., P) concentration in the bed layer, mg/L
C_d	dissolved inorganic P (or chemical) concentration in the water column, mg/L
C_{dp}	dissolved inorganic P (or chemical) concentration in the sediment pore water, mg/L
C_i	pollutant concentration of flow entering at point i, mg/L or g/m^3
C_p	particulate inorganic P (or chemical) concentration in the water column, mg/L
D	particle diameter, m
DOC	dissolved organic carbon concentration, mg/L
D_m	molecular diffusivity of dissolved chemical, m^2/sec
F_{dp}	fraction of dissolved pore water inorganic P (or chemical) to total sediment inorganic P (or chemical)
F_{dw}	fraction of dissolved inorganic P (or chemical) to total inorganic P (or chemical) in the water column
F_{pw}	fraction of particulate inorganic P (or chemical) to total inorganic P (or chemical) in the water column
f_{dp}	fraction of dissolved phosphorus in the sediment layer pore water to total P in the sediment layer
f_{dw}	fraction of dissolved to total P in the water column
f_i	fraction of total inorganic P to total P
f_o	fraction of total organic P to total P
f_{oc}	weight fraction of organic carbon in solids
f_{pw}	fraction of particulate to total P in the water column
g	gravitational acceleration (9.82 m/sec^2)

H	average water depth, m
K	bulk loss or removal rate, day^{-1}
K_B	bulk removal rate for TCB, day^{-1}
K_d	distribution (i.e., partitioning) coefficient for a contaminant, L/kg
K_d'	the apparent distribution coefficient for an organic chemical, accounting for effects of organic colloids, i.e., DOC, L/kg
K_{dw}	distribution (i.e., partitioning) coefficient for phosphorus in the water column, L/g; also contaminant distribution coefficient in the water column, L/kg
K_{dm}	minimum water column distribution coefficient for trace metals, L/kg
K_{d0}	maximum water column distribution coefficient (i.e., without any suspended solids) for trace metals, L/kg
K_{ds}	distribution (i.e., partitioning) coefficient for phosphorus in the sediment bed, L/g; also contaminant distribution coefficient in the sediment bed, L/kg
K_{DOC}	DOC partition coefficient, i.e., distribution of organic chemical between DOC and water, L/kg
K_{oc}	organic carbon partition coefficient, i.e., distribution of organic chemical between carbon and water, L/kg
K_{ow}	octanol-water partition coefficient, i.e., distribution of chemical between octanol and water, L/kg
K_r	bulk removal rate for BOD, day^{-1}
K_s	bulk removal rate for TSS, day^{-1}
K_{TN}	bulk removal rate for TN, day^{-1}
K_{TP}	bulk removal rate for TP, day^{-1}
K_{20}	bulk removal rate at 20 °C
L	average length of the wetland, m
m	Langmuir model constant related to the bonding energy for sorption, L/mg
NO_3	nitrate concentration, mg/L
Q	total average water flow rate exiting the wetland, m^3/sec
Q_i	water flow rate entering the wetland at point i, m^3/sec
RE	removal efficiency, %
S	suspended solids concentration, g/L
S_g	specific gravity of the particles
T	water temperature, °C
t	time, days
t^*	time to reach P saturated conditions in the sediments, years
TCB	total coliform bacteria
TSS	total supended solids
TP	total phophorus
TN	total nitrogen and total nitrogen concentration, mg/L
U	average velocity of flow in the wetland, m/sec
u_*	average flow shear velocity along the bed, m/sec
V	total water volume of the wetland, m^3
V_a	surficial sediment accretion rate, m/day
V_b	active sediment layer burial velocity, m/day

V_d	mass transfer velocity across the sediment-water interface resulting from diffusion of chemical, m/day
V_r	active sediment layer resuspension velocity, m/day
V_s	settling velocity, m/day
W	average width of the wetland, m
W_L	total loading of pollutant entering the wetland, i.e., $\sum Q_iC_i$, mass/time
θ	temperature correction factor
ν	kinematic viscosity of water at temperature T, m^2/sec
ν	sorbed chemical mass per mass of solids, mg/g
ν_m	Langmuir model constant for sorption maximum, mg/g
ρ_a	surficial sediment bulk density, $\rho_a = \rho_s (1-\phi_a)$, g/L
ρ_b	active sediment layer bulk density, $\rho_b = \rho_s (1-\phi_b)$, g/L
τ	hydraulic residence time (V/Q, days) for full mixed wetland or plug flow wetland with large L/W; otherwise true detention time, days
ρ_s	dry sediment density, g/L
ϕ	sediment porosity or water content, fraction
ϕ_a	surficial sediment porosity or water content, fraction
ϕ_b	active sediment layer porosity or water content, fraction
subscript b	refers to the sediment bed, i.e., active sediment layer

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13. ABSTRACT *(Maximum 200 words)*

This report describes the theoretical basis for a screening-level mathematical model for estimating the amount of pollutant removal provided by wetlands. The amount of pollution removed from the receiving water is quantitatively expressed in terms of the removal efficiency (RE), where RE is a percentage between 0 and 100 percent, and RE = 100 percent represents total removal of the pollutant. The approach was to develop a screening-level model that can be rapidly applied with minimal input data for estimating the amount of water quality improvement provided by wetlands. The primary assumption made with this model to achieve simplicity is that the wetland is at steady-state. Either of two conditions are assumed for spatial gradients in concentration: (a) fully mixed (i.e., no gradients); and (b) gradients along the main flow axis (i.e., longitudinal gradients). Given basic characteristics about the wetland, RE can be computed for total suspended solids, total coliform bacteria, biochemical oxygen demand, total nitrogen, total phosphorus, and contaminants (e.g., organic chemicals and trace metals). The RE depends on the wetland detention time and the removal rate, K (day^{-1}), for the constituent. The removal rates depend on a number of processes, such as microbial metabolism, adsorption, volatilization, denitrification, settling, etc., and ambient conditions, such as water temperature. The approach here was to focus on the dominant long-term

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removal mechanisms, making use of literature values of mathematical formulations for those mechanisms when possible. Methods for estimating K values are discussed, and examples of literature estimates are provided. These techniques have been programmed into an interactive, user-friendly, PC-based computer program, which is also described in the report. Comparisons of predicted versus observed REs for the Cache River wetland, Arkansas, are made for total suspended solids, total nitrogen, and total phosphorus.