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THE WATER QUALITY ANALYSIS

SIMULATION PROGRAM, WASP5

PART A:

MODEL DOCUMENTATION

by

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CHAPTER 1

INTRODUCTION TO THE WASP5 MODEL

The Water Quality Analysis Simulation Program--5 (WASP5), an enhancement of the original WASP (Di Toro et al., 1983; Connolly and Winfield, 1984; Ambrose, R.B. et al., 1988). This model helps users interpret and predict water quality responses to natural phenomena and man-made pollution for various pollution management decisions. WASP5 is a dynamic compartment modeling program for aquatic systems, including both the water column and the underlying benthos. The time-varying processes of advection, dispersion, point and diffuse mass loading, and boundary exchange are represented in the basic program.

This version of the WASP program was developed for the Maine Department of Environmental Protection with funding from U.S. EPA Region I. The program for modeling eutrophication was modified to provide a variety of new capabilities needed to model estuaries and rivers in Maine. These modifications include: adding salinity as a system variable; modifying the transport algorithms to allow automatic computation of tidal flows; increasing the model's dimensionality limits; incorporating a submodel of periphyton and macrophytes; providing an alternative capability for post-processing WASP output; providing an alternative means of specifying nonpoint source loads; allowing some model kinetic constants to vary by model segment; creating a benthic source for CBOD; increasing the number of time functions for temperature; allowing light limitation to be calculated on time scales shorter than one day; and providing two new light-limitation functions. These updates are incorporated in Version 5.2-MDEP of the WASP EUTRO code.

Water quality processes are represented in special kinetic subroutines that are either chosen from a library or written by the user. WASP is structured to permit easy substitution of kinetic subroutines into the overall package to form problem-specific models. WASP5 comes with two such models -- TOXI5 for toxicants and EUTRO5 for conventional water quality. Earlier versions of WASP have been used to examine eutrophication and PCB pollution of the Great Lakes (Thomann, 1975; Thomann et al., 1976; Thomann et al, 1979; Di Toro and Connolly, 1980), eutrophication of the Potomac Estuary (Thomann and Fitzpatrick, 1982), kepone pollution of the James River Estuary (O'Connor et al., 1983), volatile organic pollution of the Delaware Estuary

(Ambrose, 1987), and heavy metal pollution of the Deep River, North Carolina (JRB, 1984). In addition to these, numerous applications are listed in Di Toro et al., 1983.

The flexibility afforded by the Water Quality Analysis Simulation Program is unique. WASP5 permits the modeler to structure one, two, and three dimensional models; allows the specification of time-variable exchange coefficients, advective flows, waste loads and water quality boundary conditions; and permits tailored structuring of the kinetic processes, all within the larger modeling framework without having to write or rewrite large sections of computer code. The two operational WASP5 models, TOXI5 and EUTRO5, are reasonably general. In addition, users may develop new kinetic or reactive structures. This, however requires an additional measure of judgment, insight, and programming experience on the part of the modeler. The kinetic subroutine in WASP (denoted "WASPB"), is kept as a separate section of code, with its own subroutines if desired.

1.1 OVERVIEW OF THE WASP5 MODELING SYSTEM

The WASP5 system consists of two stand-alone computer programs, DYNHYD5 and WASP5, that can be run in conjunction or separately (Figure 1.1). The hydrodynamics program, DYNHYD5, simulates the movement of water while the water quality program, WASP5, simulates the movement and interaction of pollutants within the water. While DYNHYD5 is delivered with WASP5, other hydrodynamic programs have also been linked with WASP. RIVMOD handles unsteady flow in one-dimensional rivers, while SED3D handles unsteady, three-dimensional flow in lakes and estuaries (contact CEAM for availability).

WASP5 is supplied with two kinetic sub-models to simulate two of the major classes of water quality problems: conventional pollution (involving dissolved oxygen, biochemical oxygen demand, nutrients and eutrophication) and toxic
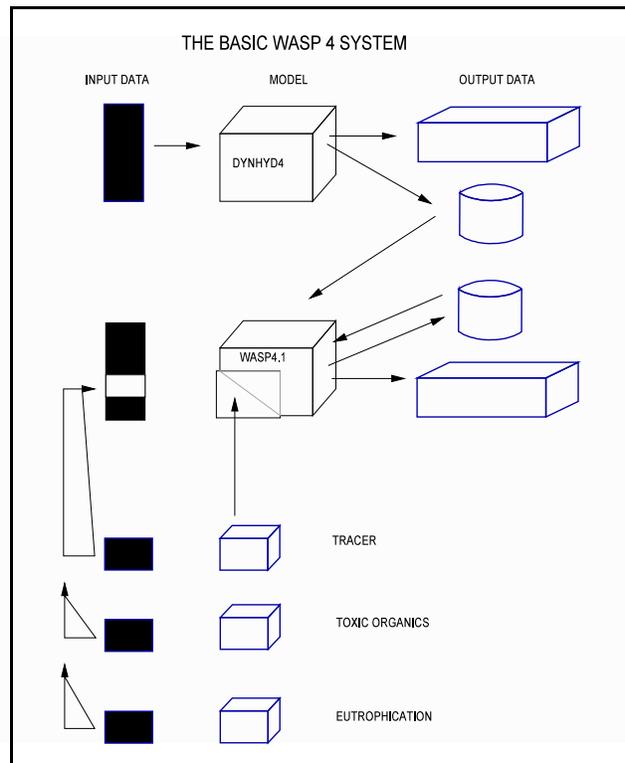
Figure 1.1 The basic WASP5 system.

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pollution (involving organic chemicals, metals, and sediment). The linkage of either sub-model with the WASP5 program gives the models EUTRO5 and TOXI5, respectively. This is illustrated in Figure 1.1 with blocks to be substituted into the incomplete WASP5 model. The tracer block can be a dummy sub-model for substances with no kinetic interactions. In most instances, TOXI5 is used for tracers by specifying no decay.

The basic principle of both the hydrodynamics and water-quality program is the conservation of mass. The water volume and water-quality constituent masses being studied are tracked and accounted for over time and space using a series of mass balancing equations. The hydrodynamics program also conserves momentum, or energy, throughout time and space.

1.2 THE BASIC WATER QUALITY MODEL

WASP5 is a dynamic compartment model that can be used to analyze a variety of water quality problems in such diverse water bodies as ponds, streams, lakes, reservoirs, rivers, estuaries, and coastal waters. This section presents an overview of the basic water quality model. Subsequent chapters detail the transport and transformation processes in WASP5 for various water quality constituents.

The equations solved by WASP5 are based on the key principle of the conservation of mass. This principle requires that the mass of each water quality constituent being investigated must be accounted for in one way or another. WASP5 traces each water quality constituent from the point of spatial and temporal input to its final point of export, conserving mass in space and time. To perform these mass balance computations, the user must supply WASP5 with input data defining seven important characteristics:

> simulation and output control
> model segmentation
> advective and dispersive transport
> boundary concentrations
> point and diffuse source waste loads
> kinetic parameters, constants, and time functions
> initial concentrations

These input data, together with the general WASP5 mass balance equations and the specific chemical kinetics equations, uniquely define a special set of water quality equations. These are numerically integrated by WASP5 as the simulation proceeds in time. At user-specified print intervals, WASP5 saves the values of all display variables for subsequent retrieval by the post-processor programs W4DSPLY and W4PLOT. These programs allow the user to interactively produce graphs and tables of variables of all display variables.

1.3 THE GENERAL MASS BALANCE EQUATION

A mass balance equation for dissolved constituents in a body of water must account for all the material entering and leaving through direct and diffuse loading; advective and dispersive transport; and physical, chemical, and biological transformation. Consider the coordinate system shown in Figure 1.2, where the x- and y-coordinates are in the horizontal plane, and the
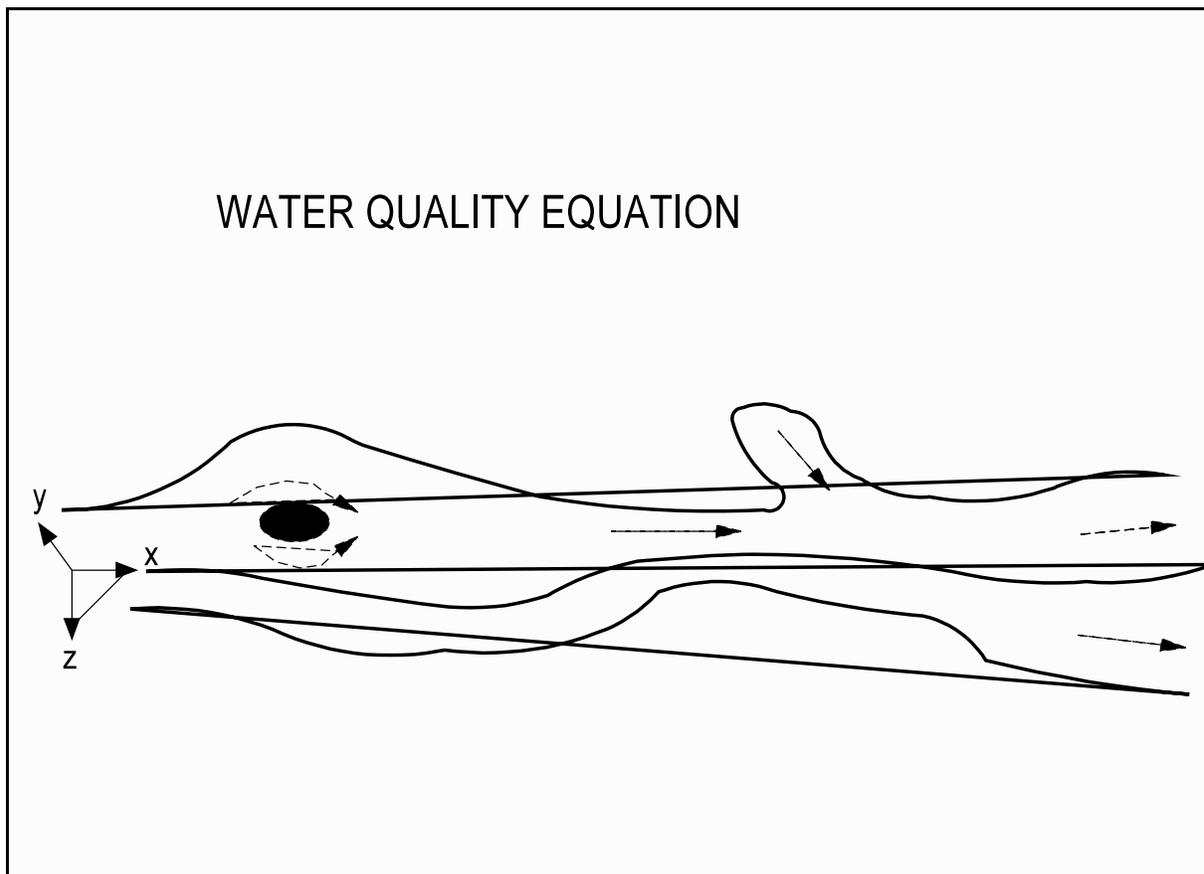
Figure 1.2 Coordinate system for mass balance equation.

z-coordinate is in the vertical plane. The mass balance equation around an infinitesimally small fluid volume is:

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(U_x\, C) - \frac{\partial}{\partial y}(U_y\, C) - \frac{\partial}{\partial z}(U_z\, C)$$

$$+ \frac{\partial}{\partial x}\left(E_x\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y\frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(E_z\frac{\partial C}{\partial z}\right) \qquad \textbf{1.1}$$

$$+ S_L + S_B + S_K$$

where:

       C =   concentration of the water quality constituent, mg/L or g/m^3

       t =   time, days

       U_x, U_y, U_z =   longitudinal, lateral, and vertical advective velocities, m/day

       E_x, E_y, E_z =   longitudinal, lateral, and vertical diffusion coefficients, m^2/day

       S_L =   direct and diffuse loading rate, g/m^3-day

       S_B =   boundary loading rate (including upstream, downstream, benthic, and atmospheric), g/m^3-day

       S_K =   total kinetic transformation rate; positive is source, negative is sink, g/m^3-day

By expanding the infinitesimally small control volumes into larger adjoining "segments," and by specifying proper transport, loading, and transformation parameters, WASP implements a finite-difference form of equation 1.1. For brevity and clarity, however, the derivation of the finite-difference form of the mass balance equation will be for a one-dimensional reach. Assuming vertical and lateral homogeneity, we can integrate equation 1.1 over y and z to obtain

$$\frac{\partial}{\partial t}(AC) = \frac{\partial}{\partial x}\left(-U_x AC + E_x A \frac{\partial C}{\partial x}\right) + A(S_L + S_B) + AS_K \qquad \textbf{1.2}$$

where:

       A   =   cross-sectional area, m^2

This equation represents the three major classes of water quality processes -- transport (term 1), loading (term 2), and transformation (term 3). The finite-difference form is derived in Appendix E. The model network and the major processes are discussed in the following sections.

1.4 THE MODEL NETWORK

The model network is a set of expanded control volumes, or "segments," that together represent the physical configuration of the water body. As Figure 1.3 illustrates, the network may subdivide the water body laterally and vertically as well as longitudinally. Benthic segments can be included along with water column segments. If the water quality model is being linked to the hydrodynamic model, then water column segments must correspond to the hydrodynamic junctions. Concentrations of
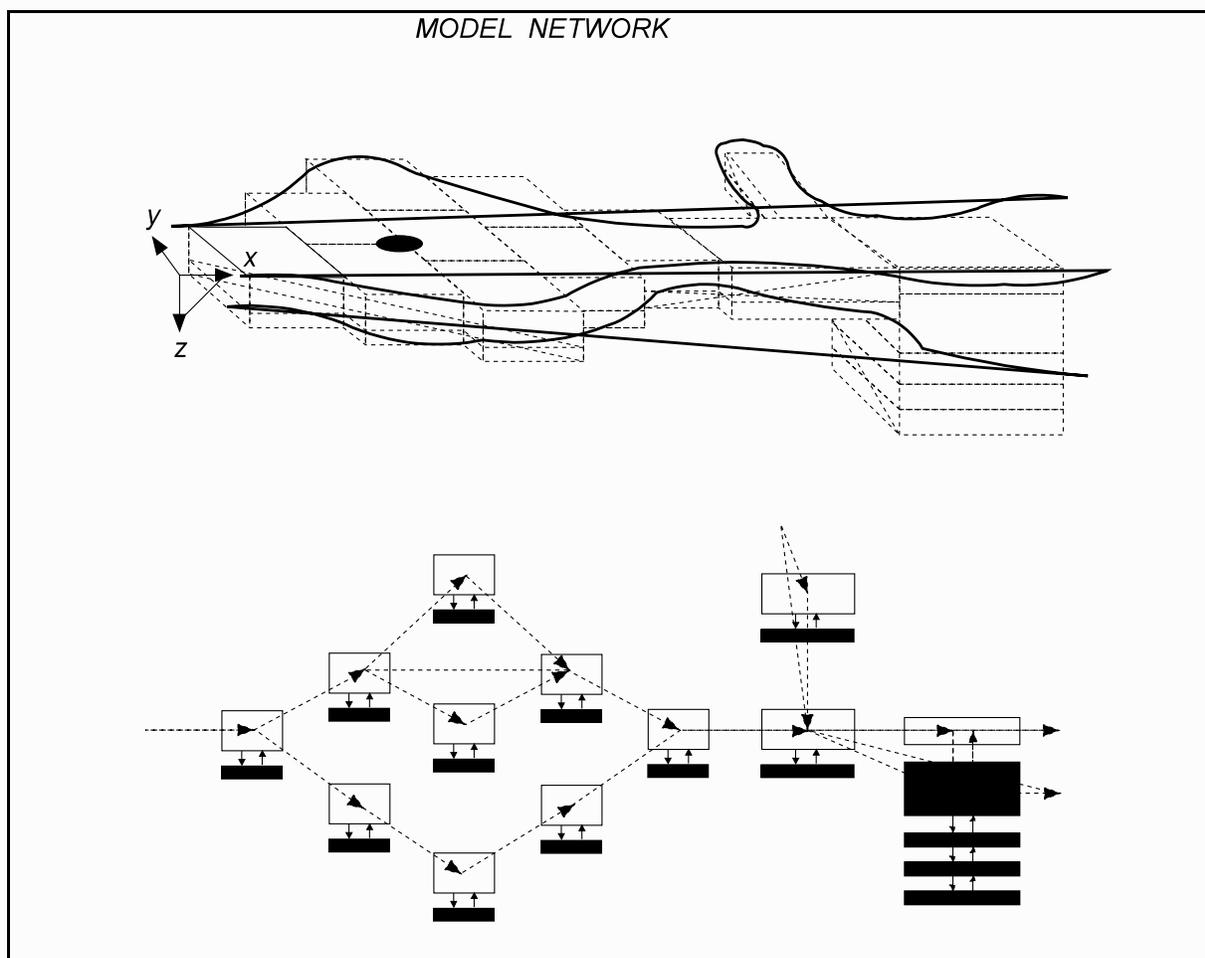
Figure 1.3 Model segmentation.

MODEL DESIGNATION		NUMBER OF SEGMENTS	HORIZONTAL SCALE (km^2) EPILIMNION SEGMENTS
LAKE 1		2	13,000
LAKE 3		67	200-1000
ROCHESTER EMBAYMENT		72	10-100
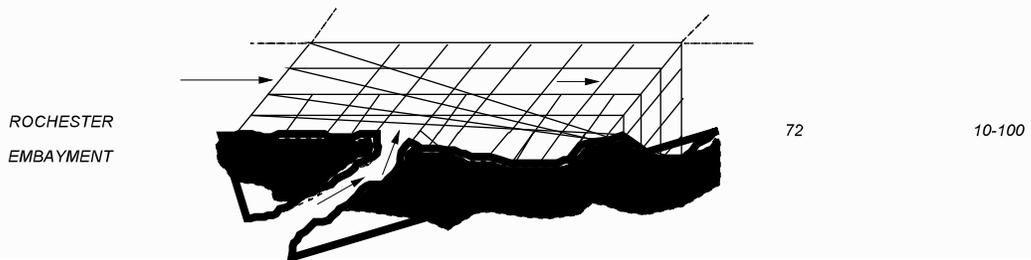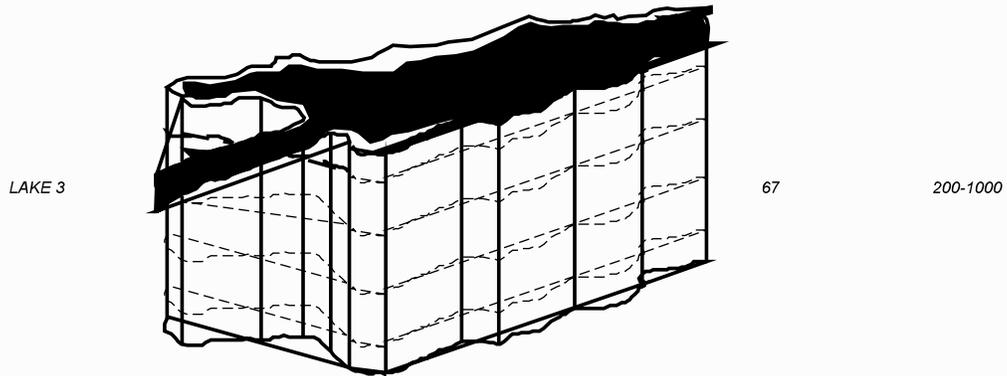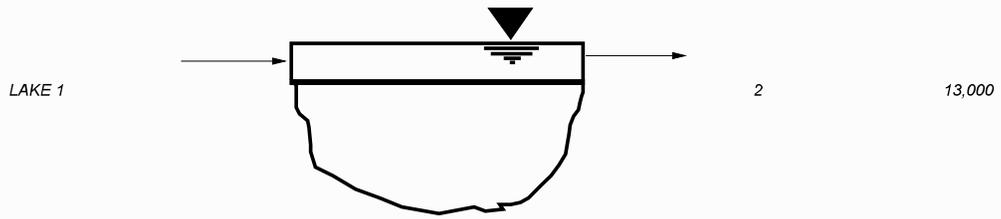
Figure 1.4 Spatial scales used in Lake Ontario analysis.

water quality constituents are calculated within each segment. Transport rates of water quality constituents are calculated across the interface of adjoining segments.

Segments in WASP may be one of four types, as specified by the input variable ITYPE. A value of 1 indicates the epilimnion (surface water), 2 indicates hypolimnion layers (subsurface), 3 indicates an upper benthic layer, and 4 indicates lower benthic layers. The segment type plays an important role in bed sedimentation and in certain transformation processes. The user should be careful to align segments properly. The segment immediately below each segment is specified by the input variable IBOTSG. This alignment is important when light needs to be passed from one segment to the next in the water column, or when material is buried or eroded in the bed.

As part of the problem definition, the user must determine how much of the water quality frequency distribution must be predicted. For example, a daily-average dissolved oxygen concentration of 5 mg/L would not sufficiently protect fish if fluctuations result in concentrations less than 2 mg/L for 10% of the time. Predicting extreme concentration values is generally more difficult than predicting average values. Figure 1.5 illustrates typical frequency distributions predicted by three model time scales and a typical distribution observed by rather thorough sampling as they would be plotted on probability paper. The straight lines imply normal distributions. Reducing the model time step (and consequently segment size) allows better simulation of the frequency distribution. This increase in predictive ability, however, also entails an increase in the resolution of the input data.

Once the nature of the problem has been determined, then the temporal variability of the water body and input loadings must be considered. Generally, the model time step must be somewhat less than the period of variation of the important driving variables. In some cases, this restriction can be relaxed by averaging the input over its period of variation. For example, phytoplankton growth is driven by sunlight, which varies diurnally. Most eutrophication models, however, average the light input over a day, allowing time steps on the order of a day.

Care must be taken so that important non-linear interactions do not get averaged out. When two or more important driving variables have a similar period of variation, then averaging may not be possible. One example is the seasonal variability of light, temperature, nutrient input, and transport in lakes subject to eutrophication. Another example involves discontinuous batch discharges. Such an input into a large lake might safely be averaged over a day or week, because large scale transport variations are relatively infrequent. The same batch input into a tidal estuary cannot safely be averaged, however,

FREQUENCY DISTRIBUTION OF OBSERVED AND

CALCULATED VALUES OF A QUALITY VARIABLE

OBSERVED

TIME SCALE 2

TIME SCALE1

STEADY-STATE

WATER QUALITY VARIABLE

5   50   95

CUMULATIVE PROBABILITY
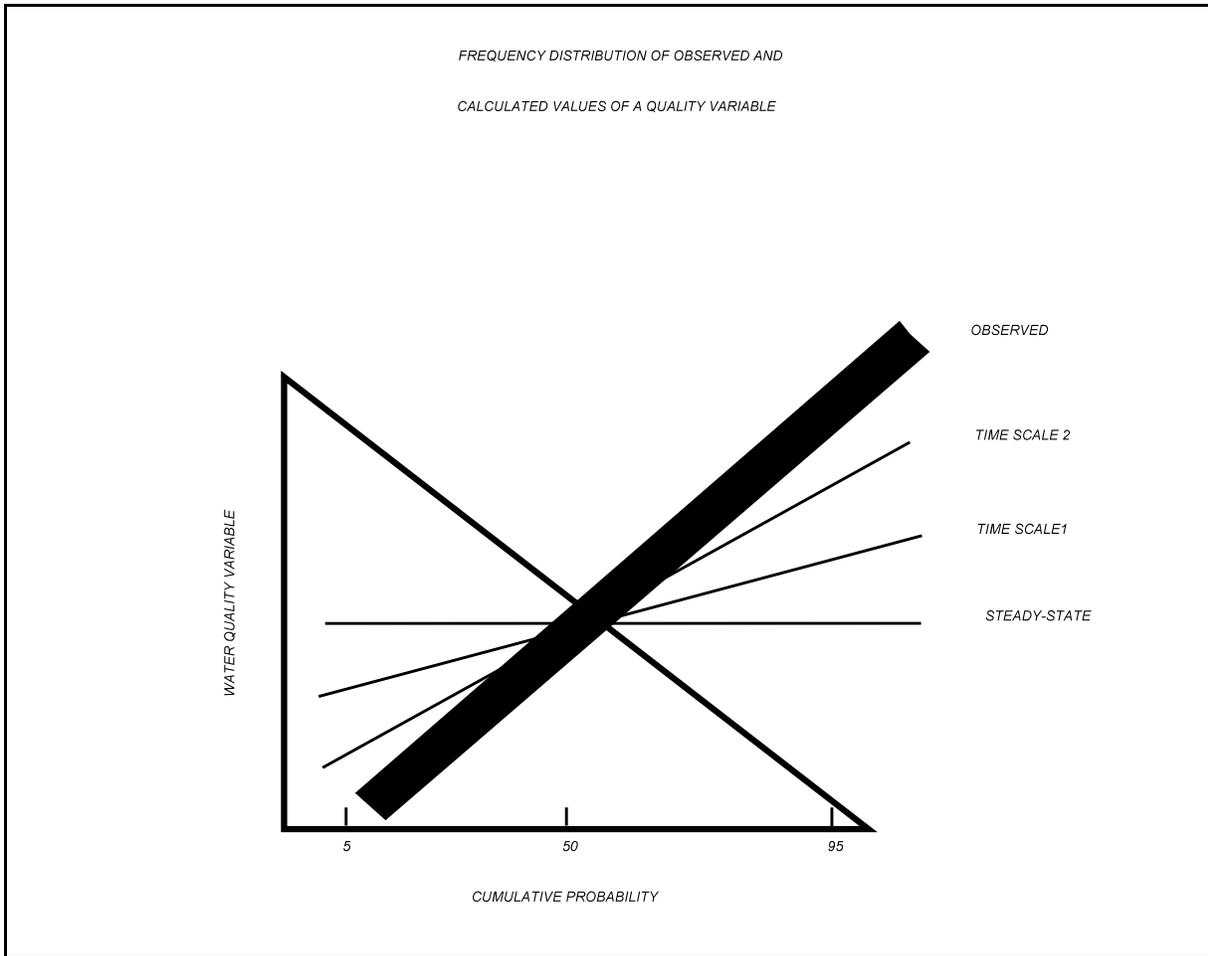
Figure 1.5   Frequency distribution of observed and calculated values of a quality variable.

because of the semi-diurnal or diurnal tidal variations. A third example is salinity intrusion in estuaries. Tidal variations in flow, volume, and dispersion can interact so that accurate long-term predictions require explicit simulation at time steps on the order of hours.

Once the temporal variability has been determined, then the spatial variability of the water body must be considered. Generally, the important spatial characteristics must be homogeneous within a segment. In some cases, this restriction can be relaxed by judicious averaging over width, depth, and/or length. For example, depth governs the impact of reaeration and sediment oxygen demand in a column of water. Nevertheless, averaging the depth across a river would generally be acceptable in a conventional waste load allocation, whereas averaging the depth across a lake would not generally be acceptable. Other important spatial characteristics to consider (depending upon the problem being analyzed) include temperature, light penetration,

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velocity, pH, benthic characteristics or fluxes, and sediment concentrations.

The expected spatial variability of the water quality concentrations also affects the segment sizes. The user must determine how much averaging of the concentration gradients is acceptable. Because water quality conditions change rapidly near a loading point and stabilize downstream, studying the effects on a beach a quarter-mile downstream of a discharge requires smaller segments than studying the effects on a beach several miles away.

A final, general guideline may be helpful in obtaining accurate simulations: water column volumes should be roughly the same. If flows vary significantly downstream, then segment volumes should increase proportionately. The user should first choose the proper segment volume and time step in the critical reaches of the water body (V_c, t_c), then scale upstream and downstream segments accordingly:

$$V_i = V_c \, Q_i / Q_c \qquad\qquad\qquad \textbf{1.3}$$

Of course, actual volumes specified must be adjusted to best represent the actual spatial variability, as discussed above. This guideline will allow larger time steps and result in greater numerical accuracy over the entire model network, as explained in the section on "Simulation Parameters" in Chapter 2.

1.5 THE MODEL TRANSPORT SCHEME

Transport includes advection and dispersion of water quality constituents. Advection and dispersion in WASP are each divided into six distinct types, or "fields." The first transport field involves advective flow and dispersive mixing in the water column. Advective flow carries water quality constituents "downstream" with the water and accounts for instream dilution. Dispersion causes further mixing and dilution between regions of high concentrations and regions of low concentrations.

The second transport field specifies the movement of pore water in the sediment bed. Dissolved water quality constituents are carried through the bed by pore water flow and are exchanged between the bed and the water column by pore water diffusion.

The third, fourth, and fifth transport fields specify the transport of particulate pollutants by the settling, resuspension, and sedimentation of solids. Water quality constituents sorbed onto solid particles are transported between the water column and the sediment bed. The three solids fields

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can be defined by the user as size fractions, such as sand, silt, and clay, or as inorganic, phytoplankton, and organic solids.

The sixth transport field represents evaporation or precipitation from or to surface water segments.

Most transport data, such as flows or settling velocities, must be specified by the user in a WASP input dataset. For water column flow, however, the user may "link" WASP with a hydrodynamics model. If this option is specified, during the simulation WASP will read the contents of a hydrodynamic file for unsteady flows, volumes, depths, and velocities.

1.6 MODEL TRANSPORT WITH TIDAL FLOW

Introduction

WASP5 (version 5.1, 1993) computes volume from the advective flow balance and depth as a function of flow from the exponential hydraulic geometry equations. Bottom area for SOD is implicitly computed as volume divided by depth and is equal to the segment surface area. The computed depth may not accurately reflect the actual depth, nor the computed bottom area the actual bottom area. The new transport representation in WASP 5.2-MDEP is intended to fix this.

WASP 5.2-MDEP provides two new options, specified by a new flag IDOPT in Record-1 of Data Block C1 (for detail, please refer to the Users Manual, Part B). The flag, IDOPT = 0 would be the default to WASP5 to preserve backward compatibility and flow would be specified entirely using Data Group D. In WASP5, flows must be specified as a WASP program input, using the DYNHYD program, or by some other means to determine flows a priori.

The flag, IDOPT = 1 would require input of available field data to compute flows in estuarine environments using simple tidal prism calculations based on a user-specified sinusoidal depth function or depth-time functions. The flag IDOPT = 2 would be similar except that only depth, and not flows, are calculated. With all options, flows may still be specified under Data Group D even when the tidal flow calculation is specified. For IDOPT = 0 or 2, the specified flows are those used in the WASP calculations. For IDOPT = 1, tidal flow volumes are adjusted to account for the flows specified under Data Group D. An automatic internal calculation of a sinusoidal depth-time variation is included in WASP 5.2-MDEP.

Tidal Flow Calculation

The tidal prism is the volume of water between low and high tide levels or between the high tide elevation and the bottom of the tidal waterway. Advective flow computations based on the

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tidal prism were added to the model to capture the ebb and flood tide elevations. The ebb and flood tide elevations can be approximated by a sine curve. A sine curve starts at mean water level at time zero but with a phase lag can be structured to start at any point in the tidal cycle. The equation for tide elevation is:

$$y = a \sin \theta + z$$
<div align="right">**1.4**</div>

where, y = elevation of tide above mean water level at a given time, t; a = maximum amplitude of elevation (ASEGD in the computer program inputs) of the tide or storm surge defined as half the tidal range or half the height of the storm surge;   = angle subdividing the tidal cycle, one tidal cycle is equal to 360° or 2 ; and Z = mean water (mean tide) elevation (DSEGD) at a particular segment.

Where,

$$\theta = 2\pi[(t - \phi_1 - \phi_2)/\lambda]$$
<div align="right">**1.5**</div>

and,

t = time; $_1$ = phase lag (PHASED) = time lag of sinusoidal depth-time function; $_2$ = time lag (TSEGD) = time lag of tidal range at a particular model segment; and   = tidal period (PERD) = total time for one complete tidal cycle.

The computation of flow based on tidal prism calculation using depth computed either from sinusoidal depth-time variation or from user specified depth-time functions is as follows:

Step 1:   The model computes the depth (say, D_{new}) at any given time (say, $t+\Delta t$) using equation 1.4 or a user specified depth-time function.

Step 2:   Based on the computed depth, D_{new} the model determines the change in depth using the available depth from previous time step as follows:
  $D = D_{new} - D_{old}$

Step 3:   Based on the computed change in depth, D the model determines the change in volume, V, in a particular segment at time, $t+ t$ as follows:

$$V = D * A$$
where A = surface area.

Step 4   Based on the computed change in volume, V the model determines the rate of change of storage, S, in a particular segment at time, $t + t$ as follows:
$$S/ t \approx dS/dt = V/ t$$

Step 5   At last the model applies continuity equation 1.6 (conservation of mass applied to a fluid volume) to a particular model segment and solves the equation for tidal flow at time, $t + t$ as follows:

$$Q_{Tidal} = dS/dt - Q_{In} + Q_{Out} \qquad\qquad \textbf{1.6}$$

where, Q_{tidal} is the computed tidal flow; Q_{in} is the inflow associated with non-tidal flows (such as fresh-water inflow); and Q_{out} is the outflow associated with non-tidal flows.

1.7 APPLICATION OF THE MODEL

The first step in applying the model is analyzing the problem to be solved. What questions are being asked? How can a simulation model be used to address these questions? A water quality model can do three basic tasks--describe present water quality conditions, provide generic predictions, and provide site-specific predictions. The first, descriptive task is to extend in some way a limited site-specific data base. Because monitoring is expensive, data seldom give the spatial and temporal resolution needed to fully characterize a water body. A simulation model can be used to interpolate between observed data, locating, for example, the dissolved oxygen sag point in a river or the maximum salinity intrusion in an estuary. Of course such a model can be used to guide future monitoring efforts. Descriptive models also can be used to infer the important processes controlling present water quality. This information can be used to guide not only monitoring efforts, but also model development efforts.

Providing generic predictions is a second type of modeling task. Site-specific data may not be needed if the goal is to predict the types of water bodies at risk from a new chemical. A crude set of data may be adequate to screen a list of chemicals for potential risk to a particular water body. Generic predictions may sufficiently address the management problem to be

solved, or they may be a preliminary step in detailed site-specific analyses.

Providing site-specific predictions is the most stringent modeling task. Calibration to a good set of monitoring data is definitely needed to provide credible predictions. Because predictions often attempt to extrapolate beyond the present data base, however, the model also must have sufficient process integrity. Examples of this type of application include waste load allocation to protect water quality standards and feasibility analysis for remedial actions, such as tertiary treatment, phosphate bans, or agricultural best-management practices.

Analysis of the problem should dictate the spatial and temporal scales for the modeling analysis. Division of the water body into appropriately sized segments was discussed in Section "Model Network." The user must try to extend the network upstream and downstream beyond the influence of the waste loads being studied. If this is not possible, the user should extend the network far enough so that errors in specifying future boundary concentrations do not propogate into the reaches being studied.

The user also should consider aligning the network so that sampling stations and points of interest (such as water withdrawals) fall near the center of a segment. Point source waste loads in streams and rivers with unidirectional flow should be located near the upper end of a segment. In estuaries and other water bodies with oscillating flow, waste loads are best centered within segments. If flows are to be input from DYNHYD5, then a WASP5 segment must coincide with each hydrodynamic junction. Benthic segments, which are not present in the hydrodynamic network, may nevertheless be included in the WASP5 network. WASP5 segment numbering does not have to be the same as DYNHYD5 junction numbering. Segments stacked vertically do not have to be numbered consecutively from surface water segments down.

Once the network is set up, the model study will proceed through four general steps involving, in some manner, hydrodynamics, mass transport, water quality transformations, and environmental toxicology. The first step addresses the question of where the water goes. This can be answered by a combination of gaging, special studies, and hydrodynamic modeling. Flow data can be interpolated or extrapolated using the principle of continuity. Very simple flow routing models can be used; very complicated multi-dimensional hydrodynamic models can also be

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used with proper averaging over time and space. At present, the most compatible hydrodynamic model is DYNHYD5.

The second step answers the question of where the material in the water is transported. This can be answered by a combination of tracer studies and model calibration. Dye and salinity are often used as tracers.

The third step answers the question of how the material in the water and sediment is transformed and what its fate is. This is the main focus of many studies. Answers depend on a combination of laboratory studies, field monitoring, parameter estimation, calibration, and testing. The net result is sometimes called model validation or verification, which are elusive concepts. The success of this step depends on the skill of the user, who must combine specialized knowledge with common sense and skepticism into a methodical process.

The final step answers the question of how this material is likely to affect anything of interest, such as people, fish, or the ecological balance. Often, predicted concentrations are simply compared with water quality criteria adopted to protect the general aquatic community. Care must be taken to insure that the temporal and spatial scales assumed in developing the criteria are compatible with those predicted by the model. Sometimes principles of physical chemistry or pharmacokinetics are used to predict chemical body burdens and resulting biological effects. The biaccumulation model FGETS (Barber, et al., 1991) and the WASTOX food chain model (Connolly and Thomann, 1985) are good examples of this.

CHAPTER 2

CHEMICAL TRACER TRANSPORT

2.1 MODEL DESCRIPTION

<u>Introduction</u>

A chemical tracer is a nonreactive chemical that is passively transported throughout the water body. Examples include salinity or chlorides. Special dyes are used as tracers, although these often decay at a slow rate. Setting up and calibrating a tracer is the first step in simulating more complex water quality variables.

<u>Overview of WASP5 Tracer Transport</u>

A conservative tracer is generally simulated using the TOXI5 program. TOXI5 simulates the transport and transformation of one to three chemicals and one to three types of solids classes (Table 2.1). To simulate a tracer, the user should bypass solids and simulate chemical 1 with no decay. A tracer is affected by transport, boundary, and loading processes only, as described below.

WASP5 uses a mass balance equation to calculate chemical mass and concentrations for every segment in a specialized network that may include surface water, underlying water, surface bed, and underlying bed. Simulated chemicals undergo several transport processes as specified by the user in the input dataset. Chemicals are advected and dispersed among water segments, and exchanged with surficial benthic segments by

Table 2.1 WASP5 State Variables for Toxicants.

SYSTEM	VARIABLE
1	CHEMICAL 1
2	SOLIDS 1
3	SOLIDS 2
4	SOLIDS 3
5	CHEMICAL 2
6	CHEMICAL 3

dispersive mixing. Dissolved chemicals migrate downward or
upward through percolation and pore water diffusion.

The transport, boundary, and loading processes for tracer
chemicals are described below. These same processes are also
applied to the water quality variables desribed in subsequent
chapters.

Transport Processes

Water Column Advection

Advective water column flows directly control the transport
of dissolved and particulate pollutants in many water bodies. In
addition, changes in velocity and depth resulting from variable
flows can affect such kinetic processes as reaeration,
volatilization, and photolysis. An important early step in any
modeling study is to describe or simulate water column advection
properly. In WASP5, water column flow is input via transport
field one in Data Group D. Circulation patterns may be described
(flow options 1 and 2) or simulated by a hydrodynamic model, such
as DYNHYD5 (flow option 3). Flow options are specified in the
first record of Data Group D.

For descriptive flows, WASP5 tracks each separate inflow
specified by the user from its point of origin through the model
network. For each inflow, the user must supply a continuity or
unit flow response function and a time function. The time
function describes the inflow as it varies in time. The
continuity function describes the unit flow response as it varies
throughout the network. The actual flow between segments that
results from the inflow is the product of the time function and
the continuity function.

If several inflow functions are specified, then the total
flow between segments is the sum of the individual flow
functions. Segment volumes are adjusted to maintain continuity.
In this manner, the effect of several tributaries, density
currents, and wind-induced gyres can be described.

In flow option 1, WASP5 sums all the flows at a segment
interface to determine the direction of net flow, and then moves
mass in the **ONE** direction. In flow option 2, WASP5 moves mass
independently of net flow. For example, if opposite flows are
specified at an interface, WASP5 will move mass in **BOTH**
directions. This option allows the user to describe large
dispersive circulation patterns.

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Hydrodynamic Linkage

    For unsteady flow in long networks, lag times may become
significant, and hydrodynamic simulations may be necessary to
obtain sufficient accuracy. Realistic simulations of unsteady
transport can be accomplished by linking WASP5 to a compatible
hydrodynamic simulation. This linkage is accomplished through an
external file chosen by the user at simulation time. The
hydrodynamic file contains segment volumes at the beginning of
each time step, and average segment interfacial flows during each
time step. WASP5 uses the interfacial flows to calculate mass
transport, and the volumes to calculate constituent
concentrations. Segment depths and velocities may also be
contained in the hydrodynamic file for use in calculating
reaeration and volatilization rates.

    The first step in the hydrodynamic linkage is to develop a
hydrodynamic calculational network that is compatible with the
WASP5 network. The easiest linkage is with link-node
hydrodynamic models that run on equivalent spatial networks. An
example is given in Figure 2.1. Note that each WASP5 segment
corresponds exactly to a hydrodynamic volume element, or node.
Each WASP5 segment interface corresponds exactly to a
hydrodynamic link, denoted in the figure with a connecting line.

    The hydrodynamic model calculates flow through the links and
volume within the nodes. Within the hydrodynamic model, the user
must specify the water quality time step, or the number of
hydrodynamic time steps per water quality time step. The
hydrodynamic model must then write out node volumes at the
beginning of each water quality time step, and average link flows
during each water quality time step. A network map such as the
one in Figure 2.1 must be supplied by the user in the
hydrodynamic model or in an external interface program. This map
is used to create a hydrodynamic file that WASP5 can read and
interpret. The hydrodynamic model DYNHYD5, supplied with WASP5,
contains subroutines to produce a proper WASP5 hydrodynamic file.

    It is important to note that the hydrodynamic model has
additional nodes outside of the WASP5 network. These additional
nodes correspond to WASP5 boundaries, denoted by nominal segment
number "0." These extra hydrodynamic nodes are necessary because
while flows are calculated only within the hydrodynamic network,
WASP5 requires boundary flows from outside its network.

    Multidimensional hydrodynamic models can also be linked to
WASP5. A compatible two-dimensional network is illustrated in
Figure 2.2. For the beginning of each water quality time step,

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Link-Node
Hydrodynamic
Network

WASP5
Network

Network Mapping	
Hydrodynamic Volume Elements	WASP4 Segments
1	0
2	1
3	2
4	3
5	4
6	5
7	6
8	7
9	0
10	8
11	0
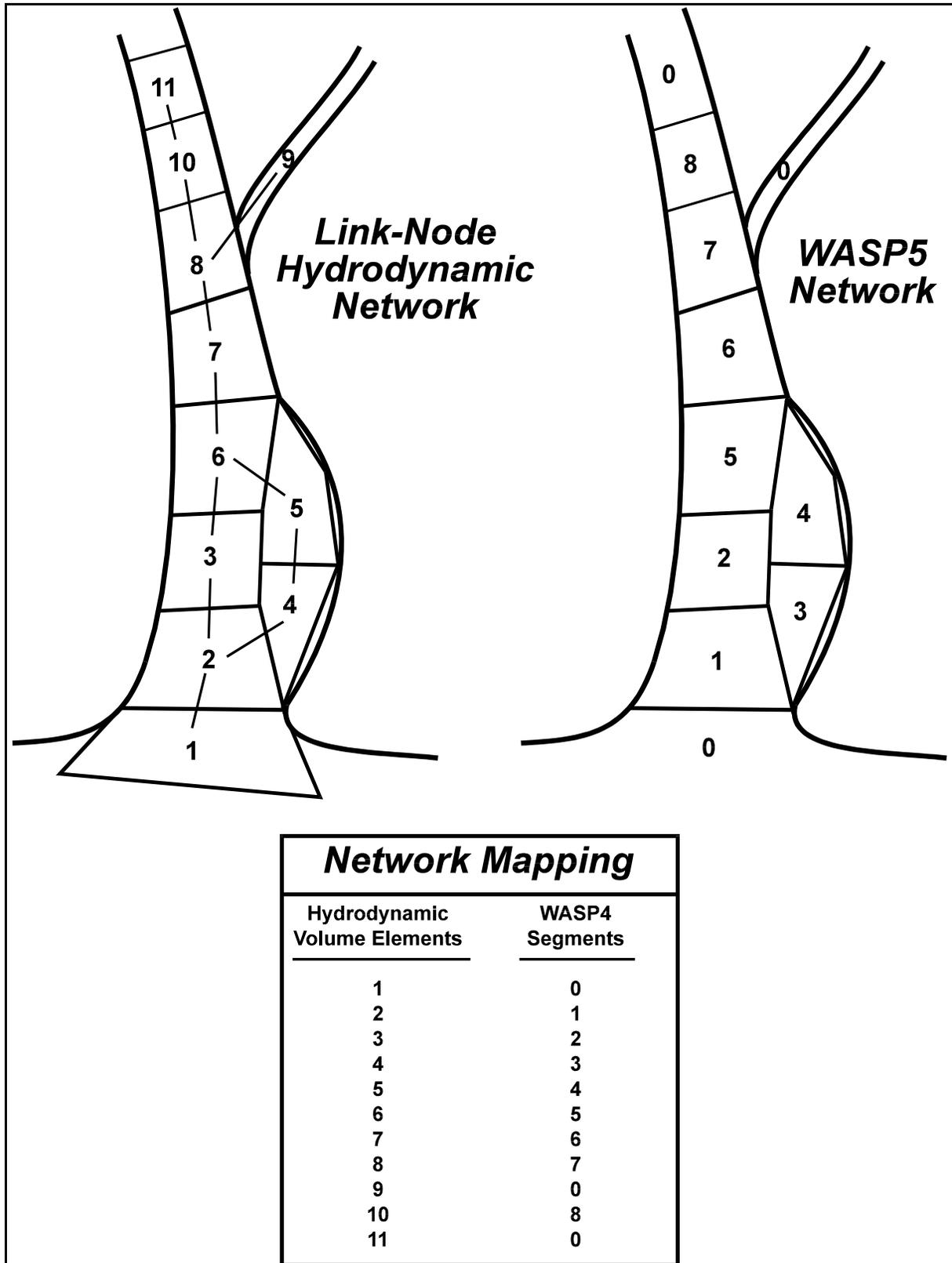
Figure 2.1   Link-node hydrodynamic linkage.

the volumes within a WASP5 segment must be summed and written to the hydrodynamic file. For the duration of each water quality time step, flows across the WASP5 segment boundaries must be averaged. All of the averaged flows across a boundary must then be summed and written to the hydrodynamic file. Again, it is important to note the presence of hydrodynamic elements outside the WASP5 network generating boundary flows.

To implement the hydrodynamic linkage, the user must specify flow option 3 in the input dataset. If IQOPT is set to 3, a menu of previously prepared hydrodynamic files (*.HYD) is presented.
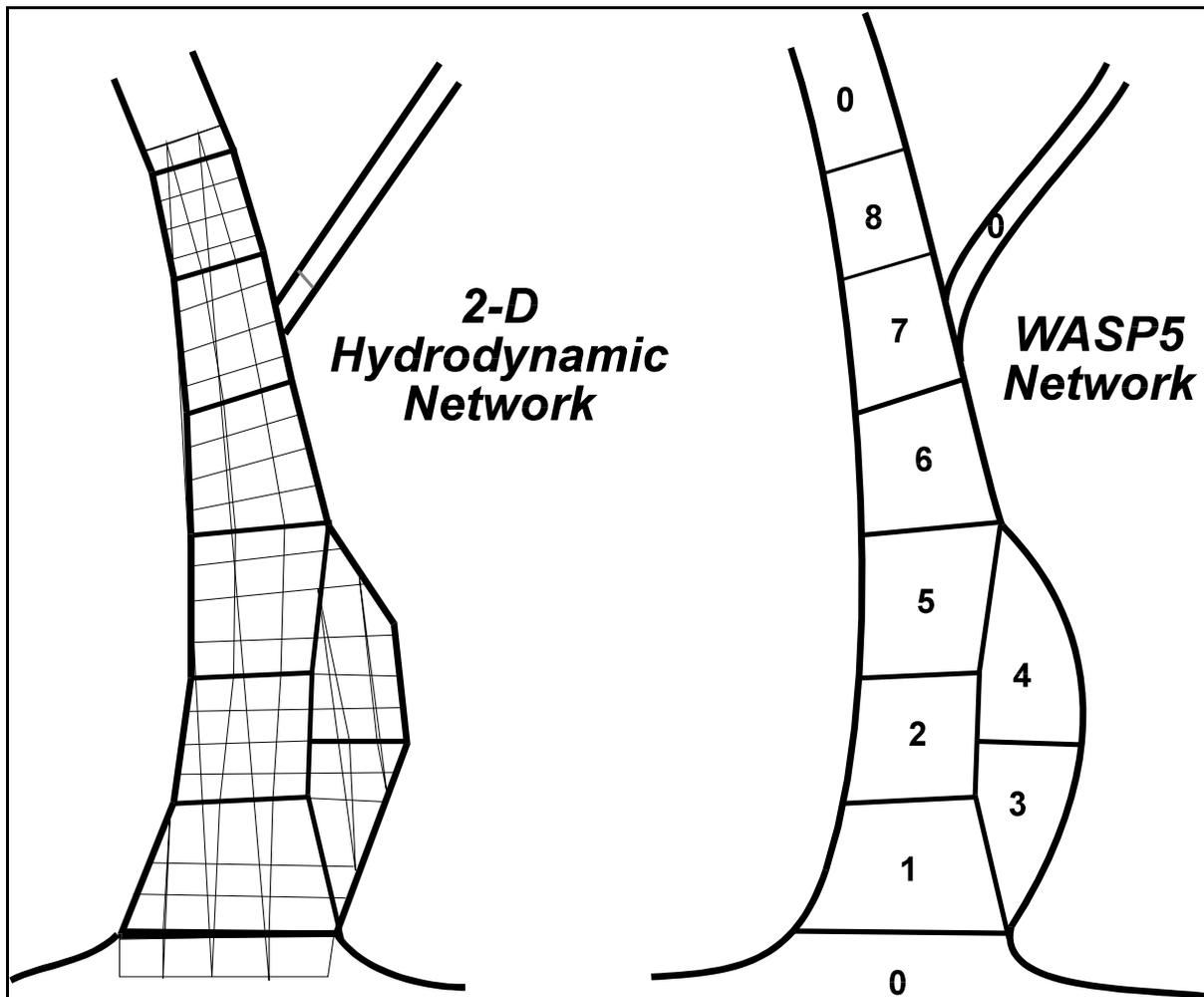
Figure 2.2 Multidimensional hydrodynamic linkage.

Following the choice of a proper file, the simulation time step will be reset by the hydrodynamic file. The time steps read in Data Group A will be ignored. Similarly, water column segment volumes will be read from the hydrodynamic file. The user must nevertheless enter a time step and volumes for each segment in the usual location. During the simulation, flows and volumes are read every time step.

The contents and format of the hydrodynamic file are detailed in Part B, The WASP5 Input Dataset, Section 5.2.

Hydraulic Geometry

A good description of segment geometry as a function of flow conditions can be important in properly using WASP5 to simulate rivers. For flow option 3, velocity and depth are computed within the hydrodynamic model, and are read by WASP5. For flow options 1 and 2, a set of user-specified hydraulic discharge coefficients from Data Group C defines the relationship between velocity, depth, and stream flow in the various segments. This method, described below, follows the implementation in QUAL2E (Brown and Barnwell, 1987). In WASP5, these segment velocities and depths are only used for calculations of reaeration and volatilization rates; they are not used in the transport scheme.

Discharge coefficients giving depth and velocity from stream flow are based on empirical observations of the stream flow relationship with velocity and depth (Leopold and Maddox, 1953). It is important to note that these coefficients are only important when calculating reaeration or volatilization. The velocity calculations are not used in time of travel, and will not affect the simulation of tracers. The equations relate velocity, channel width, and depth to streamflow through power functions:

$$V = a\, Q^b \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{2.1}$$

$$D = c\, Q^b \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{2.2}$$

$$B = e\, Q^f \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{2.3}$$

where:

D is average depth, m

B is average width, m

a, b, c, d, e, and f are empirical coefficients or exponents

Given that area is a function of average width (B) and average depth (D),

$$A = D\,B \qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{2.4}$$

it is clear from continuity that:

$$Q = U{\cdot}A = U{\cdot}D{\cdot}B = (a\,Q^{b}){\cdot}(c\,Q^{d}){\cdot}(e\,Q^{f}) = (a{\cdot}c{\cdot}e)\,Q^{b+d+f} \qquad \textbf{2.5}$$

and, therefore, the following relationships hold:

$$a\,c\,e = 1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{2.6}$$

$$b + d + f = 1 \qquad\qquad\qquad\qquad\qquad\qquad \textbf{2.7}$$

WASP5 only requires specification of the relationships for velocity, Equation 2.1, and depth, Equation 2.2; the coefficients for Equation 2.3 are implicitly specified by Equations 2.6 and 2.7.

These options can be put into perspective by noting that, for a given specific channel cross-section, the coefficients (a, c, e) and exponents (b, d, f) can be derived from Mannings equation. For example, if a channel of rectangular cross-section is assumed, then width (B) is not a function of streamflow (Q), the exponent (f) is zero (0.00) and the coefficient (e) is the width of the rectangular channel (B). By noting that hydraulic radius (R) is approximately equal to depth (D) for wide streams and that A = D B, the discharge coefficients for rectangular cross sections can be shown to be 0.4 for velocity and 0.6 for width.

Leopold et al. (1964) have noted that stream channels in humid regions tend towards a rectangular cross-section because

cohesive soils promote steep side slopes whereas noncohesive soils encourage shallow sloped, almost undefined banks.

Table 2.2 Comparison of Hydraulic Exponents

Channel Cross-Section	Exponent for (b) Velocity	Exponent for (d) Depth	Exponent for (f) Width
Rectangular	0.40	0.60	0.00
Average of 158 U.S. Gaging Stations	0.43	0.45	0.12
Average of 10 Gaging Stations on Rhine River	0.43	0.41	0.13
Ephemeral Streams in Semiarid U.S.	0.34	0.36	0.29

Table 2.2 compares hydraulic exponents for a rectangular channel with data reported by Leopold et al. (1964). Note that the average velocity exponent is relatively constant for all channel cross sections. The major variation occurs as a decrease in the depth exponent and concomitant increase in the width exponent as channel cross-sections change from the steep side slopes characteristic of cohesive soils to the shallow slopes of arid regions with noncohesive soils.

For bodies of water such as ponds, lakes, and reservoirs, velocity and depth may not be a function of flow. For these cases, both the velocity and depth exponents (b and d) can be chosen to be zero (0.00). Because Q to the zero power is equal to one (1.0), the coefficients a and c must be the velocity and depth, i.e.,

IF b = 0.0   THEN a = V, and

IF d = 0.0   THEN c = D.

When the depth exponent is zero, WASP5 will adjust segment depths with segment volumes assuming rectangular sides.

For site-specific river or stream simulations, hydraulic coefficients and exponents must be estimated. Brown and Barnwell

(1987) recommended estimating the exponents (b and d) and then calibrating the coefficients (a and c) to observed velocity and depth. The exponents may be chosen based on observations of channel shape noted in a reconnaissance survey. If cross sections are largely rectangular with vertical banks, the first set of exponents shown in Table 2.2 should be useful. If channels have steep banks typical of areas with cohesive soils, then the second set of exponents is appropriate. If the stream is in an arid region with typically noncohesive soils and shallow sloping banks, then the last set of exponents is recommended.

The key property of the channel that should be noted in a reconnaissance survey is the condition of the bank slopes or the extent to which width would increase with increasing streamflow. Clearly the bank slopes and material in contact with the streamflow at the flow rate(s) of interest are the main characteristics to note in a reconnaissance. Table 2.2 gives general guidance but it should be noted that values are derived for bankful flows. Even in streams with vertical banks, the low flows may be in contact with a sand bed having shallow sloped, almost nonexistent banks more representative of ephemeral streams in semi-arid areas.

Pore Water Advection

Pore water flows into or out of the bed can significantly influence benthic pollutant concentrations. Depending on the direction of these flows and the source of the pollutants, pore water advection may be a source or sink of pollutants for the overlying water column.

If benthic segments are included in the model network, the user may specify advective transport of dissolved chemicals in the pore water. In WASP5, pore water flows are input via transport field two. Pore water advection transports water and dissolved chemical; sediment and particulate chemical are not transported. The mass derivative of chemical due to pore water flow from segment j to segment i is given by:

$$\frac{\partial M_{ik}}{\partial t} = Q_{ji} \; f_{Dj} \; C_{jk}/n_j \qquad\qquad\qquad \textbf{2.8}$$

where:

M_{ik} = mass of chemical "k" in segment "i," g

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C_{jk} = total concentration of chemical "k" in segment "j," mg/L (g/m^3)

n_j = porosity of segment j, L_w/L

f_{Dj} = dissolved fraction of chemical in segment "j"

Q_{ji} = pore water flow rate from j to i, m^3/day

Dissolved fractions f_D may be input by the user in Data Group J. In TOXI5, these are recomputed from sorption kinetics each time step.

WASP5 tracks each separate pore water inflow through the benthic network. For each inflow (or outflow), the user must supply a continuity function and a time function. The actual flow through benthic segments that results from each inflow is a product of the time function and the continuity function. If a flow originates in or empties into a surface water segment, then a corresponding surface water flow function must be described in flow field 1 that matches the pore water function.

Water Column Dispersion

Dispersive water column exchanges significantly influence the transport of dissolved and particulate pollutants in such water bodies as lakes, reservoirs, and estuaries. Even in rivers, longitudinal dispersion can be the most important process diluting peak concentrations that may result from unsteady loads or spills. Natural or artificial tracers such as dye, salinity, or even heat are often used to calibrate dispersion coefficients for a model network.

In WASP5, water column dispersion is input via transport field one in Data Group B. Several groups of exchanges may be defined by the user. For each group, the user must supply a time function giving dispersion coefficient values (in m^2/sec) as they vary in time. For each exchange in the group, the user must supply an interfacial area, a characteristic mixing length, and the adjoining segments between which the exchange takes place. The characteristic mixing length is typically the distance between the segment midpoints. The interfacial area is the area normal to the characteristic mixing length shared by the exchanging segments (cross-sectional area for horizontal exchanges, or surface area for vertical exchanges). The actual

dispersive exchange between segments i and j at time t is given by:

$$\frac{\partial M_{ik}}{\partial t} = \frac{E_{ij}(t) \cdot A_{ij}}{L_{cij}} (C_{jk} - C_{ik})$$ **2.9**

where:

M_{ik} =   mass of chemical "k" in segment "i," g

C_{ik}, C_{jk} =   concentration of chemical "k" in segment "i" and "j," mg/L (g/m^3)

$E_{ij}(t)$ =   dispersion coefficient time function for exchange "ij", m^2/day

A_{ij} =   interfacial area shared by segments "i" and "j," m^2

L_{cij} =   characteristic mixing length between segments "i" and "j," m

Pore Water Diffusion

Diffusive pore water exchanges can significantly influence benthic pollutant concentrations, particularly for relatively soluble chemicals and water bodies with little sediment loading. Depending on the dissolved concentration gradient, pore water diffusion may be a source or sink of pollutants for the overlying water column.

If benthic segments are included in the model network, the user may specify diffusive transport of dissolved chemicals in the pore water. In WASP5, pore water diffusion is input via transport field two in Data Group B. Several groups of exchanges may be defined by the user.

For each exchange group, the user must supply a time function giving dispersion coefficient values (in m^2/sec) as they vary in time. For each exchange in the group, the user must supply an interfacial area, a characteristic mixing length, and the segments between which exchange takes place. The characteristic mixing length is typically the distance between two benthic segment midpoints (multiplied internally by the

tortuosity, which is roughly the inverse of porosity). For pore
water exchange with a surface water segment, the characteristic
mixing length is usually taken to be the depth of the surficial
benthic segment.   The interfacial area is the surficial area of
the benthic segment (which is input by the user) multiplied
internally by porosity.

There may be several surficial benthic segments underlying a
water column segment, representing discrete benthic deposits (or
habitats). The concentration of chemical diffusing is the
dissolved fraction per unit pore water volume. The actual
diffusive exchange between benthic segments i and j at time t is
given by:

$$\frac{\partial M_{ik}}{\partial t} = \frac{E_{ij}(t)\ A_{ij}\ n_{ij}}{L_{cij}/n_{ij}} \left(\frac{f_{Djk}\ C_{jk}}{n_j} - \frac{f_{Dik}\ C_{ik}}{n_i} \right) \qquad \textbf{2.10}$$

where:

     f_{Dik}, f_{Djk} =   dissolved fraction of chemical "k" in
                             segments "i" and "j"

     n_{ij} =   average porosity at interface "ij", L_w/L

     $E_{ij}(t)$ =   diffusion coefficient time function for
                             exchange "ij", m^2/day

     A_{ij} =   interfacial area shared by segments "i" and
                             "j," m^2

     L_{cij} =   characteristic mixing length between segments
                             "i" and "j," m

Boundary Processes

A boundary segment is characterized by water exchanges from
outside the network, including tributary inflows, downstream
outflows, and open water dispersive exchanges. WASP5 determines
its boundary segments by examining the advective and dispersive
segment pairs specified by the user. If an advective or
dispersive segment pair includes segment number "0," the other
segment number is a boundary segment. Thus, for advective flows,
the segment pair (0,1) denotes segment 1 as an upstream boundary

segment; segment pair (5,0) denotes segment 5 as a downstream boundary segment.

Boundary concentrations C_{Bik} (mg/L) must be specified for each simulated variable "k" at each boundary segment "i". These concentrations may vary in time. At upstream boundary segments, WASP5 applies the following mass loading rates:

$$V_i S_{Bik} = Q_{0i}(t) \cdot C_{Bik} \qquad\qquad\qquad 2.11$$

where:

S_{Bik}	=	boundary loading rate response of chemical "k" in segment "i," g/m^3-day
V_i	=	volume of boundary segment "i," m^3
$Q_{0i}(t)$	=	upstream inflow into boundary segment "i," m^3/day

At downstream boundary segments, WASP5 applies the following mass loading rates:

$$V_i S_{Bik} = -Q_{i0}(t) \cdot C_{ik} \qquad\qquad\qquad 2.12$$

where:

$Q_{i0}(t)$	=	downstream outflow from boundary segment "i," m^3/day
C_{ik}	=	internal concentration of chemical "k" in segment "i," mg/L

Notice that the specified boundary concentration is not used to calculate the boundary loading rate for the downtream boundary segment. If, however, the downstream outflow becomes negative, it becomes in reality an inflow. In this case, Equation 2.11 applies where $Q_{0i} = -Q_{i0}$.

At exchange boundary segments, WASP5 applies the following mass loading rates:

$$V_i S_{Bi} = \frac{E_{i0}(t) \cdot A_{i0}}{L_{ci0}} (C_{Bk} - C_{ik})$$

<div align="right">2.13</div>

where terms are as defined above. When a boundary concentration exceeds the internal concentration, mass is added to the boundary segment; when the boundary concentration falls below the internal concentration, mass is lost from the boundary segment.

Loading Processes

WASP5 allows the user to specify loading rates for each variable. Two types of loadings are provided for -- point source loads and runoff loads. The first set of loads is specified by the user in the input dataset. The second set of loads is read by WASP5 from a nonpoint source loading file created by an appropriate loading model. Both kinds of loads, in kg/day, are added to the designated segments at the following rates:

$$V_i S_{Lik} = 1000 \cdot L_{ik}(t)$$

<div align="right">2.14</div>

where:

S_{Lik} = loading rate response of chemical "k" in segment "i," g/m^3-day

$L_{ik}(t)$ = loading rate of chemical "k" into segment "i," kg/day

Point source loads are input as a series of loading versus time values. During a simulation, WASP5 interpolates between these points to provide time-variable loadings. The WASP5 calculational time step should be set by the user to a value that is divisible into the difference in time entries in the point source loading functions. If evenly divisible time steps cannot be specified, the user should specify maximum time steps at least 5 times smaller than the point source time entries. If the user is specifying daily load variations, for example, the maximum time step should be 0.2 days.

The user should understand that mass entered as loads is not directly accompanied with inflow. No significant errors are introduced if the inflow associated with a loading is small

compared with the water body flow. If a loading is associated
with significant inflow, then the user should generally enter the
associated flows separately under water column advection, and
treat the loading as a model boundary by specifying the boundary
concentration accompanying the inflow. If a large number of
diffuse loads are being read in, the user can provide for the
incremental flows using a flow continuity function that increases
downstream.

Nonpoint Source Linkage

     Realistic simulations of nonpoint source loadings can be
accomplished by linking WASP5 to a compatible surface runoff
simulation. This linkage is accomplished through a formatted
external file chosen by the user at simulation time. The
nonpoint source loading file contains information on which WASP5
systems and segments receive nonpoint source loads, and a record
of the nonzero loads by system, segment, and day.

     If the user sets the nonpoint source loading flag (Data
Group F, Record 5) to 1, a menu of previously prepared nonpoint
source files (*.NPS) is presented. Following the choice of a
proper file, nonpoint source loads are read once a day throughout
a simulation from a loading file generated by a previous loading
model simulation. These loads are treated as step functions that
vary daily. When the user implements the nonpoint source loading
option, model time steps should be divisible into 1 day. (Time
steps do not have to be exactly divisible into a day; if time
steps are small, any errors associated with carrying the previous
day's loading rate into a new day will be small.)

     The contents and format of the nonpoint source file are
detailed in Part B, The WASP5 Input Dataset, Section 7.2.

Initial Conditions

     Because WASP5 is a dynamic model, the user must specify
initial conditions for each variable in each segment. Initial
conditions include the chemical concentrations at the beginning
of the simulation. The product of the initial concentrations and
the initial volumes give the initial constituent masses in each
segment. For steady simulations, where flows and loadings are
held constant and the steady-state concentration response is
desired, the user may specify initial concentrations that are
reasonably close to what the final concentrations should be. For
dynamic simulations where the transient concentration response is
desired, initial concentrations should reflect measured values at
the beginning of the simulation.

In addition to chemical concentrations, the dissolved fractions must be specified for each segment at the beginning of the simulation. For tracers, the dissolved fractions will normally be set to 1.0. For tracers, as well as dissolved oxygen, eutrophication, and sediment transport, the initial dissolved fractions remain constant throughout the simulation. For organic chemical simulations, the dissolved fraction will be internally calculated from partition coefficients and sediment concentrations.

The density of each constituent must be specified under initial conditions. For tracers, this value should be set to 1.0.

2.2 MODEL IMPLEMENTATION

Introduction

To simulate a tracer with WASP5, use the preprocessor or text editor to create a TOXI5 input file. The preprocessor will create an input file with parameters in the proper fields. Using a text editor, the user must take care to enter parameters into the proper fields. A general description of the input dataset is given in Part B of this document. The model input parameters are organized below as they are presented in the preprocessor. The data group, record number, and input parameter name are also given for reference.

Model Input Parameters

This section summarizes the input parameters that must be specified in order to solve the WASP5 mass balance equation. Input parameters are prepared for WASP5 in four major sections of the preprocessor -- environment, transport, boundaries, and transformations.

Environment Parameters

These parameters define the basic model identity, including the segmentation, and control the simulation.

Simulation Type-- The user must specify which WASP5 model will be run with the dataset. The present choices are "TOXI5" or "EUTRO5." (Group A, Record 1, SIMTYP)

Simulation Titles-- The user may specify a 2-line title for the simulation. This title may include any descriptive information on the water body, time frame, pollutants, simulation parameters, etc. The user may also specify the properly positioned names of the simulation switches input in Record 4. This is for user convenience only. (Group A, Records 1, 2, 3; TITLE1, TITLE2, HEADER)

Number of Segments-- The user must specify the number of segments in the model network. (Group A, Record 4, NOSEG)

Number of Systems-- The user must specify the number of model systems (state variables) in the simulation. In the preprocessor, select "simulate" for Chemical 1, and "bypass" for Chemicals 2 and 3 and Solids 1-3. For bypassed variables, the bypass option SYSBY(I) is set to 1. (Group A, Record 4, NOSYS; Record 10, SYSBY(I))

Restart Option-- The user must specify the restart option, which controls the use of the simulation restart file. This restart file stores the final conditions from a simulation, and can be used to input initial conditions in a sequential simulation. 0 = neither read from nor write to the restart file; 1 = write final simulation results to restart file; 2 = read initial conditions from restart file created by earlier simulation, and write final simulation results to new restart file. The restart file created with Option 1 is named RESTART.OUT. The file restart file read with Option 2 is named x.RST, where x is the same name as used in the primary input file, x.INP. Thus, to use a restart file, the file must renamed from RESTART.OUT to x.RST. (Group A, Record 4, ICFL)

Message Flag-- The user must specify the option controlling messages printed to screen during the simulation. 0 = all messages printed, including data input and simulated concentrations; 1 = simulated concentrations only printed; 2 = no messages printed to screen. (Group A, Record 4, MFLG)

Mass Balance Analysis-- The user should specify the system number for which a global mass balance analysis will be performed. A value of 0 will result in no mass balance table being generated. (Group A, Record 4, JMAS)

Negative Solution Option-- Normally, concentrations are not allowed to become negative. If a predicted concentration at t +
 t is negative, WASP maintains its positive value by instead halving the concentration at time t. The negative solution option lets the user bypass this procedure, allowing negative

concentrations. This may be desirable for simulating dissolved oxygen deficit in the benthos, for example. 0 = prevents negative concentrations; 1 = allows negative concentrations. (Group A, Record 4, NSLN)

Time Step Option-- The user must specify how time steps will be determined during the simulation. 0 = user inputs time step history; 1 = model calculates time step. (Group A, Record 4, INTY)

Advection Factor, dimensionless-- The advection factor   can be specified to modify the finite difference approximation of $\partial c/\partial x$ used in the advection term by WASP. For   = 0, the backward difference approximation is used. This is most stable, and is recommended for most applications. For   = 0.5, the central difference approximation is used. This is unstable in WASP, and is not recommended.

A nonzero advection factor is helpful in situations where the network size and time step produce large numerical dispersion. A nonzero advection factor reduces the numerical dispersion produced by a particular velocity, length, and time step combination. According to Bella and Grenney (1970):

$$E_{num} = \frac{U}{2} \; [(1-2 \; \nu) \; L - U \; \Delta t]$$
2.15

Note that a   of 0 reduces this to Equation 2.20. Values of E_{num} for a length of 2000 meters and various combinations of velocity and time step are provided in Table 2.3. For a particular velocity, say 0.4 m/sec, numerical dispersion can be reduced by increasing the time step. For   = 0, increasing the time step from 1000 to 4000 seconds decreases E_{num} from 320 to 80 m^2/sec. If the time step must be 1000 seconds, however, numerical dispersion can still be reduced by increasing . In this case, increasing   from 0 to 0.4 decreases E_{num} from 320 to 0 m^2/sec. (Group A, Record 4, ADFC)

Initial Time, day, hour, minute-- The time at the beginning of the simulation must be specified in order to synchronize all the time functions. The day, hour, and minute can be input. The beginning of the simulation is day 1. (Group A, Record 4, ZDAY, ZHR, ZMIN)

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Table 2.3 Values of Numerical Dispersion (m^2/sec)

	U (m/sec)					
	0.1	0.2	0.4	0.6	0.8	1.0
t = 1000 sec						
0.0	95	180	320	420	480	500
0.1	75	140	240	300	320	300
0.2	55	100	160	180	160	100
0.3	35	60	80	60	0	--
0.4	15	20	0	--	--	--
t = 2000 sec						
0.0	90	160	240	240	160	0
0.1	70	120	160	120	0	--
0.2	50	80	80	0	--	--
0.3	30	40	0	--	--	--
0.4	10	0	--	--	--	--
t = 4000 sec						
0.0	80	120	80	--	--	--
0.1	60	80	0	--	--	--
0.2	40	40	--	--	--	--
0.3	20	0	--	--	--	--
0.4	0	--	--	--	--	--
t = 8000 sec						
0.0	60	40	--	--	--	--
0.1	40	0	--	--	--	--
0.2	20	--	--	--	--	--
0.3	0	--	--	--	--	--
0.4	--	--	--	--	--	--

Final Time, days--The elapsed time at the end of the simulation must be specified in days (including decimal fraction). The end of the simulation occurs when the final time from the integration time step history is encountered. The final time is entered on the same record as the time step. (Group A, Record 7, T(NOBRK))

Transport Analysis Flag-- The user should specify whether the transport analysis file will be generated during the simulation. A value of 0 causes the file to be generated; a value of 1 prevents the file from being generated. (Group A, Record 4, TFLG)

Runtime Display Segments-- The user must specify up to six segments for display on the screen during the simulation. Concentrations in these segments will be written and updated on the screen. These segments can be changed during the simulation. (Group A, Record 5, ISEGOUT)

Integration Time Step, days--A sequence of integration time steps (t) must be specified, along with the time interval over which they apply. If time step option (INTY) was set to 0, these time steps will be used during the simulation. If the time step option was set to 1, the model will calculate time steps internally; the time steps given here are the maximum allowed.

Given specific network and transport parameters, time steps are constrained within a specific range to maintain stability and minimize numerical dispersion, or solution inaccuracies. To maintain stability at a segment, the advected, dispersed, and transformed mass must be less than the resident mass:

$$(\Sigma \ Q \ C_j + \Sigma \ R \ C_j + \Sigma \ S_K \ V_j) \ \Delta t < V_j \ C_j \qquad\qquad \textbf{2.16}$$

Solving for t and applying the criterion over the entire network with appropriate factors gives the maximum stable step size used by WASP5:

$$\Delta t_{max} = 0.9 \ Min \left(\frac{V_j}{\sum_{i} Q_{ij} \ + \sum_{i} R_{ij} \ + \ 5\sum_{k} (S_{Kjk} \ V_j/C_j)} \right) \qquad\qquad \textbf{2.17}$$

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For purely advective systems, Equation 2.17 sets the time step to 90% of the minimum segment travel time. For purely dispersive systems, Equation 2.17 sets the time step to 90% of the minimum segment flushing time. For a linear reactive system with no transport, Equation 2.17 sets the time step to 18% of the reaction time. Usually t is controlled by advective or dispersive flows.

Numerical dispersion is artificial mixing caused by the finite difference approximation used for the derivatives. If the advection factor = 0, the backward difference approximation of $\partial c/\partial x$ is used in the advection term, and

$$E_{num} = \frac{U\ L}{2}$$ **2.18**

where:

   L   =   length of the segment, m

For the Euler scheme, the forward difference approximation of c/ t is used, and

$$E_{num} = \frac{U^2\ \Delta t}{2}$$ **2.19**

The total numerical dispersion, then, is

$$E_{num} = \frac{U}{2}\ (L - U\ \Delta t)$$ **2.20**

Note that increasing the time step up to x/U (or V/Q) decreases numerical dispersion to 0. The conditions for stability discussed above require a time step somewhat less than V/Q for most segments. So to maintain stability and minimize numerical dispersion in a water body subject to unsteady flow, the sequence of time steps must be as large as possible, but always less than t_{max} given in Equation 2.17. (Group A, Record 6, NOBRK; Record 7, DTS, T)

Print Intervals, days-- The user must specify the print
intervals controlling the output density in the print file
transferred to the post-processor. The model will store all
display variables in all segments after each print interval
throughout the simulation. Different print intervals can be
specified for different phases in the simulation. At least two
print intervals must be specified, one for time 0 and one for the
final time. NPRINT is the number of different print intervals to
input. PRINT(I) is the print interval to be used until time
TPRINT(I). TPRINT(I) is the time up to when print interval
PRINT(I) will be used. (Group A, Record 8, NPRINT; Record 9,
PRINT(I), TPRINT(I))

Segment Volumes, m^3--Initial volumes for each segment must
be specified. These can be calculated from navigation charts or
from a series of transects measuring depth versus width along the
river. Sometimes, volumes can be estimated from the travel time
of a well-mixed cloud of dye through a reach. For simulations
using hydrodynamic results from DYNHYD5, volumes from the
hydrodynamic summary file (#.HYD) are used and continuity is
maintained. (Group C, Record 3, BVOL(ISEG))

Transport Parameters

This group of parameters defines the advective and
dispersive transport of simulated model variables. Input
parameters include advective flows, sediment transport
velocities, dispersion coefficients, cross-sectional areas, and
characteristic lengths. Although the nominal units expected by
the model are SI, English or other units can be used along with
proper specification of conversion factors.

Number of Flow Fields-- Under advection, the user has a
choice of up to six flow fields. To simulate surface water
transport, select water column flow in the preprocessor or set
the number of flow fields to 1. When simulating pore water
flow, select this option in the preprocessor or set the number of
flow fields to 2. (Group D, Record 1, NFIELD)

Advective Flow, m^3/sec--Steady or unsteady flows can be
specified between adjoining segments, as well as entering or
leaving the network as inflow or outflow. The user must be
careful to check for continuity errors, as the model does not
require that flow continuity be maintained. For example, the
user may specify that more flow enters a segment than leaves.
For simulations using hydrodynamic results from DYNHYD5, flows

from the *.HYD file are used and flow continuity is automatically maintained. (Group D, Record 4, BQ; Record 6, QT(K), TQ(K))

Number of Exchange Fields-- Under dispersion, the user has a choice of up to two exchange fields. To simulate surface water toxicant and solids dispersion, select water column dispersion in the preprocessor or set the number of exchange fields to 1. To simulate exchange of dissolved toxicants with the bed, the user should also select pore water diffusion in the preprocessor or set the number of exchange fields to 2. (Group B, Record 1, NRFLD)

Dispersion Coefficients, m^2/sec--Dispersive mixing coefficients can be specified between adjoining segments, or across open water boundaries. These coefficients can model pore water diffusion in benthic segments, vertical diffusion in lakes, and lateral and longitudinal dispersion in large water bodies. Values can range from 10^{-10} m^2/sec for molecular diffusion to $5x10^2$ m^2/sec for longitudinal mixing in some estuaries. Values are entered as a time function series of dispersion and time, in days. (Group B, Record 6, RT(I), TR(I))

Cross-Sectional Area, m^2--Cross-sectional areas are specified for each dispersion coefficient, reflecting the area through which mixing occurs. These can be surface areas for vertical exchange, such as in lakes or in the benthos. Areas are not modified during the simulation to reflect flow changes. (Group B, Record 4, A(K))

Characteristic Mixing Length, m--Mixing lengths are specified for each dispersion coefficient, reflecting the characteristic length over which mixing occurs. These are typically the lengths between the center points of adjoining segments. A single segment may have three or more mixing lengths for segments adjoining longitudinally, laterally, and vertically. For surficial benthic segments connecting water column segments, the depth of the benthic layer is a more realistic mixing length than half the water depth. (Group B, Record 4, EL(K))

Boundary Parameters

This group of parameters includes boundary concentrations, waste loads, and initial conditions. Boundary concentrations must be specified for any segment receiving flow inputs, outputs, or exchanges. Initial conditions include not only initial concentrations, but also the density and solids transport field for each solid, and the dissolved fraction in each segment.

Boundary Concentrations, mg/L--Steady or time-variable concentrations must be specified for each water quality constituent at each boundary. A boundary is either a tributary inflow, a downstream outflow, or an open water end of the model network across which dispersive mixing can occur. Advective and dispersive flows across boundaries are specified by the transport parameters. Values are entered as a time function series of concentrations and time, in days. (Group E, Record 4, BCT(K), T(K))

Waste Loads, kg/day--Steady or time-variable loads may be specified for each water quality constituent at several segments. These loads represent municipal and industrial wastewater discharges, urban and agricultural runoff, precipitation, and atmospheric deposition of pollutants. Values are entered as a time function series of loads and time, in days. (Group F, Record 4, WKT(K), T(K))

Initial Concentrations, mg/L--Concentrations of each constituent in each segment must be specified for the time at which the simulation begins. For those water bodies with low transport rates, the initial concentrations of conservative substances may persist for a long period of time. Accurate simulation, then, would require accurate specification of initial concentrations. If initial concentrations cannot be determined accurately, then longer simulations should be run, and early predictions discounted. (Group J, Record 2, C(ISYS,J))

Dissolved Fractions--The initial fraction of chemical dissolved in the water portion of a segment is input as a fraction of total chemical concentration. The dissolved fraction is important in determining the amount of chemical transported by pore water flow and dispersion, and by solids transport. Dissolved fractions may be computed from sorption kinetics in the transformation subroutines. (Group J, Record 2, DISSF(ISYS,J))

Solid Densities, g/cm^3--The density of each type of solid is needed to compute the porosity of bed segments. Porosity will be a function of sediment concentration and the density of each solid type. (Group J, Record 1, DSED(K))

Maximum Concentrations, mg/L--Maximum concentrations must be specified for each water quality constituent. The simulation is automatically aborted if a calculated concentration falls outside these limits. This usually indicates computational instability, and the time step must usually be reduced. (Group J, Record 1, CMAX(K))

Transformation Parameters

    This group of parameters includes spatially variable
parameters, constants, and kinetic time functions for the water
quality constituents being simulated. None are necessary for
dissolved, conservative chemicals.

External Input Files

    At the user's option, two external input files may be called
upon and used by WASP5 during a simulation. These formatted
files may be created by a simulation model, or by output from a
spreadsheet. As formatted ASCII files, they may be edited using
standard text editors. Hydrodynamic files are denoted by *.HYD,
where the user specifies a 1 to 8 character name for *. Nonpoint
source loading files are denoted by *.NPS. The contents and
format for these files are specified in Part B, Sections 5.2 and
7.2.

CHAPTER 3

SEDIMENT TRANSPORT

3.1 MODEL DESCRIPTION

Introduction

Sediment transport is potentially a very important process
in aquatic systems. Excess sediment can affect water quality
directly. Water clarity and benthic habitats can be degraded.
Sediment transport also influences chemical transport and fate.
Many chemicals sorb strongly to sediment and thus undergo
settling, scour, and sedimentation. Sorption also affects a
chemical's transfer and transformation rates. Volatilization and
base-catalyzed hydrolysis, for example, are slowed by sorption.
Both sediment transport rates and concentrations must be
estimated in most toxic chemical studies.

In general, the stream transport capacity for suspended
sediment is in excess of its actual load, and the problem is one
of estimating sediment source loading--namely, watershed erosion.
In areas of backwater behind dams or in sluggish reaches, the
stream transport capacity may drop enough to allow net
deposition. Strongly sorbed pollutants may build up
significantly. Because sediment transport can be complex,
site-specific calibration of the settling, scour, and
sedimentation rates is usually necessary.

Overview of WASP5 Sediment Transport

Sediment size fractions, or solids types, are simulated
using the TOXI5 program. Simulations may incorporate total
solids as a single variable, or, alternately, represent from one
to three solids types or fractions. The character of the three
solids types is user-defined. They may represent sand, silt, and
clay, or organic solids and inorganic solids. The user defines
each solid type by specifying its settling and erosion rates, and
its organic content.

WASP5 performs a simple mass balance on each solid variable
in each compartment based upon specified water column advection
and dispersion rates, along with special settling, deposition,
erosion, burial, and bed load rates. Mass balance computations

are performed in benthic compartments as well as water column compartments. Bulk densities or benthic volumes are adjusted throughout the simulation.

All solids transport rates can be varied in space and time by the user. There are, however, no special process descriptions for solids transport. Erosion rates, for example, are not programmed as a function of sediment shear strength and water column shear stress. Consequently, the TOXI5 sediment model should be considered descriptive, and must be calibrated to site data.

Sediment Transport Processes

Water Column Transport

Sediment and particulate chemicals in the water column may settle to lower water segments and deposit to surficial bed segments. Settling, deposition, and scour rates in WASP5 are described by velocities and surface areas in transport fields 3, 4, and 5. Particulate transport velocities may vary both in time and in space, and are multiplied by cross-sectional areas to obtain flow rates for solids and the particulate fractions of chemicals.

Settling velocities should be set within the range of Stoke's velocities corresponding to the suspended particle size distribution:

$$V_s = \frac{8.64\ g}{18\ \mu} (\rho_p - \rho_w)\ d_p^2 \qquad\qquad\qquad 3.1$$

where:

V_s = Stokes velocity for particle with diameter d_p and density ρ_p, m/day

g = acceleration of gravity = 981 cm/sec^2

μ = absolute viscosity of water = 0.01 poise (g/cm^3-sec) at 20 °C

ρ_p = density of the solid, g/cm^3

Table 3.1 Stoke's Settling Velocities (in m/day) at 20 °C

Particle Diameter, mm	Particle Density, g/cm^3			
	1.80	2.00	2.50	2.70
Fine Sand				
0.3	300.00	400.00	710.00	800.00
0.05	94.00	120.00	180.00	200.00
Silt				
0.05	94.00	120.00	180.00	200.00
0.02	15.00	19.00	28.00	32.00
0.01	3.80	4.70	7.10	8.00
0.005	0.94	1.20	1.80	2.00
0.002	0.15	0.19	0.28	0.32
Clay				
0.002	0.15	0.19	0.28	0.32
0.001	0.04	0.05	0.07	0.08

ρ_w = density of water, 1.0 g/cm^3

d_p = particle diameter, mm

Values of V_s for a range of particle sizes and densities are provided in Table 3.1.

Benthic Exchange

Benthic exchange of sediment and particulate chemicals is driven by the net scour and deposition velocities:

$$W_{Bs} = A_{ij} \; (w_R \; S_i - w_D \; S_j) \qquad\qquad \textbf{3.2}$$

where:

W_Bs   =   net sediment flux rate, g/day

S   =   sediment concentration, g/m^3

w_D   =   deposition velocity, m/day

w_R   =   scour velocity, m/day

A_ij   =   benthic surface area, m^2

i   =   benthic segment

j   =   water segment

The deposition velocity can be calculated as the product of the Stokes settling velocity and the probability of deposition:

$$w_D = V_s \, \alpha_D \qquad\qquad\qquad\qquad \textbf{3.3}$$

where:

$_D$ =   probability of deposition upon contact with the bed.

The probability of deposition depends upon the shear stress on the benthic surface and the suspended sediment size and cohesiveness. Likewise, the scour velocity depends upon the shear stress, the bed sediment size and cohesiveness, and the state of consolidation of surficial benthic deposits. Figure 3.1 is offered as initial guidance in specifying initial deposition and scour velocities. For example, coarse silt of 0.05 mm diameter may settle at 100 to 200 m/day, but should not deposit where mean stream velocity is above 0.5 cm/sec. Where mean velocity rises above 30 cm/sec, erosion is expected, and nonzero scour velocities should be specified. For fine silt of 0.005 mm diameter settling at 1 to 2 m/day, deposition is not expected, even under quiescent conditions. Nonzero scour velocities should be specified where mean velocity is above 2 m/sec. Site specific calibration is necessary to refine the initial estimates.
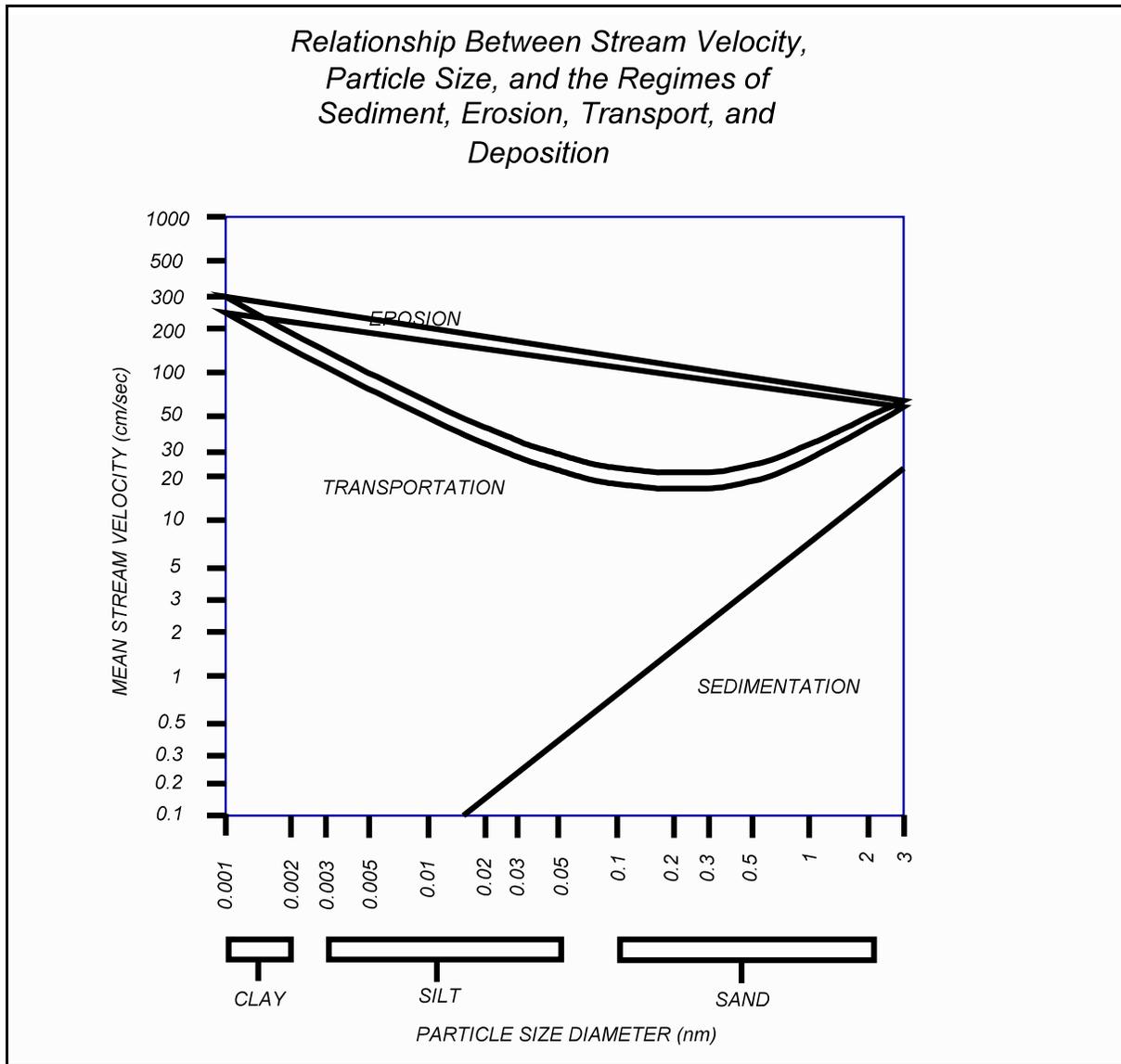
Figure 3.1 Sediment transport regimes (Graf, 1971).

Sediment Loading

     Sediment loading derives primarily from watershed erosion and bank erosion. These can be measured or estimated by several techniques, and input into each segment as a point source load. For some problems, long term average sediment loads can be calculated using the Universal Soil Loss Equation (Wischmeier and Smith, 1978). A useful treatment of this process is given by Mills et al. (1985). This technique works poorly for short term or inherently dynamic problems because much of the sediment loading occurs during a few extreme storm or snow melt events.

If available, suspended sediment data at local gaging stations
can be extrapolated to provide areawide loading estimates.
Alternatively, daily runoff loads can be simulated with a
watershed model and read in directly from an appropriately
formatted nonpoint source loading file.

The Sediment Bed

     The bed sediment plays an important role in the transport
and fate of water quality constituents. Sediment-sorbed
pollutants may be buried in the bed by deposition and
sedimentation, or they may be released to the water column by
scour. In WASP5, the movement of sediment in the bed is governed
by one of two options. In the first option, bed segment volumes
remain constant and sediment concentrations vary in response to
deposition and scour. No compaction or erosion of the segment
volume is allowed to occur. In the second option, the bed
segment volume is compacted or eroded as sediment is deposited or
scoured. Sediment concentration in the bed remains constant. In
both options chemical may be transported through the bed by pore
water flow and dispersion.

     The Constant Bed Volume Option--The first bed option,
referred to as the constant volume option, allows the sediment
concentration of the bed to change according to the net flux of
sediment. Bed segments are located in reference to the rising or
falling bed surface. The rate at which the bed rises or falls is
represented by a sedimentation velocity, input in flow fields 3,
4, and 5 for each sediment size fraction. Sediment in the bed is
added through deposition and lost through scour and
sedimentation.

     Assuming the depth of the bed remains constant and
neglecting dispersive mixing, the mass balance of sediment in a
stationary upper bed is given by:

$$d_i \frac{\partial S_i}{\partial t} = w_D S_j - (w_R + w_s) S_i \qquad\qquad \textbf{3.4}$$

where:

      w_s =   sedimentation velocity of the upper bed, m/day

      S_i =   sediment concentration in the upper bed, g/m^3

S_j = sediment concentration in the water, g/m^3

d_i = depth of the upper bed, m

For a lower bed layer,

$$d_k \frac{\partial S_k}{\partial t} = w_s S_i - w_{sk} S_k \qquad\qquad 3.5$$

where:

S_k = sediment concentration in the lower bed, g/m^3

w_{sk} = sedimentation velocity of the lower bed, m/day

d_k = depth of the lower bed, m

In most applications the sediment concentration of the bed will be nearly constant over time. In this case the mass derivative S/t will be zero. The resulting mass balance in the upper bed is:

$$w_D S_j = (w_R + w_s) \; S_i \qquad\qquad 3.6$$

In the lower bed,

$$w_s S_i = w_{sk} S_k \qquad\qquad 3.7$$

It should be noted that under the constant volume option WASP5 does not require a balance of sediment fluxes into and out of a bed segment. The user should, therefore, take care that deposition, scour, and sedimentation velocities reflect the intended mass flux of sediment in the bed.

The constant volume option also has a provision for a movable upper bed layer. This layer is modeled by specifying a total advective flow rate (flow field one) between upper bed segments. Thus, when a flow rate Q_{ij} is specified from upper bed segment j to upper bed segment i, the sediment, pore water, and chemical in j are transported to i. To maintain a mass balance in segment i, a similar flow rate should be specified out of i.

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This option allows for the lateral transport of sediment across the upper bed, and can be used to represent bed load transport.

The Variable Bed Volume Option--The second bed volume option, referred to as the variable bed volume option, allows bed volumes to change in response to deposition and scour. Two types of bed layers are assumed: an upper uncompacted layer, and one or more lower compacted layers. When deposition exceeds scour, the upper layer increases in volume as the surface of the bed rises. After a period of time, the added volume of upper bed compresses and becomes part of the lower bed. When scour exceeds deposition, the volume of the upper layer decreases as the surface of the bed drops. When the upper layer erodes completely, the next layer of bed is exposed to scour.

In locations where sediment deposition exceeds scour (Figure 3.2), bed compaction is triggered by a sedimentation time step. This sedimentation time step is input by the user and will generally be much larger than the simulation time step. As sediment and sorbed chemical settle from the water column, the top bed segment increases in volume, sediment mass, and chemical mass. Sediment concentrations remain constant. The volume of the upper bed continues to increase until the end of the sedimentation time step. At this time, the volume of the upper bed that has been added by net deposition is compressed to the density of the lower bed. Since the porosity of the uncompressed bed is greater than the porosity of the compressed bed, pore water and dissolved chemical are squeezed into the water column.

During compression, the lower bed segments rise to include the compressed portion of the upper bed. The volumes and sediment concentrations of these lower bed segments remain constant. A portion of the bottom bed segment is buried out of the network, however, as bed segments rise in response to sedimentation. Thus, chemical mass in the lower bed is added through compression of the upper bed, and lost through sediment burial.

After compression, the top bed segment returns to its original predeposition volume. Sediment and chemical concentrations in the upper bed are not changed by compaction. In the lower beds, segment volumes and sediment concentrations are unchanged. Chemical mass from the compacted portion of the bed is added to the lower bed, and chemical mass in the bottom bed segment is buried out of the model network.

Over several sedimentation time steps, the density and volume of the upper bed segment remain constant, so that:

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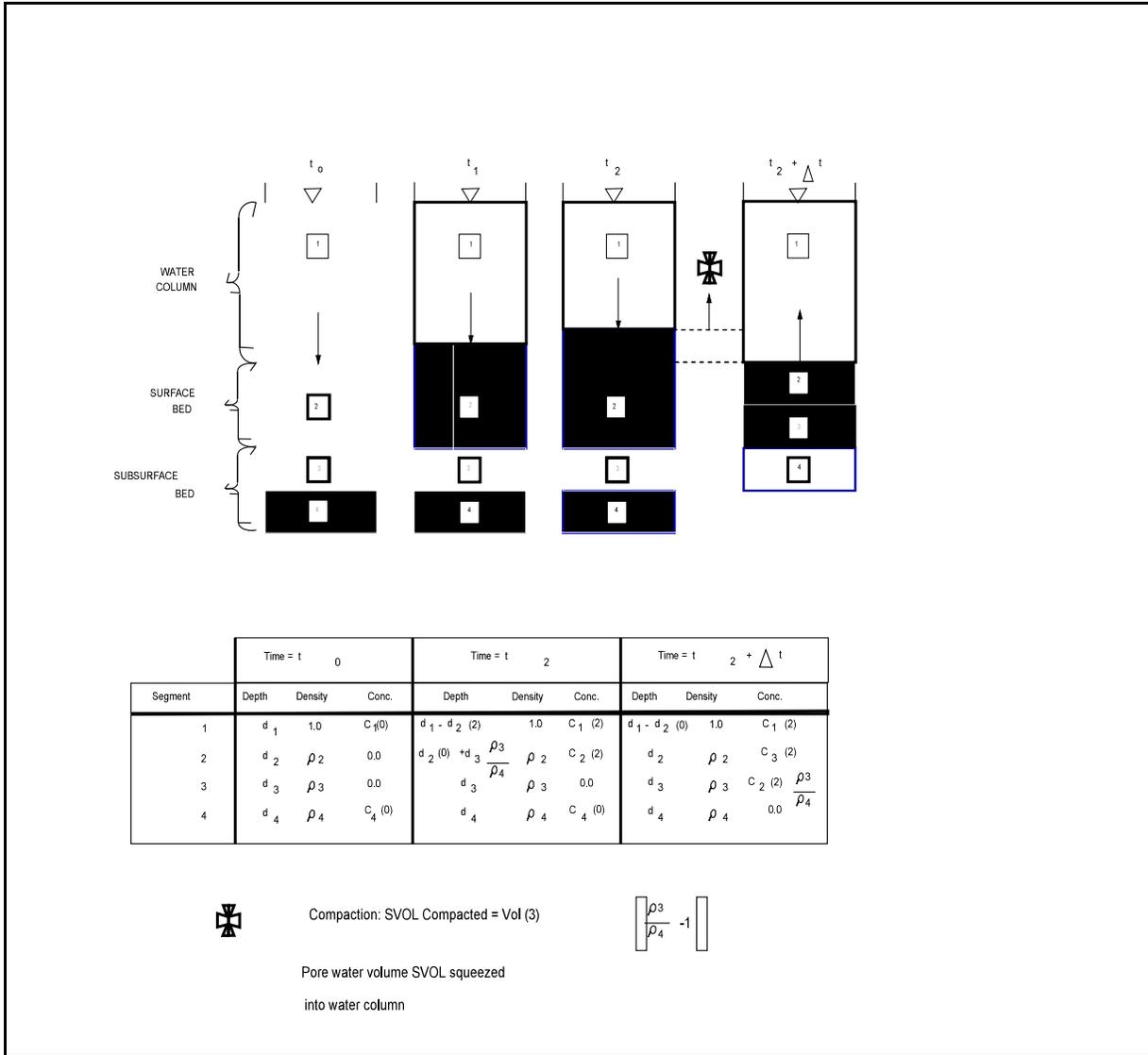
Figure 3.2 WASP5 sediment burial (variable volume option).

Segment	Time = t_0			Time = t_2			Time = $t_2 + \Delta t$		
	Depth	Density	Conc.	Depth	Density	Conc.	Depth	Density	Conc.
1	d_1	1.0	$C_1(0)$	$d_1 - d_2 (2)$	1.0	$C_1 (2)$	$d_1 - d_2 (0)$	1.0	$C_1 (2)$
2	d_2	ρ_2	0.0	$d_2 (0) + d_3 \frac{\rho_3}{\rho_4}$	ρ_2	$C_2 (2)$	d_2	ρ_2	$C_3 (2)$
3	d_3	ρ_3	0.0	d_3	ρ_3	0.0	d_3	ρ_3	$C_2 (2) \frac{\rho_3}{\rho_4}$
4	d_4	ρ_4	$C_4 (0)$	d_4	ρ_4	$C_4 (0)$	d_4	ρ_4	0.0

Compaction: SVOL Compacted = Vol (3) $\left[\dfrac{\rho_3}{\rho_4} - 1 \right]$

Pore water volume SVOL squeezed into water column

$$S_i \frac{\partial V_i}{\partial t} = A_{ij} w_D S_j - A_{ij} (w_R + w_s) S_i = 0 \qquad \text{3.8}$$

and

$$w_s = (w_D S_j - w_R S_i)/S_i \qquad \text{3.9}$$

For a lower bed layer, volumes are held constant along with density. To maintain mass balance, the average sedimentation velocity is, effectively:

$$w_{sk} = w_s S_i / S_k \qquad\qquad 3.10$$

For locations where sediment scour exceeds deposition, WASP responds as in Figure 3.3. As sediment and sorbed chemical erode from the bed, the top bed segment decreases in volume, depth, chemical mass, and sediment mass. Its density remains constant. When the sediment mass in the top bed layer equals zero, then segment renumbering is triggered. All the properties of the remaining bed segments, including chemical concentration, remain unaffected by renumbering. The new top bed segment, for example, has the same depth, volume, sediment and chemical concentration as the old second bed segment. A new bottom bed segment is

	t_0	t_1	t_2	$t_2 + \Delta t$
WATER COLUMN	1	1	1	1
SURFACE BED	2	2		2
SUBSURFACE BED	3	3	3	3
	4	4	4	4

	Time = t_0			Time = t_2			Time = $t_2 + \Delta t$		
Segment	Depth	Density	Conc.	Depth	Density	Conc.	Depth	Density	Conc.
1	d_1	1.0	0.0	$d_1 + d_2(0)$	1.0	$C_1(2)$	$d_1 + d_2(0)$	1.0	1
2	d_2	ρ_2	$C_2(0)$	0	ρ_2	$C_2(0)$	d_2	ρ_2	$C_3(2)$
3	d_3	ρ_3	$C_3(0)$	d_3	ρ_3	$C_3(0)$	d_3	ρ_3	$C_4(2)$
4	d_4	ρ_4	$C_4(0)$	d_4	ρ_4	$C_4(0)$	d_4	ρ_4	0.0
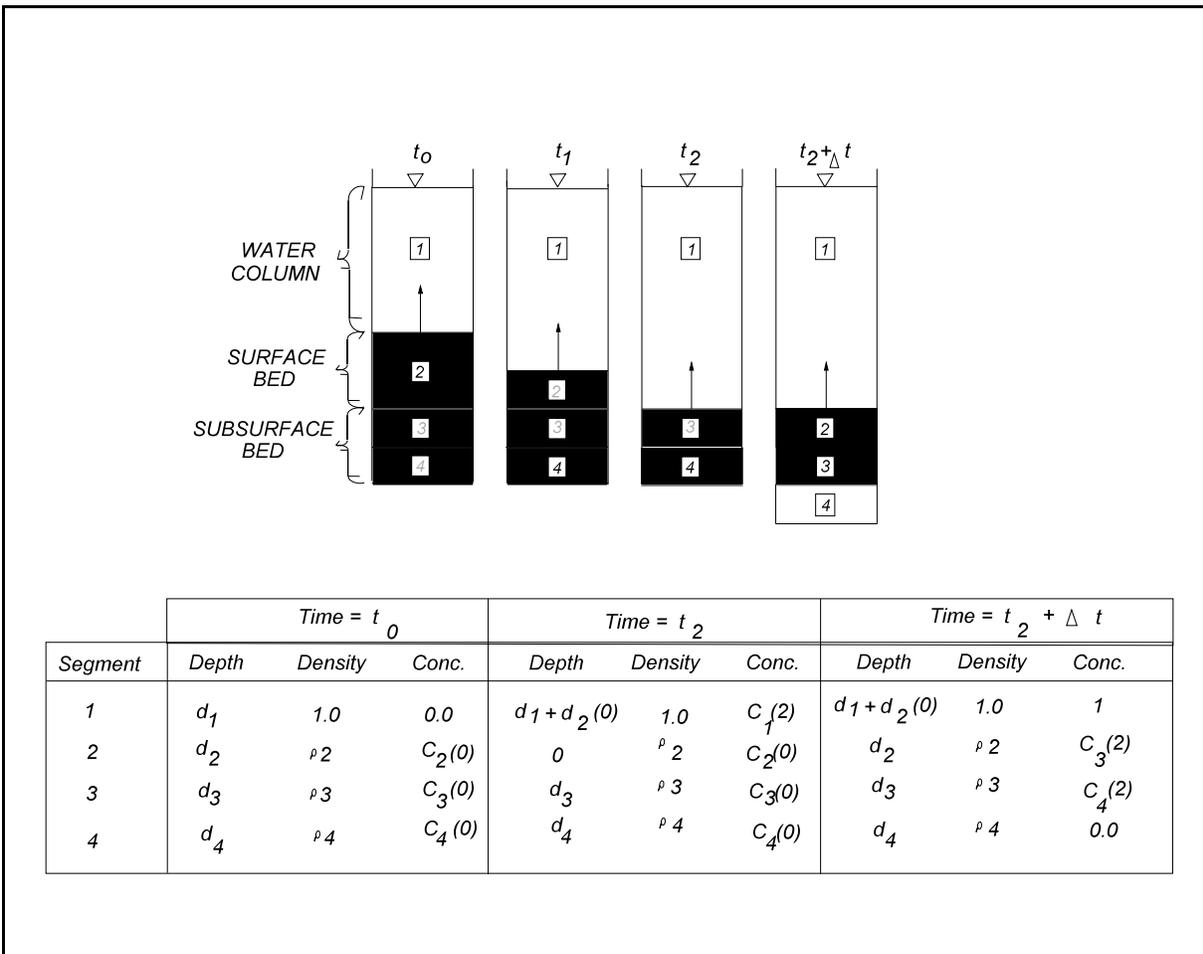
Figure 3.3 WASP sediment erosion (variable volume option).

created with the same physical properties as the other bed segments. Its chemical concentration, however, is zero. Renumbering and creation of a new bottom segment completes the WASP5 erosion cycle (or time step).

As a consequence of the way the variable bed volume option treats sedimentation, certain constraints are imposed on the bed segment properties defined in the input data set. The density (or sediment concentration) of a top bed segment must be less than or equal to the density of the lower bed segments within a vertical stack. Since the compaction routine implicitly handles sedimentation, no sedimentation velocities to lower beds may be specified in the sediment transport fields. Finally, the user must simulate sediment as a state variable in order to use this option. Sediment is a state variable in the toxics program, but not the eutrophication program.

3.2 MODEL IMPLEMENTATION

Introduction

To simulate sediment transport with WASP5, use the preprocessor or a text editor to create a TOXI5 input file. Simple datasets are provided for use as templates to edit and adapt. The model input dataset and the input parameters will be similar to those for the conservative tracer model as described in Chapter 2. To those basic parameters, the user will add benthic segments and solids transport rates. During the simulation, solids variables will be transported both by the water column advection and dispersion rates and by these solids transport rates.

In WASP5, solids transport rates in the water column and the bed are input via up to three solids transport fields. These fields describe the settling, deposition, scour, and sedimentation flows of three kinds of solids. The transport of particulate chemicals or the particulate fraction of simulated chemicals follows the solids flows. The user must specify the dissolved fraction (i.e. 0.0) and the solids transport field for each simulated solid under initial conditions. To simulate total solids, solids 1 must be used.

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Model Input Parameters

     This section summarizes the input parameters that must be
specified in order to solve the sediment balance equations in
TOXI5. Input parameters are prepared for WASP5 in four major
sections of the preprocessor -- environment, transport,
boundaries, and transformation. Basic model parameters are
described in Chapter 2, and will not be repeated here.

Environment Parameters

     These parameters define the basic model identity, including
the segmentation, and control the simulation.

     Systems-- To simulate total solids only, select "simulate"
for Solids 1 and "bypass" for the other five systems. To
simulate two solids types, select "simulate" for both Solids 1
and Solids 2. To simulate three solids types, select "simulate"
for all three. The chemical systems can be simulated or
bypassed. (Group A, Record 4, NOSYS; Record 9, SYSBY)

     Bed Volume Option-- The user must determine whether bed
volumes are to be held constant or allowed to vary. Volumes may
be held constant by specifying 0, in which case sediment
concentrations and porosities in the bed segments will vary.
Alternatively, sediment concentrations and porosities may be held
constant by specifying 1, in which case surficial bed segment
volumes will vary. (Group C, Record 1, IBEDV)

     Bed Time Step-- While mass transport calculations are
repeated every model time step, certain benthic calculations are
repeated only at this benthic time step, in days. If the
constant bed volume option is chosen, sediment concentrations are
updated every model time step, but porosities are recalculated
every benthic time step. If the variable bed volume is chosen,
upper benthic segment volumes are updated every time step, with
compaction occurring every benthic time step. (Group C, Record 1,
TDINTS)

Transport Parameters

     Number of Flow Fields-- To simulate total solids, the user
should select solids 1 flow under advection. To simulate three
sediment types, the user should select solids 1 flow, solids 2
flow, and solids 3 flow. In addition, the user should select
water column flow. (Group D, Record 1, NFIELD)

Sediment Transport Velocities, m/sec-- Time variable settling, deposition, scour, and sedimentation velocities can be specified for each type of solid. If the units conversion factor is set to 1.157e-5, then these velocities are input in units of m/day. These velocities are multiplied internally by cross-sectional areas and treated as flows that carry solids and sorbed chemical between segments. Settling velocities are important components of suspended sediment transport in the water column. Scour and deposition velocities determine the transfer of solids and sorbed chemical between the water column and the sediment bed. Sedimentation velocities represent the rate at which the bed is rising in response to net deposition. (Group D, Record 6, QT)

Cross-Sectional Areas, m^2-- The interfacial surface area must be specified for adjoining segments where sediment transport occurs. These surface areas are multiplied internally by sediment transport velocities to obtain sediment transport flows. (Group D, Record 4, BQ)

Boundary Parameters

This group of parameters includes boundary concentrations, waste loads, and initial conditions. Boundary concentrations must be specified for any segment receiving flow inputs, outputs, or exchanges. Initial conditions includes not only initial concentrations, but also the density and solids transport field for each solid, and the dissolved fraction in each segment.

Boundary Concentrations, mg/L-- At each segment boundary, time variable concentrations must be specified for total solids, or for each solids type simulated. A boundary segment is characterized by water exchanges from outside the network, including tributary inflows, downstream outflows, and open water dispersive exchanges. (Group E, Record 4, BCT)

Waste Loads, kg/day-- For each point source discharge, time variable sediment loads can be specified for total solids, or for each solids type simulated. These loads can represent municipal and industrial wastewater discharges, or urban and agricultural runoff. (Group F.1, Record 4, WKT)

Solids Transport Field-- The transport field associated with total solids or each solids type must be specified under initial conditions. (Group J, Record 1, IFIELD)

Solid Density, g/cm^3-- The average density of the total sediment, or the density of each solids type must be specified. This information is used to compute the porosity of benthic segments. Porosity is a function of sediment concentration and the density of each solids type. (Group J, Record 1, DSED)

Initial Concentrations, mg/L-- Concentrations of total sediment or of each solids type in each segment must be specified for the time at which the simulation begins. If the variable benthic volume option is used, the benthic sediment concentrations specified here will remain constant for the entire simulation. (Group J, Record 2, C)

Dissolved Fraction-- The dissolved fraction of each solid in each segment should be set to 0. (Group J, Record 2, DISSF)

Transformation Parameters

This group of parameters includes spatially variable parameters, constants, and kinetic time functions for the water quality constituents being simulated. None are necessary for sediment transport.

Data Group Descriptions

An input dataset to simulate three sediment types in a river is given with the model software. A comprehensive listing of the WASP5 data groups, records, and variables is given in Part B of this documentation.

CHAPTER 4

DISSOLVED OXYGEN

4.1 MODEL DESCRIPTION

Introduction

Dissolved oxygen (DO) is one of the most important variables in water quality analysis. Low concentrations directly affect fish and alter a healthy ecological balance. Because DO is affected by many other water quality parameters, it is a sensitive indicator of the health of the aquatic system.

DO has been modeled for over 70 years. The basic steady-state equations were developed and used by Streeter and Phelps (1925). Subsequent development and applications have added terms to their basic equation and provided for time-variable analysis. The equations implemented here are fairly standard. As explained below, the user may implement some or all of the processes that are described with terms in these equations.

Overview of WASP5 Dissolved Oxygen

Dissolved oxygen and associated variables are simulated using the EUTRO5 program. Several physical-chemical processes can affect the transport and interaction among the nutrients, phytoplankton, carbonaceous material, and dissolved oxygen in the aquatic environment. Figure 4.1 presents the principal kinetic interactions for the nutrient cycles and dissolved oxygen.

EUTRO5 can be operated by the user at various levels of complexity to simulate some or all of these variables and interactions. To simulate only carbonaceous biochemical oxygen demand (BOD) and DO, for example, the user may bypass calculations for the nitrogen, phosphorus, and phytoplankton variables. Simulations may incorporate carbonaceous biochemical oxygen demand (CBOD) and either ammonia (NH3) or nitrogenous biochemical oxygen demand (NBOD) expressed as ammonia. Sediment oxygen demand may be specified, as well as photosynthesis and respiration rates.

Four levels of complexity are identified and documented at the end of this section: (1) Streeter-Phelps, (2) modified Streeter-Phelps, (3) full linear DO balance, and (4) nonlinear DO
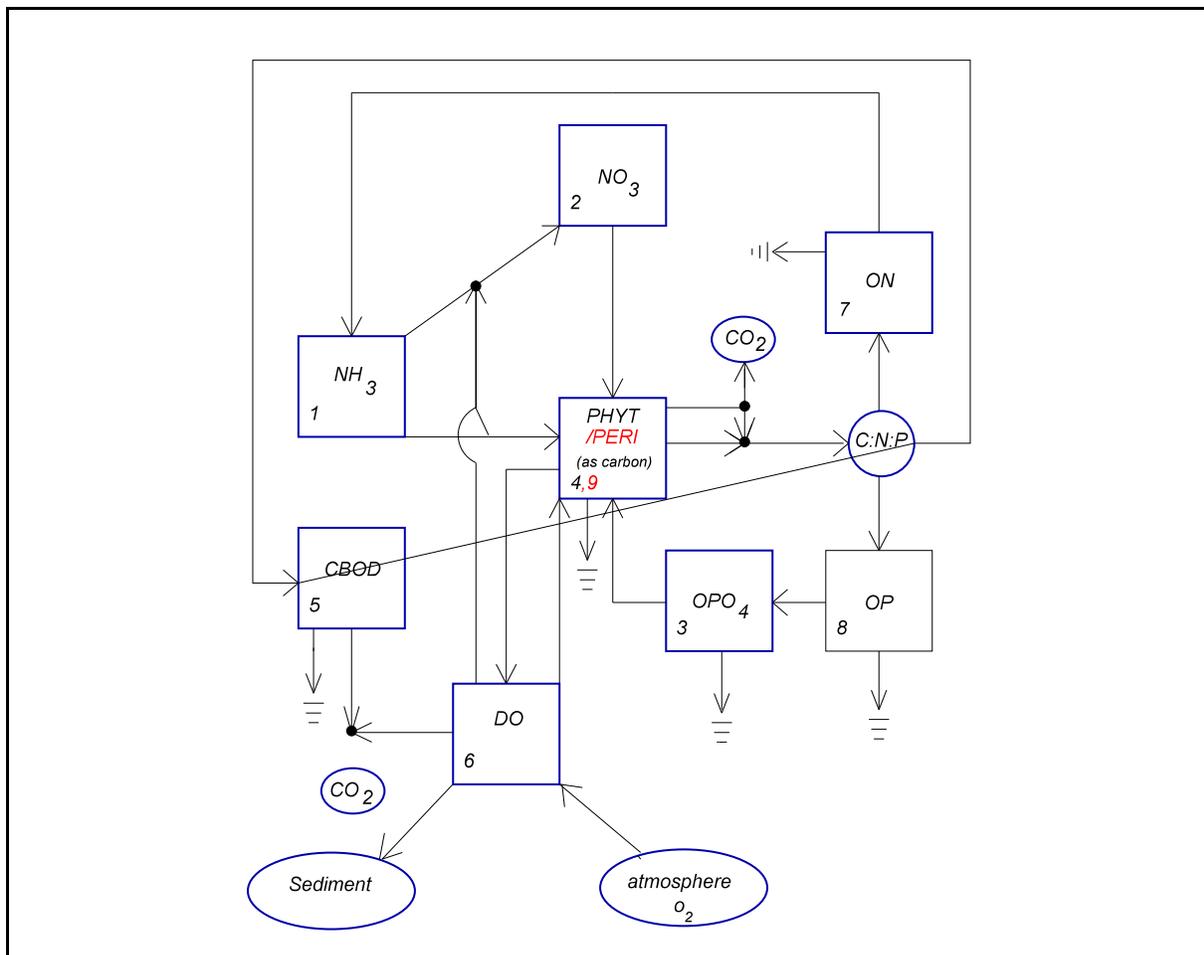
Figure 4.1   EUTRO5 state variable interactions.

balance. The actual simulation of phytoplankton is described in Chapter 5.

Dissolved Oxygen Processes

     Six EUTRO5 state variables can participate directly in the DO balance: phytoplankton carbon, periphyton carbon, ammonia, nitrate, carbonaceous biochemical oxygen demand, and dissolved oxygen. The reduction of dissolved oxygen is a consequence of the aerobic respiratory processes in the water column and the anaerobic processes in the underlying sediments. Because both these sets of processes can contribute significantly, it is necessary to formulate their kinetics explicitly.
     The methodology for the analysis of dissolved oxygen dynamics in natural waters, particularly in streams, rivers, and estuaries is reasonably well-developed (O'Connor and Thomann,

1972). The major and minor processes incorporated into EUTRO5 are discussed below. The reader should refer to the kinetic equations summarized in Figure 4.2, and the reaction parameters and coefficients in Table 4.1. In Figure 4.2, the factor $f_A A/V$ is applied to the periphyton term to convert C_9 from biomass per unit bottom area to biomass per unit volume. The terms f_A and f_{2WC} are defined in Table 5.5.

---

5. CARBONACEOUS BIOCHEMICAL OXYGEN DEMAND

$$\frac{\partial C_5}{\partial t} = a_{oc} K_{1D} C_4 - k_D \Theta_D^{(T-20)} \left(\frac{C_6}{K_{BOD}+C_6} \right) C_5 - \frac{v_{s3}(1-f_{D5})}{D} C_5$$

$\qquad\qquad$ *phytop. death* $\qquad\qquad$ *oxidation* $\qquad\qquad\qquad$ *settling*

$$- \frac{5}{4} \frac{32}{14} k_{2D} \Theta_{2D}^{(T-20)} \left(\frac{K_{NO3}}{K_{NO3}+C_6} \right) C_2 + f_{2WC}\, a_{2OC}\, K_{2D}\, f_A \frac{A}{V} C_9 + \frac{f_{CBOD}}{D}$$

$\qquad\qquad$ *denitrification* $\qquad\qquad\qquad$ *perip. death* $\qquad$ *benthic flux*

---

6. DISSOLVED OXYGEN

$$\frac{\partial C_6}{\partial t} = k_2(C_s - C_6) - k_d \Theta_d^{T-20} \left(\frac{C_6}{K_{BOD}+C_6} \right) C_5 - \frac{64}{14} k_{12} \Theta_{12}^{T-20} \left(\frac{C_6}{K_{NIT}+C_6} \right) C_1$$

$\qquad\qquad$ *reaeration* $\qquad\qquad$ *oxidation* $\qquad\qquad\qquad$ *nitrification*

$$- \frac{SOD}{D} \Theta_s^{T-20} + G_{P1} \left(\frac{32}{12} + \frac{48}{14} \frac{14}{12} (1-P_{NH3}) \right) C_4 - \frac{32}{12} k_{1R} \Theta_{1R}^{T-20} C_4$$

sediment demand $\qquad$ *phytoplankton growth* $\qquad\qquad$ *respiration*

$$+ G_{M1} \left(\frac{32}{12} + \frac{48}{14} \frac{14}{12} (1-P_{2NH3}) \right) f_A \frac{A}{V} C_9 - \frac{32}{12} k_{2R} \Theta_{2R}^{T-20} f_A \frac{A}{V} C_9$$

$\qquad\qquad\qquad$ *periphyton growth* $\qquad\qquad$ *respiration*

Figure 4.2 Oxygen balance equations.

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Table 4.1 CBOD and DO Reaction Terms

Description	Notation	Value from Potomac Estuary Model	Units
Oxygen to carbon ratio	a_{OC}	32/12	mg O_2/mg C
Phytoplankton nitrogen-carbon ratio	a_{NC}	0.25	mg N/mg C
Deoxygenation rate at 20°C, Temp. coeff.	k_d $_d$	0.21-0.16 1.047	day^{-1} -
Half saturation constant for oxygen limitation	K_{BOD}	0.5	mg O_2/L
Nitrification rate at 20°C, Temp. coeff.	k_{12} $_{12}$	0.09-0.13 1.08	day^{-1} -
Half saturation constant for oxygen limitation	K_{NIT}	0.5	mg N/L
Denitrification rate at 20°C, Temp. coeff.	k_{2D} $_{2D}$	- 1.08	day^{-1} -
Half saturation constant for oxygen limitation	K_{NO3}	0.1	mg N/L
Phytoplankton growth rate	G_{P1}	0.1-0.5	day^{-1}
Phytoplankton respiration rate, 20°C, Temperature coeff.	k_{1R} $_{1R}$	0.125 1.045	day^{-1} -
Sediment Oxygen Demand, Temp. coeff.	SOD $_s$	0.2-4.0 1.08	g/m^2-day -
Reaeration rate at 20°C, Temp. coeff.	k_2 $_a$	Eq. 4.1-4.7 1.028	day^{-1} -
DO saturation	C_s	Eq. 4.8	mg O_2/L
Fraction dissolved CBOD	f_{D5}	0.5	none
organic matter settling velocity	v_{s3}	-	m/day
Oxygen to carbon ratio for periphyton	a_{2OC}	32/12	mg O_2/mg C
Flux of CBOD from the sediment	f_{CBOD}	-	mg/m^2-day

Reaeration

     Oxygen deficient, i.e., below saturation, waters are
replenished via atmospheric reaeration. The reaeration rate
coefficient is a function of the average water velocity, depth,
wind, and temperature. In EUTRO5, the user may specify a single
reaeration rate constant, spatially-variable reaeration rate
constants, or allow the model to calculate variable reaeration
rates based upon flow or wind. Calculated reaeration will follow
either the flow-induced rate or the wind-induced rate, whichever
is larger.

     EUTRO5 calculates flow-induced reaeration based on the Covar
method (Covar, 1976). This method calculates reaeration as a
function of velocity and depth by one of three formulas -- Owens,
Churchill, or O'Connor- Dobbins, respectively:

$$k_{qj}(20°C) = 5.349 \ v_j^{0.67} \ D_j^{-1.85} \qquad\qquad \textbf{4.2}$$

$$k_{qj}(20°C) = 5.049 \ v_j^{0.97} \ D_j^{-1.67} \qquad\qquad \textbf{4.3}$$

or

$$k_{qj}(20°C) = 3.93 \ v_j^{0.50} \ D_j^{-1.50} \qquad\qquad \textbf{4.4}$$

where:

     k_{qj} =   flow-induced reaeration rate coefficient at 20°C,
                  day^{-1}

     v_j =   average water velocity in segment j, m/sec

     D_j =   average segment depth, m

     The Owens formula is automatically selected for segments
with depth less than 2 feet. For segments deeper than 2 feet,

the O'Connor-Dobbins or Churchill formula is selected based on a consideration of depth and velocity. Deeper, slowly moving rivers require O'Connor-Dobbins; moderately shallow, faster moving streams require Churchill. Segment temperatures are used to adjust the flow-induced k_{qj}(20 °C) by the standard formula:

$$k_{qj}(T) = k_{qj}(20°C) \; \Theta_a^{T-20} \qquad\qquad\qquad\qquad\qquad \textbf{4.5}$$

where:

T	=	water temperature, °C
k_{qj}(T)	=	reaeration rate coefficient at ambient segment temperature, day^{-1}
Θ_a	=	temperature coefficient, unitless

Wind-induced reaeration is determined by O'Connor (1983). This method calculates reaeration as a function of wind speed, air and water temperature, and depth using one of three formulas:

$$k_{wj} = \frac{86400}{100\,D_j} \left(\frac{D_{OW}}{\nu_W} \right)^{2/3} \left(\frac{\rho_a}{\rho_W} \right)^{1/2} \frac{\kappa^{1/3}}{\Gamma} \sqrt{C_d} \; (100 \cdot W) \qquad\qquad \textbf{4.6}$$

$$k_{wj} = \frac{86400}{100\,D_j} \left[(TERM1 \cdot 100\,W)^{-1} + (TERM2\sqrt{100\,W})^{-1} \right]^{-1}$$

$$where$$

$$TERM1 = \left(\frac{D_{OW}}{\nu_W} \right)^{2/3} \left(\frac{\rho_a}{\rho_W} \right)^{1/2} \frac{\kappa^{1/3}}{\Gamma_u} \sqrt{C_d} \qquad\qquad\qquad \textbf{4.7}$$

$$TERM2 = \left(\frac{D_{OW}}{\kappa\,z_0} \frac{\rho_a \nu_a}{\rho_W \nu_W} \sqrt{C_d} \right)^{1/2}$$

or

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$$k_{wj} = \frac{86400}{100\,D_j} \left(\frac{D_{OW}}{\kappa\,z_e} \frac{\rho_a \nu_a}{\rho_w \nu_w} \sqrt{C_d} \right)^{1/2} \sqrt{100\,W} \qquad\qquad \textbf{4.8}$$

where:

k_{wj} =   wind-induced reaeration rate coefficient, day^{-1}

W =   time-varying wind speed at 10 cm above surface, m/sec

T_a =   air temperature, °C

ρ_a =   density of air, a function of T_a, g/cm^3

ρ_w =   density of water, 1.0 g/cm^3

ν_a =   viscosity of air, a function of T_a, cm^2/s

ν_w =   viscosity of water, a function of T, cm^2/s

D_{OW} =   diffusivity of oxygen in water, a function of T, cm^2/s

κ =   von Karman's coefficient, 0.4

v_t =   transitional shear velocity, set to 9, 10, and 10 for small, medium, and large scales, cm/s

v_c =   critical shear velocity, set to 22, 11, and 11 for small, medium, and large scales, cm/s

z_e =   equivalent roughness, set to 0.25, 0.35, and 0.35 for small, medium, and large scales, cm

z_0 =   effective roughness, a function of z_e, κ, C_d, v_t, ν_a, and W, cm

λ =   inverse of Reynold's number, set to 10, 3, and 3 for small, medium, and large scales

γ =   nondimensional coefficient, set to 10, 6.5, and 5 for small, medium, and large scales

$_u$ = nondimensional coefficient, a function of , v_c, C_d, and W

C_d = drag coefficient, a function of z_e, , $_a$, , v_t, and W

Equation 4.5 is used for wind speeds of up to 6 m/sec, where interfacial conditions are smooth and momentum transfer is dominated by viscous forces. Equation 4.7 is used for wind speeds over 20 m/sec, where interfacial conditions are rough and momentum transfer is dominated by turbulent eddies. Equation 4.6 is used for wind speeds between 6 and 20 m/sec, and represents a transition zone in which the diffusional sublayer decays and the roughness height increases.

The user is referred to O'Connor (1983) for details on the calculation of air density, air and water viscosity, the drag coefficient, the effective roughness, and $_u$. Small scale represents laboratory conditions. Large scale represents open ocean conditions. Medium scale represents most lakes and reservoirs.

The program allows a maximum value of the reaeration coefficient of 24 day^{-1}. If the calculated flow-induced or wind-induced reaeration coefficient is higher than this, the program automatically reduces it to 24 day^{-1}.

Dissolved oxygen saturation, C_s, is determined as a function of temperature, in degrees K, and salinity S, in ppt (parts per thousand) (APHA, 1985):

$$\ln C_s = -139.34 + (1.5757 \cdot 10^5)\, T_K^{-1} - (6.6423 \cdot 10^7)\, T_K^{-2}$$

$$+ (1.2438 \cdot 10^{10})\, T_K^{-3} - (8.6219 \cdot 10^{11})\, T_K^{-4} \qquad \textbf{4.9}$$

$$- 0.5535\, S\, (0.031929 - 19.428\, T_K^{-1} + 3867.3\, T_K^{-2})$$

Carbonaceous Oxidation

The long history of applications have focused primarily on the use of BOD as the measure of the quantity of oxygen demanding material and its rate of oxidation as the controlling kinetic

reaction. This has proven to be appropriate for waters receiving a heterogeneous combination of organic wastes of municipal and industrial origin since an aggregate measure of their potential effect is a great simplification that reduces a complex problem to one of tractable dimensions.

The oxidation of carbonaceous material is the classical BOD reaction. Internally the model uses ultimate carbonaceous biochemical oxygen demand CBOD as the indicator of equivalent oxygen demand for the carbonaceous material. A principal source of CBOD, other than man-made sources and natural runoff, is detrital phytoplankton carbon, produced as a result of algal death. The primary loss mechanism associated with CBOD is oxidation:

$$C_x H_y O_z \rightarrow CO_2 + H_2O \qquad\qquad\qquad\qquad\qquad\qquad \textbf{4.10}$$

The kinetic expression for carbonaceous oxidation in EUTRO5 contains three terms -- a first order rate constant, a temperature correction term, and a low DO correction term. The first two terms are standard. The third term represents the decline of the aerobic oxidation rate as DO levels approach 0. The user may specify the half-saturation constant K_{BOD}, which represents the DO level at which the oxidation rate is reduced by half. The default value is zero, which allows this reaction to proceed fully even under anaerobic conditions.

Direct comparisons between observed BOD_5 data and model output cannot be made using the internal CBOD computed by EUTRO5, since field measurements may be tainted by algal respiration and the decay of algal carbon. Therefore a correction must be made to the internally computed model CBOD so that a valid comparison to the field measurement may be made. This results in a new variable, known as the bottle BOD_5, which is computed via equation 4.10.

$$Bottle\ BOD_5 = C_5\,(1-e^{-5k_{dbot}})\ +\ \frac{64}{14}\,C_1\,(1-e^{-5k_{nbot}})$$
$$+\ a_{oc}C_4\,(1-e^{-5k_{1R}}) \qquad\qquad \textbf{4.11}$$

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where:

C_5 = the internally computed CBOD, mg/L

C_1 = the internally computed NH_3, mg/L

C_4 = the phytoplankton biomass in carbon units, mg/L

a_{oc} = the oxygen to carbon ratio, 32/12 mg O_2/mg C

k_{dbot} = the laboratory "bottle" deoxygenation rate constant, day^{-1}

k_{nbot} = the laboratory "bottle" nitrification rate constant, day^{-1}

k_{1R} = the algal respiration rate constant at 20°C, day^{-1}

Equation 4.10 can provide a low estimate of the observed bottle BOD because it does not include a correction for the decay of detrital algal carbon, which in turn depends upon the number of non-viable phytoplankton. Please note that laboratory "bottle" CBOD and nitrification rates are used here, as specified by the user. The default laboratory rate constant for nitrification is 0, reflecting the use of a nitrifying inhibitor.

Nitrification

Additional significant losses of oxygen can occur as a result of nitrification:

$$NH_3^+ + 2\,O_2 \rightarrow NO_3 + H_2O + H^+ \qquad\qquad \textbf{4.12}$$

Thus for every mg of ammonia nitrogen oxidized, 2 (32/14) mg of oxygen are consumed.

The kinetic expression for nitrification in EUTRO5 contains three terms -- a first order rate constant, a temperature correction term, and a low DO correction term. The first two terms are standard. The third term represents the decline of the nitrification rate as DO levels approach 0. The user may specify the half-saturation constant K_{NIT}, which represents the DO level at which the nitrification rate is reduced by half. The default

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value is zero, which allows this reaction to proceed fully even under anaerobic conditions.

Denitrification

Under low DO conditions, the denitrification reaction provides a sink for CBOD:

$$5\,CH_2O + 5\,H_2O + 4\,NO_3 + 4\,H^+ \rightarrow 5\,CO_2 + 2\,N_2 + 12\,H_2O \qquad \textbf{4.13}$$
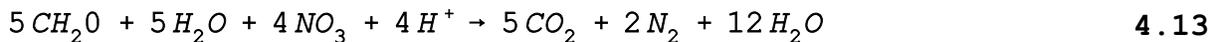
Thus for each mg of nitrate nitrogen reduced, 5/4 (12/14) mg of carbon are consumed, which reduces CBOD by 5/4 (12/14) (32/12) mg. Denitrification is not a significant loss in the water column, but can be important when simulating anaerobic benthic conditions.

The kinetic expression for denitrification in EUTRO5 contains three terms -- a first order rate constant (with appropriate stoichiometric ratios), a temperature correction term, and a DO correction term. The first two terms are standard. The third term represents the decline of the denitrification rate as DO levels rise above 0. The user may specify the half-saturation constant K_{NO3}, which represents the DO level at which the denitrification rate is reduced by half. The default value is zero, which prevents this reaction at all DO levels.

Settling

Under quiescent flow conditions, the particulate fraction of CBOD can settle downward through the water column and deposit on the bottom. In water bodies, this can reduce carbonaceous deoxygenation in the water column significantly. The deposition of CBOD and phytoplankton, however, can fuel sediment oxygen demand in the benthic sediment. Under high flow conditions, particulate CBOD from the bed can be resuspended.

The kinetic expression for settling in EUTRO5 is driven by the user-specified particulate settling velocity v_{s3} and the CBOD particulate fraction $(1 - f_{D5})$, where f_{D5} is the dissolved fraction. Settling velocities that vary with time and segment can be input as part of the advective transport field. Resuspension can also be input using a separate velocity time

function. Segment-variable dissolved fractions are input with initial conditions.

Phytoplankton Growth

A byproduct of photosynthetic carbon fixation is the production of dissolved oxygen. The rate of oxygen production (and nutrient uptake) is proportional to the growth rate of the phytoplankton since its stoichiometry is fixed. Thus, for each mg of phytoplankton carbon produced by growth, 32/12 mg of O_2 are produced. An additional source of oxygen from phytoplankton growth occurs when the available ammonia nutrient source is exhausted and the phytoplankton begin to utilize the available nitrate. For nitrate uptake the initial step is a reduction to ammonia which produces oxygen:

$$2\,NO_3 \rightarrow 2\,NH_3 + 3O_2 \qquad\qquad\qquad \textbf{4.14}$$

Thus, for each mg of phytoplankton carbon produced by growth using nitrate, a_{NC} mg of phytoplankton nitrogen are reduced, and $(48/14)$ a_{NC} mg of O_2 are produced.

Phytoplankton Respiration

Oxygen is diminished in the water column as a result of phytoplankton and periphyton respiration, which is basically the reverse process of photosynthesis:

$$C_4 + C_9V/A + O_2 \rightarrow CO_2 \qquad\qquad\qquad \textbf{4.15}$$

where C_4 is phytoplankton carbon, in mg/L, C_9 is periphyton carbon in mg/m^2 of bottom area, V is water-column volume, and A is bottom area. Thus for every mg of phytoplankton carbon consumed by respiration, 32/12 mg of oxygen are also consumed.

Phytoplankton and Periphyton Death

The death of phytoplankton and periphyton provides organic carbon, which can be oxidized. The kinetic expression in EUTRO5

recycles phytoplankton carbon to CBOD using a first order death rate and the stoichiometric oxygen to carbon ratio 32/12.

Periphyton death is handled in a manner that recognizes that periphyton are anchored to the bottom and associated with the sediment. A fractional coefficient, f_{2WC}, is specified by the user to allocate dead periphyton between the fraction in the water column (f_{2WC}, generally a small fraction or zero), and the fraction in the underlying sediment ($1-f_{2WC}$).

Sediment Oxygen Demand

The decomposition of organic material in benthic sediment can have profound effects on the concentrations of oxygen in the overlying waters. The decomposition of organic material results in the exertion of an oxygen demand at the sediment-water interface. As a result, the areal fluxes from the sediment can be substantial oxygen sinks to the overlying water column.

EUTRO5 provides two options for oxygen fluxes: descriptive input and predictive calculations. The first option is used for networks composed of water column segments only. The kinetic equation is given in Figure 4.2. Observed sediment oxygen demand fluxes must be specified for water segments in contact with the benthic layer. Seasonal changes in water temperature can affect SOD through the temperature coefficient. In the MDEP version of the code, the user can also specify fluxes of CBOD from the benthic layer to the water column. As with SOD and the similar fluxes for ammonium and phosphate, this specified flux is only implemented in the model if there are no sediment segments. If a single sediment segment is present in the model, then it is assumed that the benthic calculation discussed below is to be implemented instead.

The calculational framework incorporated for benthic-water column exchange draws principally from a study of Lake Erie, which incorporated sediment-water column interactions, performed by Di Toro and Connolly (1980). For a single benthic layer with thickness, Dj, the CBOD and DO mass balance equations are summarized in Figure 4.3. The equivalent SOD generated for the overlying water column segment is also given. Subscripts "j" and "i" refer to a benthic segment and the overlying water column segment, respectively.

WASP5 allows a more detailed parameterization of settling into the benthos that includes not only a downward settling velocity but an upward resuspension velocity as well. In this context, then, the net particulate flux to the sediment is due to

Figure 4.3 Benthic layer oxygen balance equations.

the difference between the downward settling flux and the upward resuspension flux.

   One of the first decisions to be made regarding the benthic layer is to determine its depth. Two factors influence this decision. The first is to adequately reflect the thickness of the active layer, the depth to which the sediment is influenced by exchange with the overlying water column. Secondly one wishes the model to reflect a reasonable time history or "memory" in the sediment layer. Too thin a layer and the benthos will "remember"

or be influenced by deposition of material that would have occurred only within the last year or two of the period being analyzed; too thick a layer and the model will "average" too long a history, not reflecting substantial reductions resulting from reduced discharges from sewage treatment plants. The choice of

TABLE 4.2 Benthic Layer CBOD and DO Reaction Terms

Description	Notation	Value	Units
Organic carbon (as CBOD) decomposition rate	k_{DS}	0.0004	day^{-1}
Temperature coefficient	$_{DS}$	1.08	none
Denitrification rate	k_{2D}		day^{-1}
Temperature coefficient	$_{2D}$		none
Phytoplankton decomposition rate	k_{PzD}		day^{-1}
Temperature coefficient	$_{PzD}$		none
Diffusive exchange coefficient	E_{DIF}	2.0×10^{-4}	m^2/day
Benthic layer depth	D_j	0.2-0.7	m
Benthic layer	j		
Water column	i		

sediment thickness is further complicated by spatially variable sedimentation rates. The benthic layer depths, together with the assigned sedimentation velocities, provide for a multi-year detention time or "memory," providing a reasonable approximation of the active layer in light of the observed pore water gradients.

The decomposition reactions that drive the component mass balance equations are the anaerobic decomposition of the phytoplankton carbon, and the anaerobic breakdown of the benthic organic carbon. Both reactions are sinks of oxygen and rapidly drive its concentration negative, indicating that the sediment is reduced rather than oxidized. The negative concentrations computed can be considered the oxygen equivalents of the reduced end products produced by the chains of redox reactions occurring in the sediment.

Because the calculated concentration of oxygen is positive in the overlying water, it is assumed that the reduced carbon species (negative oxygen equivalents) that are transported across the benthic water interface combine with the available oxygen and are oxidized to CO_2 and H_2O with a consequent reduction of oxygen in the overlying water column.

Figure 4.3 and Table 4.2 summarize the benthic CBOD and DO reactions and parameters. Illustrative parameter values from an early Potomac Estuary modeling study are provided.

4.2 MODEL IMPLEMENTATION

To simulate dissolved oxygen with WASP5, use the preprocessor to create a EUTRO5 input dataset. For the portions of the dataset describing environment, transport, and boundaries, EUTRO5 model input will be similar to that for the conservative tracer model as described in Chapter 2. To those basic parameters, the user will add combinations of transformation parameters and perhaps solids transport rates.

EUTRO5 kinetics can be implemented using some or all of the processes and kinetic terms described above to analyze dissolved oxygen problems. For convenience, four levels of complexity are identified here: (1) Streeter-Phelps, (2) modified Streeter-Phelps, (3) full linear DO balance, and (4) nonlinear DO balance. Please note that the discrete levels of simulation identified here are among a continuum of levels that the user could implement.

The four implementation levels are described briefly below, along with the input parameters required to solve the DO balance equations in EUTRO5. Input parameters are prepared for WASP5 in

Table 4.3 Summary of EUTRO5 Variables Used in DO Balance

Variable	Notation	Concentration	Units
1. Ammonia Nitrogen	NH3	C_1	mg N/L
2. Nitrate Nitrogen	NO3	C_2	mg N/L
4. Phytoplankton Carbon	PHYT	C_4	mg C/L
5. Carbonaceous BOD	CBOD	C_5	mg O_2/L
6. Dissolved Oxygen	DO	C_6	mg O_2/L
7. Organic Nitrogen	ON	C_7	mg N/L
9. Periphyton Carbon	MAC	C_9	mg C/m^2

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four major sections of the preprocessor -- environment, transport, boundaries, and transformation. Basic model parameters are described in Chapter 2, and will not be repeated here. Six of the eight EUTRO5 state variables that can participate in DO balance simulations, with abbreviations used in this text, are listed in Table 4.3.

Streeter-Phelps

The simplest dissolved oxygen balance solves the Streeter-Phelps BOD-DO equations in a slightly modified form.

$$S_{k5} = -k_d \Theta_d^{T-20} C_5 - \frac{v_{s3}}{D} (1 - f_{D5}) C_5 \qquad\qquad \textbf{4.17}$$

$$S_{k6} = +k_2 \Theta_2^{T-20} (C_s - C_6) - k_d \Theta_d^{T-20} C_5 - \frac{SOD_T}{D} \qquad\qquad \textbf{4.18}$$

where S_{ki} is the source/sink term for variable "i" in a segment, in mg/L-day. Kinetic rate constants and coefficients are as defined in Table 4.1, except that C_5 is interpreted as total (not just carbonaceous) biochemical oxygen demand, BOD. These equations are usually applied in well-defined low flow design conditions.

Environment Parameters

These parameters define the basic model identity, including the segmentation, and control the simulation.

Systems-- Select "simulate" for CBOD and DO and "bypass" for the other six systems. For this implementation, the CBOD system is used to represent total ultimate BOD. (Group A, Record 4, NOSYS; Record 9, SYSBY)

Segments-- Water column segments should be defined in the standard fashion. If BOD settling is to be simulated, the user should add a single benthic segment underlying all water column segments. This benthic segment will merely act as a convenient sink for settling BOD. Model calculations within this benthic

segment should be ignored. (Group A, Record 4, NOSEG; Group C, Record 3, ISEG, IBOTSG, ITYPE, BVOL, DMULT)

Transport Parameters

    This group of parameters defines the advective and dispersive transport of simulated model variables.

    Number of Flow Fields-- To simulate settling, the user should select solids 1 flow under advection. The user should also select water column flow. (Group D, Record 1, NFIELD)

    Particulate Transport, m^3/sec-- Time variable settling and resuspension rates for particulate BOD can be input using the Solids 1 continuity array BQ and the time function QT. For each solids flow field, cross-sectional exchange areas (m^2) for adjacent segment pairs are input using the spatially-variable BQ. Time-variable settling velocities can be specified as a series of velocities, in m/sec, versus time. If the units conversion factor is set to 1.157e-5, then these velocities are input in units of m/day. These velocities are multiplied internally by cross-sectional areas and treated as flows that carry particulate organic matter out of the water column. (Group D, Record 4, BQ, JQ, IQ; Record 6, QT, TQ)

Boundary Parameters

    This group of parameters includes boundary concentrations, waste loads, and initial conditions. Boundary concentrations must be specified for any segment receiving flow inputs, outputs, or exchanges. Initial conditions include not only initial concentrations, but also the density and solids transport field for each solid, and the dissolved fraction in each segment.

    Boundary Concentrations, mg/L-- At each segment boundary, time variable concentrations must be specified for BOD and DO. A boundary segment is characterized by water exchanges from outside the network, including tributary inflows, downstream outflows, and open water dispersive exchanges. (Group E, Record 4, BCT)

    Waste Loads, kg/day-- For each point source discharge, time variable BOD and DO loads can be specified. These loads can represent municipal and industrial wastewater discharges, or urban and agricultural runoff. (Group F.1, Record 4, WKT)

Solids Transport Field-- The transport field associated with particulate BOD settling must be specified under initial conditions. Field 3 is recommended. (Group J, Record 1, IFIELD)

Solid Density, g/cm^3-- A value of 0 can be entered for the nominal density of BOD and DO. This information is not used in EUTRO5. (Group J, Record 1, DSED)

Initial Concentrations, mg/L-- Concentrations of BOD and DO in each segment must be specified for the time at which the simulation begins. Concentrations of zero for nonsimulated variables -- NH3, NO3, PO4, PHYT, ON, and OP -- will be entered by the preprocessor. (Group J, Record 2, C)

Dissolved Fraction-- The dissolved fraction of BOD and DO in each segment must be specified. Values for DO should be 1.0. Only the particulate fraction of BOD will be subject to settling. (Group J, Record 2, DISSF)

Transformation Parameters

This group of parameters includes spatially variable parameters, constants, and kinetic time functions for the water quality constituents being simulated. Parameter values are entered for each segment. Specified values for constants apply over the entire network for the whole simulation. Kinetic time functions are composed of a series of values versus time, in days.

Water Temperature, °C-- Segment variable water temperatures can be specified using the parameter TMPSG (parameter TMPFN and time functions TEMP(1-4) should be omitted). Temperatures will remain constant in time. (Group G, Record 4, PARAM(I,3))

Sediment Oxygen Demand, g/m^2-day-- Segment variable sediment oxygen demand fluxes can be specified using the parameter SOD1D. Values should be entered for water column segments that are in contact with the bottom of the water body. (Group G, Record 4, PARAM(I,9))

BOD Deoxygenation Rate, day^{-1}-- The BOD deoxygenation rate constant and temperature coefficient can be specified using constants KDC and KDT, respectively. (Group H, Record 4, CONST(72), CONST(73))

Reaeration Rate, day^{-1}-- There are three options for specifying reaeration rate constants in EUTRO5. In the first

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option, a single reaeration rate constant can be specified using constant K2 (Constant 82). An internal temperature coefficient of 1.028 is used with this option.

If K2 is not entered (or is set to 0), the second option is attempted by EUTRO5. In this option, variable reaeration rate constants can be input using parameter REARSG and time function REAR. The product of spatially-variable REARSG and time-variable REAR gives the segment and time specific reaeration rate constants used by EUTRO5. These reaeration values are not modified by a temperature function.

The third option is invoked if neither K2 nor REARSG is entered. In this option, reaeration rates will be calculated from water velocity, depth, wind velocity, and water and air temperature. The actual reaeration rate used by EUTRO5 will be either the flow or wind-induced value, whichever is largest.

For rivers, segment water velocities and depths are calculated as a function of flow using the hydraulic coefficients entered under the topic "environment" (Group C, Record 3, a, b, c, d). For lakes and estuaries, ambient velocities in m/sec can be input using parameter VELFN and time functions VEL(1-4). The parameter VELFN indicates which velocity function will be used by the model for each segment. Values of 1.0, 2.0, 3.0, or 4.0 will call time functions VELN(1), VELN(2), VELN(3), and VELN(4), respectively. Water velocities should then be entered via these time functions as a series of velocity versus time values.

For open bodies of water, wind-driven reaeration can be significant. The user should input ambient wind speed, in m/sec, and air temperature, in °C, using time functions WIND and AIRTMP. The default values for wind speed and air temperature are 0.6 m/sec and 15 C. The scale of the water body should be input using constant WTYPE. Values of 1.0, 2.0, and 3.0 indicate laboratory scale, lake and reservoir scale, and open ocean scale, respectively. The default value is 2.

For estuaries, where salinity affects DO saturation significantly, salinity values in g/L can be input using parameter SAL and time function SALFN. The product of spatially-variable SAL and time-variable SALFN gives the segment and time specific salinity values used by EUTRO5. Average segment salinity values can be input to SAL, while relative variations in time, if significant, can be input to SALFN.

For northern climates, where ice cover can affect reaeration during winter months, the user may input the fraction of water

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surface available for reaeration using time function XICECVR. A
value of 1.0 indicates that the entire surface area is available
for reaeration. The time variable value of XICECVR will be
multiplied by the reaeration rate constants for options 1 and 3.
For option 2, it is assumed that ice cover is built into the time
function REAR.

   WTYPE and K2 are identified in EUTRO5 as constants 1 and 82.
VELFN, SAL, and REARSG are identified in EUTRO5 as parameters 1,
2, and 14, respectively. WIND, VELN(1-4), SALFN, AIRTMP,
XICECVR, and REAR are identified in EUTRO5 as time functions 7,
15-18, 20, 21, 22, and 23 respectively. (Group G, Record 4,
PARAM(I,1), PARAM(I,2), PARAM(I,14); Group H, Record 4,
CONST(82); Group I, Record 2, VALT(7,K), VALT(15-18,K),
VALT(20,K), VALT(21,K), VALT(22,K), VALT(23,K))

Modified Streeter-Phelps

   The modified Streeter-Phelps equations divide biochemical
oxygen demand into carbonaceous and nitrogenous fractions, and
allow time-variable temperatures to be specified. This allows
for more realistic calibration to observed data. Waste load
allocations, however, are usually projected for design low-flow
conditions.

$$S_{k5} = -k_d \, \Theta_d^{T-20} \, C_5 - \frac{v_{s3}}{D} (1 - f_{D5}) \, C_5 \qquad \textbf{4.19}$$

$$S_{k1} = -k_n \, \Theta_n^{T-20} \, C_1 - \frac{v_{s3}}{D} (1 - f_{D1}) \, C_1 \qquad \textbf{4.20}$$

$$S_{k6} = +k_2 \, \Theta_2^{T-20} \, (C_s - C_6) - k_d \, \Theta_d^{T-20} \, C_5$$

$$- \frac{64}{14} \, k_n \, \Theta_n^{T-20} \, C_1 - \frac{SOD}{D} \, \Theta_s^{T-20} \qquad \textbf{4.21}$$

where S_{ki} is the source/sink term for variable "i" in a segment,
in mg/L-day. Kinetic rate constants and coefficients are as
defined in Table 4.1, except for the following:

C_1 =   nitrogenous biochemical oxygen demand (NBOD), as expressed by TKN, mg/L (use System 1)

k_n =   nitrogenous deoxygenation rate constant, day^{-1}

$_n$ =   temperature coefficient

f_{D1} =   NBOD dissolved fraction

To implement these equations in EUTRO5, System 1 (nominally NH3) must be interpreted as nitrogenous BOD rather than ammonia. Here, NBOD is expressed by total Kjeldahl nitrogen (TKN). If directly measured NBOD data are available, values should be divided by 4.57 before use in this model. Likewise, System 1 model predictions should be multiplied by 4.57 before comparison with NBOD data.

Environment Parameters

     These parameters define the basic model identity, including the segmentation, and control the simulation.

     Systems-- Select "simulate" for NH3, CBOD and DO and "bypass" for the other five systems. For this implementation, the NH3 system is used to represent nitrogenous BOD, as expressed by TKN. (Group A, Record 4, NOSYS; Record 9, SYSBY)

     Segments-- Water column segments should be defined in the standard fashion. If CBOD or NBOD settling is to be simulated, the user should add a single benthic segment underlying all water column segments. This benthic segment will merely act as a convenient sink for settling BOD. Model calculations within this benthic segment should be ignored. (Group A, Record 4, NOSEG; Group C, Record 3, ISEG, IBOTSG, ITYPE, BVOL, DMULT)

Transport Parameters

     This group of parameters define the advective and dispersive transport of model variables.

     Number of Flow Fields-- To simulate settling, the user should select solids 1 flow under advection. The user should also select water column flow. (Group D, Record 1, NFIELD)

     Particulate Transport, m^3/sec-- Time variable settling and resuspension rates for particulate CBOD and NBOD can be input using the Solids 1 continuity array BQ and the time function QT. For each solids flow field, cross-sectional exchange areas (m^2)

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for adjacent segment pairs are input using the spatially-variable BQ. Time-variable settling velocities can be specified as a series of velocities, in m/sec, versus time. If the units conversion factor is set to 1.157e-5, then these velocities are input in units of m/day. These velocities are multiplied internally by cross-sectional areas and treated as flows that carry particulate organic matter out of the water column. (Group D, Record 4, BQ, JQ, IQ; Record 6, QT, TQ)

Boundary Parameters

This group of parameters includes boundary concentrations, waste loads, and initial conditions. Boundary concentrations must be specified for any segment receiving flow inputs, outputs, or exchanges. Initial conditions include not only initial concentrations, but also the density and solids transport field for each solid, and the dissolved fraction in each segment.

Boundary Concentrations, mg/L-- At each segment boundary, time variable concentrations must be specified for CBOD, NBOD, and DO. The NH3 system is used to represent NBOD, which is expressed as TKN. A boundary segment is characterized by water exchanges from outside the network, including tributary inflows, downstream outflows, and open water dispersive exchanges. (Group E, Record 4, BCT)

Waste Loads, kg/day-- For each point source discharge, time variable CBOD, NBOD, and DO loads can be specified. These loads can represent municipal and industrial wastewater discharges, or urban and agricultural runoff. The NH3 system is used to represent NBOD, which is expressed as TKN. (Group F.1, Record 4, WKT)

Solids Transport Field-- The transport field associated with particulate CBOD and NBOD settling must be specified under initial conditions. Field 3 is recommended for both. (Group J, Record 1, IFIELD)

Solid Density, g/cm^3-- A value of 0 can be entered for the nominal density of CBOD, NBOD, and DO. This information is not used in EUTRO5. (Group J, Record 1, DSED)

Initial Concentrations, mg/L-- Concentrations of CBOD, NBOD, and DO in each segment must be specified for the time at which the simulation begins. The NH3 system is used to represent NBOD, which is expressed as TKN. Concentrations of zero for non-

simulated variables -- NO3, PO4, PHYT, ON, and OP -- will be entered by the preprocessor. (Group J, Record 2, C)

Dissolved Fraction-- The dissolved fraction of CBOD, NBOD, and DO in each segment must be specified. Values for DO should be 1.0. Only the particulate fraction of CBOD and NBOD will be subject to settling. (Group J, Record 2, DISSF)

Transformation Parameters

This group of parameters includes spatially variable parameters, constants, and kinetic time functions for the water quality constituents being simulated. Parameter values are entered for each segment. Specified values for constants apply over the entire network for the whole simulation. Kinetic time functions are composed of a series of values versus time, in days.

Water Temperature, °C-- Time and segment variable water temperatures can be specified using the parameters TMPSG and TMPFN, and the time functions TEMP(1-4). If temperatures are to remain constant in time, then the user should enter segment temperatures using the parameter TMPSG. TMPFN and TEMP(1-4) should be omitted.

If the user wants to enter time-variable temperatures, then values for the parameter TMPSG should be set to 1.0. The parameter TMPFN indicates which temperature function will be used by the model for each segment. Values of 1.0, 2.0, 3.0, or 4.0 will call time functions TEMP(1), TEMP(2), TEMP(3), and TEMP(4), respectively. Water temperatures should then be entered via these time functions as a series of temperature versus time values. The product of TMPSG and the selected TEMP function will give the segment and time specific water temperatures used by EUTRO5.

TMPSG and TMPFN are identified in EUTRO5 as parameters 3 and 4, respectively. TEMP(1-4) are identified in EUTRO5 as time functions 1-4. (Group G, Record 4, PARAM(I,3), PARAM(I,4); Group I, Record 2, VALT(1-4,K))

Sediment Oxygen Demand, g/m^2-day-- Segment variable sediment oxygen demand fluxes and temperature coefficients can be specified using the parameters SOD1D and SODTA, respectively. Values should be entered for water column segments that are in contact with the bottom of the water body. If temperatures

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remain constant in time, then SODTA can be omitted. (Group G, Record 4, PARAM(I,9), PARAM(I,11))

CBOD Deoxygenation Rate, day^{-1}-- The CBOD deoxygenation rate constant and temperature coefficient can be specified using constants KDC and KDT, respectively. (Group H, Record 4, CONST(72), CONST(73))

NBOD Deoxygenation Rate, day^{-1}-- The NBOD deoxygenation rate constant and temperature coefficient can be specified using constants K12C and K12T, respectively. (Group H, Record 4, CONST(11), CONST(12))

Reaeration Rate, day^{-1}-- There are three basic options for specifying reaeration -- a single rate constant, segment and time variable rate constants, and flow and wind calculated rate constants. These options are described in the Streeter-Phelps section.

Full Linear DO Balance

The full DO balance equations divide the NBOD process into mineralization and nitrification, and add the effects of photosynthesis and respiration from given phytoplankton levels:

$$s_{k7} = -k_{71}\ \Theta_{71}^{T-20}\ C_7 - \frac{v_{s3}}{D}\ (1 - f_{D7})\ C_7 \qquad\qquad \textbf{4.22}$$

$$S_{k1} = +k_{71}\ \Theta_{71}^{T-20}\ C_7 - k_{12}\ \Theta_{12}^{T-20}\ C_1 \qquad\qquad \textbf{4.23}$$

$$S_{k2} = +k_{12}\ \Theta_{12}^{T-20}\ C_1 \qquad\qquad \textbf{4.24}$$

$$S_{k5} = -k_d\ \Theta_d^{T-20}\ C_5 - \frac{v_{s3}}{D}\ (1 - f_{D5})\ C_5 \qquad\qquad \textbf{4.25}$$

$$S_{k6} = +k_2 \, \Theta_2^{T-20} \, (C_s - C_6) - k_d \, \Theta_d^{T-20} \, C_5 - \frac{64}{14} k_{12} \, \Theta_{12}^{T-20} \, C_1$$

$$-\frac{SOD}{D} \Theta_s^{T-20} + (k_{1c}\Theta_{1c}^{T-20} - k_{1R}\Theta_{1R}^{T-20}) \frac{32}{12} C_4$$

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where S_{ki} is the source/sink term for variable "i" in a segment, in mg/L-day. Kinetic rate constants and coefficients are as defined in Table 4.1. In addition, the following are used:

> k_{71} = organic nitrogen mineralization rate constant, day^{-1}

> $_{71}$ = temperature coefficient

> k_{1C} = average phytoplankton growth rate constant, day^{-1} (user must input light and nutrient limited value)

> $_{1C}$ = temperature coefficient

> f_{D7} = organic nitrogen dissolved fraction

Constant phytoplankton concentrations to be used in the DO balance are input under initial conditions as g/L chlorophyll **a**. If the carbon to chlorophyll ratio is not input, then a default value of 30 is used. The particulate fractions of CBOD and ON are associated with transport field 3, organic matter settling.

Environment Parameters

These parameters define the basic model identity, including the segmentation, and control the simulation.

Systems-- Select "simulate" for NH3, NO3, CBOD, DO, and ON. Select "constant" for PHYT, and "bypass" for PO4 and OP. (Group A, Record 4, NOSYS; Record 9, SYSBY)

Segments-- Water column segments should be defined in the standard fashion. If CBOD or ON settling is to be simulated, the user should add a single benthic segment underlying all water column segments. This benthic segment will merely act as a convenient sink for settling organic matter. Model calculations

within this benthic segment should be ignored. (Group A, Record 4, NOSEG; Group C, Record 3, ISEG, IBOTSG, ITYPE, BVOL, DMULT)

Transport Parameters

    This group of parameters define the advective and dispersive transport of model variables.

    Number of Flow Fields-- To simulate settling, the user should select solids 1 flow under advection. The user should also select water column flow. (Group D, Record 1, NFIELD)

    Particulate Transport, m^3/sec-- Time variable settling and resuspension rates for particulate CBOD and ON can be input using the Solids 1 continuity array BQ and the time function QT. For each solids flow field, cross-sectional exchange areas (m^2) for adjacent segment pairs are input using the spatially-variable BQ. Time-variable settling velocities can be specified as a series of velocities, in m/sec, versus time. If the units conversion factor is set to 1.157e-5, then these velocities are input in units of m/day. These velocities are multiplied internally by cross-sectional areas and treated as flows that carry particulate organic matter out of the water column. (Group D, Record 4, BQ, JQ, IQ; Record 6, QT, TQ)

Boundary Parameters

    This group of parameters includes boundary concentrations, waste loads, and initial conditions. Boundary concentrations must be specified for any segment receiving flow inputs, outputs, or exchanges. Initial conditions include not only initial concentrations, but also the density and solids transport field for each solid, and the dissolved fraction in each segment.

    Boundary Concentrations, mg/L-- At each segment boundary, time variable concentrations must be specified for NH3, NO3, ON, CBOD, and DO. A boundary segment is characterized by water exchanges from outside the network, including tributary inflows, downstream outflows, and open water dispersive exchanges. (Group E, Record 4, BCT)

    Waste Loads, kg/day-- For each point source discharge, time variable NH3, NO3, ON, CBOD, and DO loads can be specified. These loads can represent municipal and industrial wastewater discharges, or urban and agricultural runoff. (Group F.1, Record 4, WKT)

Solids Transport Field-- The transport field associated with particulate CBOD and ON settling must be specified under initial conditions. Field 3 is recommended for both. (Group J, Record 1, IFIELD)

Solid Density, g/cm^3-- A value of 0 can be entered for the nominal density of NH3, NO3, ON, CBOD, and DO. This information is not used in EUTRO5. (Group J, Record 1, DSED)

Initial Concentrations, mg/L-- Concentrations of NH3, NO3, ON, CBOD, and DO in each segment must be specified for the time at which the simulation begins. Average concentrations of PHYT, expressed as g/L chlorophyll a, must be specified as well. These are converted to mg/L phytoplankton carbon in EUTRO5 using a default carbon to chlorophyll ration of 30. Phytoplankton concentrations will remain constant throughout the simulation and affect DO through photosynthesis and respiration. Concentrations of zero for non-simulated variables -- PO4 and OP -- will be entered by the preprocessor. (Group J, Record 2, C)

Dissolved Fraction-- The dissolved fraction of NH3, NO3, ON, CBOD, and DO in each segment must be specified. Values for DO should be 1.0. Only the particulate fraction of CBOD and ON will be subject to settling. (Group J, Record 2, DISSF)

Transformation Parameters

This group of parameters includes spatially variable parameters, constants, and kinetic time functions for the water quality constituents being simulated. Parameter values are entered for each segment. Specified values for constants apply over the entire network for the whole simulation. Kinetic time functions are composed of a series of values versus time, in days.

Water Temperature, °C-- Time and segment variable water temperatures can be specified using the parameters TMPSG and TMPFN, and the time functions TEMP(1-4), as described in the modified Streeter-Phelps section.

Sediment Oxygen Demand, g/m^2-day-- Segment variable sediment oxygen demand fluxes and temperature coefficients can be specified using the parameters SOD1D and SODTA, respectively. Values should be entered for water column segments that are in contact with the bottom of the water body. (Group G, Record 4, PARAM(I,9), PARAM(I,12))

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Nitrogen Mineralization Rate, day^{-1}-- The mineralization rate constant and temperature coefficient for dissolved organic nitrogen can be specified using constants K71C and K71T, respectively. (Group H, Record 4, CONST(91), CONST(92))

Nitrification Rate, day^{-1}-- The nitrification rate constant and temperature coefficient for dissolved ammonia nitrogen can be specified using constants K12C and K12T, respectively. (Group H, Record 4, CONST(11), CONST(12))

CBOD Deoxygenation Rate, day^{-1}-- The CBOD deoxygenation rate constant and temperature coefficient can be specified using constants KDC and KDT, respectively. (Group H, Record 4, CONST(72), CONST(73))

Reaeration Rate, day^{-1}-- There are three basic options for specifying reaeration -- a single rate constant, segment and time variable rate constants, and flow and wind calculated rate constants. These options are described in the Streeter-Phelps section.

Photosynthesis Rate, day^{-1}-- The average phytoplankton growth rate constant and temperature coefficient can be input using constants K1C and K1T, respectively. For DO balance simulations where phytoplankton dynamics are bypassed, the growth rate constant must reflect average light and nutrient limitations in the water body. (Group H, Record 4, CONST(41), CONST(42))

Respiration Rate, day^{-1}-- The average phytoplankton respiration rate constant and temperature coefficient can be input using constants K1RC and K1RT, respectively. (Group H, Record 4, CONST(50), CONST(51))

Nonlinear DO Balance

The nonlinear DO balance equations add feedback from DO concentratons to terms in the linear DO balance equations presented above. This feedback can become important in inhibiting nitrification and carbonaceous oxidation and in promoting denitrification where low DO concentrations occur.

For this level of analysis, the linear DO balance equations presented above are supplemented with nonlinear terms for carbonaceous oxidation, nitrification, and denitrification. These terms are presented in Figure 4.2 and Table 4.1. The environment, transport, and boundary parameters required to

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implement the nonlinear DO balance are the same as those in the linear DO balance presented above. The user should supplement the transformation parameters presented above with the following.

Nitrification Rate, day^{-1}-- The nitrification rate constant and temperature coefficient for dissolved ammonia nitrogen can be specified using constants K12C and K12T, respectively. The half-saturation constant for oxygen limitation of nitrification can be specified using constant KNIT. The default value for KNIT is 0.0, indicating no oxygen limitation. (Group H, Record 4, CONST(11), CONST(12), CONST(13))

Denitrification Rate, day^{-1}-- The denitrification rate constant and temperature coefficient for dissolved nitrate nitrogen can be specified using constants K20C and K20T, respectively. The half-saturation constant for oxygen limitation of denitrification can be specified using constant KNO3. The default value for KNO3 is 0.0, indicating no denitrification at oxygen concentrations above 0.0. (Group H, Record 4, CONST(21), CONST(22), CONST(23))

CBOD Deoxygenation Rate, day^{-1}-- The CBOD deoxygenation rate constant and temperature coefficient can be specified using constants KDC and KDT, respectively. The half-saturation constant for oxygen limitation of carbonaceous deoxygenation can be specified using constant KBOD. The default value for KBOD is 0.0, indicating no oxygen limitation. (Group H, Record 4, CONST(72), CONST(73), CONST(75))

Data Group Descriptions

Input datasets to simulate DO balance in a river are given with the model software. A comprehensive listing of the WASP5 data groups, records, and variables is given in Part B of this documentation.

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CHAPTER 5

EUTROPHICATION

5.1 MODEL DESCRIPTION

Introduction

     Nutrient enrichment and eutrophication are continuing
concerns in many water bodies. High concentrations of nitrogen
and phosphorus can lead to periodic phytoplankton blooms and an
alteration of the natural trophic balance. Dissolved oxygen
levels can fluctuate widely, and low DO concentrations in bottom
waters can result.

     Eutrophication has been modeled for approximately 30 years.
The equations implemented here were derived from the Potomac
Eutrophication Model, PEM (Thomann and Fitzpatrick, 1982), and
are fairly standard. Sections of this text are modified from the
PEM documentation report.

Overview of WASP5 Eutrophication

     The nutrient enrichment, eutrophication, and DO depletion
processes are simulated using the EUTRO5 program. Several
physical-chemical processes can affect the transport and
interaction among the nutrients, phytoplankton, carbonaceous
material, and dissolved oxygen in the aquatic environment.
Figure 5.1 presents the principal kinetic interactions for the
nutrient cycles and dissolved oxygen.

     EUTRO5 can be operated by the user at various levels of
complexity to simulate some or all of these variables and
interactions. Four levels for simulating the DO balance were
described in Chapter 4. Three levels of complexity for
simulating eutrophication are identified and documented at the
end of this section: (1) simple eutrophication kinetics, (2)
intermediate eutrophication kinetics, and (3) intermediate
eutrophication kinetics with benthos. The user should become
familiar with the full capabilities of EUTRO5 even if simpler
simulations are planned.

EUTRO5 simulates the transport and transformation reactions
of up to eight state variables, illustrated in Figure 5.1. They
can be considered as four interacting systems: phytoplankton
kinetics, the phosphorus cycle, the nitrogen cycle, and the
dissolved oxygen balance. The general WASP5 mass balance
equation is solved for each state variable. To this general
equation, the EUTRO5 subroutines add specific transformation
processes to customize the general mass balance for the eight
state variables in the water column and benthos. Following a
short summary of the material cycles, the rest of Section 5.1
covers the specific details for the several transformation
sources and sinks.

Phosphorus Cycle

        Dissolved or available inorganic phosphorus (DIP) interacts
with particulate inorganic phosphorus via a sorption-desorption
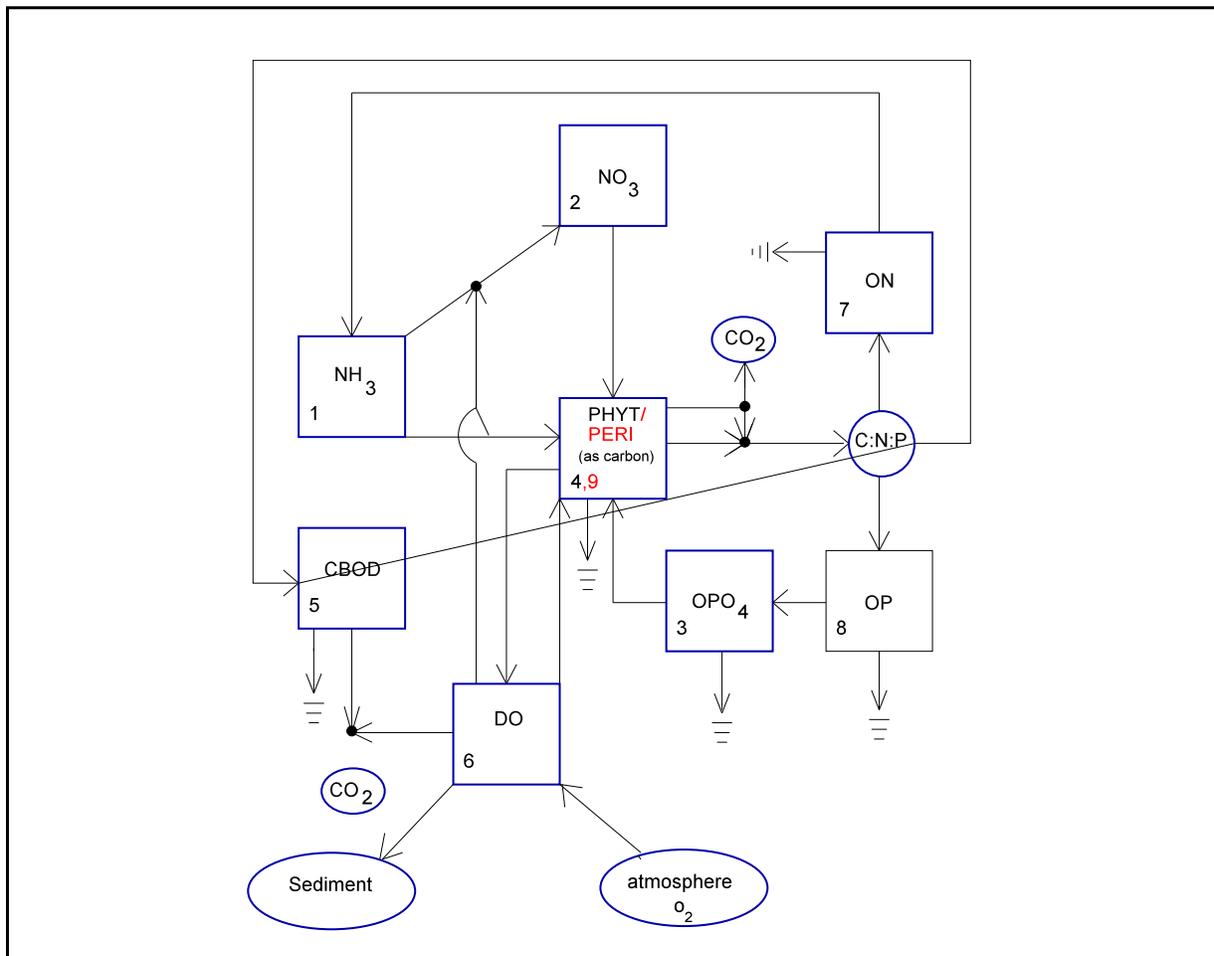
Figure 5.1   EUTRO5 state variable interactions (note that
settling occurs only for phytoplankton and not for periphyton).

mechanism. DIP is taken up by phytoplankton and periphyton for growth, and is incorporated into phytoplankton and periphyton biomass. Phosphorus is returned from the phytoplankton and periphyton biomass pool to dissolved and particulate organic phosphorus and to dissolved inorganic phosphorus through endogenous respiration and nonpredatory mortality. Organic phosphorus is converted to dissolved inorganic phosphorus at a temperature-dependent mineralization rate.

Nitrogen Cycle

The kinetics of the nitrogen species are fundamentally the same as the phosphorus system. Ammonia and nitrate are taken up by phytoplankton and periphyton for growth, and incorporated into phytoplankton and periphyton biomass. The rate at which each is taken up is a function of its concentration relative to the total inorganic nitrogen (ammonia plus nitrate) available. Nitrogen is returned from the phytoplankton and periphyton biomass pool to dissolved and particulate organic nitrogen and to ammonia through endogenous respiration and nonpredatory mortality. Organic nitrogen is converted to ammonia at a temperature dependent mineralization rate, and ammonia is then converted to nitrate at a temperature- and oxygen-dependent nitrification rate. Nitrate may be converted to nitrogen gas in the absence of oxygen at a temperature- and oxygen-dependent denitrification rate.

Dissolved Oxygen

Dissolved oxygen is coupled to the other state variables. The sources of oxygen considered are reaeration and evolution by phytoplankton during growth. The sinks of oxygen are algal respiration, oxidation of detrital carbon and carbonaceous material from waste effluents and nonpoint discharges, and nitrification. These processes are discussed in Chapter 4.

Phytoplankton Kinetics

Phytoplankton kinetics assume a central role in eutrophication, affecting all other systems. An overview of this system is given in Figure 5.2.

It is convenient to express the reaction term of phytoplankton, S_{k4j}, as a difference between the growth rate of phytoplankton and their death and settling rates in the volume V_j. That is:

$$S_{k4j} = (G_{p1j} - D_{p1j} - k_{s4j})\ P_j \hspace{4cm} \textbf{5.1}$$

where:

S_{k4j} = reaction term, mg carbon/L-day

P_j = phytoplankton population, mg carbon/L

G_{p1j} = growth rate constant, day^{-1}

D_{p1j} = death plus respiration rate constant, day^{-1}

k_{s4j} = settling rate constant, day^{-1}

j = segment number, unitless
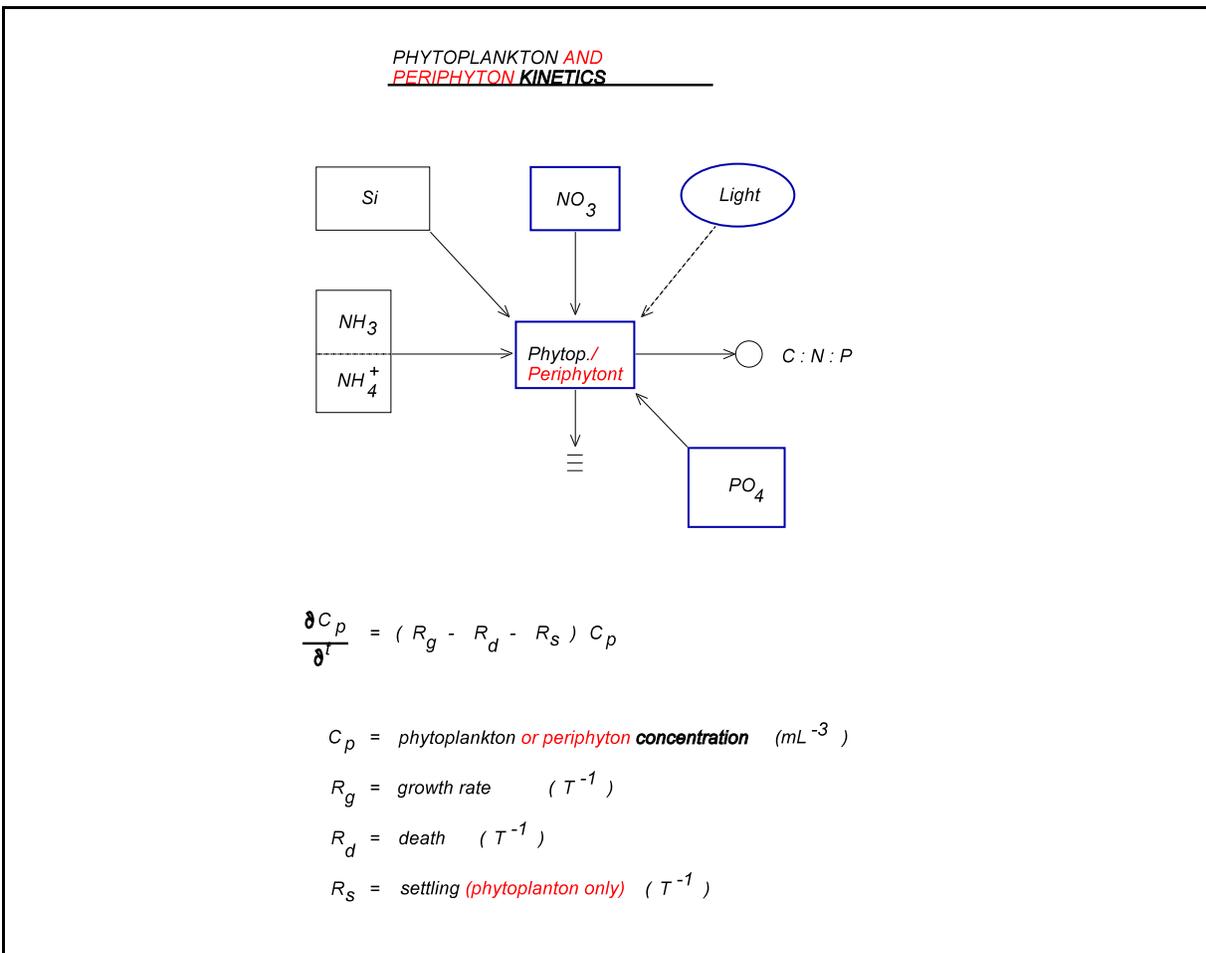
Figure 5.2   Phytoplankton and periphyton kinetics.

The subscript 1 identifies the quantities as referring to phytoplankton type 1, (only one type is considered in this particular model); the subscript j refers to the volume element being considered. The balance between the magnitude of the growth rate and death rate (together with the transport, settling, and mixing) determines the rate at which phytoplankton mass is created in the volume element V_j. In subsequent text and in figures, subscripts i and j will be omitted unless needed for clarity.

Phytoplankton Growth

The growth rate of a population of phytoplankton in a natural environment is a complicated function of the species of phytoplankton present and their differing reactions to solar radiation, temperature, and the balance between nutrient availability and phytoplankton requirements. The available information is not sufficiently detailed to specify the growth kinetics for individual algal species in a natural environment. Rather than considering the problem of different species and their associated environmental and nutrient requirements, this model characterizes the population as a whole by the total biomass of the phytoplankton present.

A simple measure of total biomass that is characteristic of all phytoplankton, chlorophyll *a*, is used as the aggregated variable. The principal advantages are that the measurement is direct; it integrates cell types and ages, and it accounts for cell viability. The principal disadvantage is that it is a community measurement with no differentiation of functional groups (e.g., diatoms, blue-greens); also, it is not necessarily a good measurement of standing crop in dry weight or carbon units because the chlorophyll-to-dry-weight and carbon ratios are variable and non-active chlorophyll (phaeopigments) must be measured to determine viable chlorophyll concentrations.

As can be seen from the above discussion, no simple aggregate measurement is entirely satisfactory. From a practical point of view, the availability of extensive chlorophyll data essentially dictates its use as the aggregate measure of the phytoplankton population or biomass for calibration and verification purposes. For internal computational purposes, however, EUTRO5 uses phytoplankton carbon as a measure of algal biomass. Using either a fixed or variable carbon to chlorophyll mechanism (discussed subsequently), phytoplankton chlorophyll *a* may be computed and used as the calibration and verification variable to be compared against observed chlorophyll *a* field data.

With a choice of biomass units established, a growth rate that expresses the rate of production of biomass as a function of the important environmental variables (temperature, light, and nutrients) may be developed. The specific growth rate, G_{P1j}, in segment j is related to k_{1c}, the maximum 20°C growth rate at optimum light and nutrients, via the following equation.

$$G_{P1j} = k_{1c}\ X_{RTj}\ X_{RIj}\ X_{RNj} \hspace{4cm} \textbf{5.2}$$

where:

X_{RTj} = the temperature adjustment factor, dimensionless

X_{RIj} = the light limitation factor as a function of I, f, D, and K_e, dimensionless (see below)

X_{RNj} = the nutrient limitation factor as a function of dissolved inorganic phosphorus and nitrogen (DIP and DIN), dimensionless (see below)

T = ambient water temperature, °C

I = incident photosynthetically active solar radiation, ly/day

f = fraction day that is daylight, unitless

D = depth of the water column or model segment, m

K_e = total light extinction coefficient, m^{-1}

DIP = dissolved inorganic phosphorus (orthophosphate) available for growth, mg/L

DIN = dissolved inorganic nitrogen (ammonia plus nitrate) available for growth, mg/L

An initial estimate of k_{1c} can be made based upon previous studies of phytoplankton dynamics and upon reported literature values (such as Bowie et al., 1985) and subsequently refined during the calibration and verification process. This maximum growth rate constant is adjusted throughout the simulation for ambient temperature, light, and nutrient conditions.

   Temperature -- Water temperature has a direct effect on the phytoplankton growth rate. The selected maximum growth rate is

temperature-corrected using temporally- and spatially-variable
water column temperatures as reported in field studies. The
temperature correction factor is computed using:

$$X_{RTj} = \Theta_{1c}^{T-20}$$
  5.3

where:

Θ_{1c} = temperature coefficient, unitless

Light -- In the natural environment, the light intensity to
which the phytoplankton are exposed is not uniformly at the
optimum value. At the surface and near-surface of the air-water
interface, photoinhibition can occur at high light intensities,
whereas at depths below the euphotic zone light is not available
for photosynthesis due to natural and algal-related turbidity.

Modeling frameworks developed by DiToro et al. (1971), and
by Smith (1980), extending upon a light curve analysis formulated
by Steele (1962), account for both the effects of supersaturating
light intensities and light attenuation through the water column.
The daily-average depth-averaged growth rate reduction developed
by DiToro based on Steele is presented in Equation 5.4 and is
obtained by integrating the specific growth rate over depth:

$$\overline{X_{RI}} = \frac{e}{K_e\,D}\,f\,\left[\exp\left\{-\frac{I_a}{I_s}\exp(-K_e\,D)\right\} - \exp\left(-\frac{I_a}{I_s}\right)\right]$$
  5.4

where:

I_a = the average incident photosynthetically available
light intensity during daylight hours just below
the surface = TFACT * H, ly/day = I/f

TFACT = the fraction of the total solar radiation that is
photosynthetically available. TFACT typically has
a value of 0.43 to 0.45 according to Brown and
Barnwell (1987). In the EPA version of WASP
Version 5, a fixed value of 0.9 is used in
Equation 5.4 instead of TFACT

H = total solar radiation, langleys/day

I_s = the saturating photosynthetically active light intensity of phytoplankton, ly/day

K_e = the light extinction coefficient, computed from the sum of the non-algal light attenuation, K_e', and the phytoplankton self-shading attenuation, K_{eshd} (as calculated by Equation 5.5), m^{-1}

$$K_{eshd} = 0.0088\,P_{Chl} + 0.054\,P_{Chl}^{0.67}$$
5.5

P_{Chl} = phytoplankton chlorophyll concentration, g/L

Table 5.1 Calculated Solar Radiant Energy Flux to a Horizontal Surface Under a Clear Sky (langleys/day)[1]

Latitude	Time of Day	Season				Annual Mean
		Spring	Summer	Fall	Winter	
30°N	Mean[2]	680	750	530	440	600
	Mid-Day[3]	2100	2200	1700	1400	1900
40°N	Mean	650	740	440	320	540
	Mid-Day	1900	2100	1400	1000	1600
50°N	Mean	590	710	330	190	460
	Mid-Day	1700	1900	1000	650	1300

[1]total solar radiation, which is greater than the photosynthetically active radiation

[2]calculated seasonal means under a clear sky, representing upper limits for solar radiant energy at sea level. Reference: Weast and Astle (1980).

[3]Mid-day flux extended over a 24-hour period, assuming an atmospheric turbidity of 0, precipitable water content of 2 cm, and an atmospheric ozone content of .34 cm NTP. Reference: Robinson (1966).

Typical clear sky values of total solar radiation for different latitudes and months are provided in Table 5.1.

Equation 5.4 is quite similar in form to that developed by Smith (1980), which is also available as an option in this model:

$$X_{RI}(t) = \frac{e}{K_e D} \left[\exp\left\{ -\frac{I_o}{I_s} \exp(-K_e D) \right\} - \exp\left(-\frac{I_o}{I_s} \right) \right] \qquad \textbf{5.6}$$

where:

$$I_o(t) = \left(\frac{\pi}{2} \frac{I}{f} \right) SIN\left(\frac{\pi\, t}{f} \right), \qquad t = 0 - f$$

$$\qquad\qquad = 0, \qquad\qquad\qquad\qquad t = f - 1 \qquad \textbf{5.7}$$

and

$$I_s = \frac{k_{1c}\, X_{RT}\, \Theta_c\, e}{\Phi_{max}\, K_c\, f_u} \qquad \textbf{5.8}$$

where:

I_o = the time variable incident photosynthetically active light intensity just below the surface, assumed to follow a half sin function over daylight hours, ly/day

Φ_{max} = the quantum yield, mg carbon fixed per mole of light quanta absorbed

K_c = the extinction coefficient per unit of chlorophyll, m^2/mg chlorophyll a

K_e = the light extinction coefficient, computed from the sum of the non-algal light attenuation, K_e', and the phytoplankton self-shading attenuation, K_{eshd} (as calculated by Equation 5.9), m^{-1}

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$$K_{eshd} = K_c \; P_{Chl} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{5.9}$$

f_u = units conversion factor (= 0.19 TFACT, assuming TFACT is the fraction of incident light that is photosynthetically active and 1 mole photons is equivalent to 52,000 cal), mole photons/m^2-ly

$_c$ = the ratio of carbon to chlorophyll in the phytoplankton, (mg carbon/mg chlorophyll a)

e = the base of natural logarithms (2.71828), unitless

Equations 5.6 - 5.9 give a light limitation coefficient that varies over the day with incident light. This term is numerically integrated over the day within the computer program to obtain daily average light limitation:

$$\overline{X_{RI}} = \int_{o}^{1} X_{RI}(t)\,dt \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{5.10}$$

The term I_s, the temperature-dependent light saturation parameter is an unknown in the DiToro/Steele light formulation, and must be determined via the calibration-verification process. In the Smith formulation, this term is calculated from parameters that are reasonably well documented in the literature. As Smith (1980) points out, since the early experiments of Warburg and Negelein (1923), maximum photosynthetic quantum yield ($_{max}$) has been measured for a wide range of conditions (reviewed by Kok, 1960), and a nearly temperature-independent value of 0.08 to 0.1 mole O_2 per mole of photons absorbed is now widely accepted for photosynthesizing plants in general in the laboratory. Bannister (1974a) gives good arguments for adopting 0.06 mole carbon (0.07 mole O_2) per mole of photons as the maximum yield for plankton in nature. Reported values for K_c generally fall in the range 0.01 to 0.02 m^2mg^{-1}, and 0.016 m^2mg^{-1} has been suggested as the approximate average (Bannister, 1974b).

A second feature incorporated in the modeling framework derived from Smith's work is the calculation of a variable carbon to chlorophyll ratio based on the assumption that adaptive changes in carbon to chlorophyll occur so as to maximize the specific growth rate for ambient conditions of light and

temperature. Smith found that phytoplankton adjust chlorophyll composition so that I_s roughly equals 30% of the average available light. The expression used to calculate the carbon to chlorophyll ratio is presented in Equation 5.11:

$$\Theta_c = 0.3 \cdot \frac{\Phi_{max}\ K_c\ f_u}{k_{1c}\ X_{RT}\ e} \cdot I_a \left[\frac{1-e^{-K_e D}}{K_e \cdot D} \right]$$

5.11

where the latter term is the average daily solar radiation within a segment during daylight hours, in ly/day. Note that substituting Equation 5.11 into 5.8 gives an I_s equal to 30% of the average available light.

A review of reported carbon/chlorophyll ratios in nature (Eppley and Sloane, 1966) suggests that physiological factors (in part the energy cost of synthesizing chlorophyll as compared with other cellular compounds) come into play to prevent $_c$ from going much below 20, even in very low light. This lower limit of 20 has been included when determining a value for $_c$. Previously

Table 5.2 Carbon to Chlorophyll a Ratio

Sampling Period	Carbon/Chlorophyll **a** g C/ g Chlorophyll **a**		
	Observed Mean	Observed Range	Predicted Range
July 20-Oct. 6,1970[1]	45	25-68	24-28
August 1-29, 1977[2]	28	12-37	23-26
Sept. 7-28, 1978[2]	21	15-27	26-30
Sept. 7-28, 1978[3]		26-30	

1. Elemental analysis of blue-green algae
2. Laboratory elemental analysis of overall phytoplankton population
3. Estimates of cell composition based upon field data

reported values of $_c$ from algal composition studies conducted by EPA Region III's Central Regional Laboratory (CRL) are compared in Table 5.2 to calculated values of using Equation 5.11. There is general agreement between the measured and calculated values. Unfortunately, no winter algae composition studies were available for comparison purposes.

The Maine DEP version of WASP adds two additional light limitation functions as available options, a half-saturation equation and a formula by Smith (1936). Further discussion of these formulations is available in Bowie et al. (1985). The half-saturation formula does not exhibit photoinhibition effects at higher light levels. It is given as the following for the instantaneous incident light:

$$X_{RI} = \frac{I_o}{I_s + I_o} \qquad\qquad\qquad 5.12$$

where:

$\quad$ I_s $\quad = \quad$ the half-saturation constant for photosynthetically available light, ly/day

Integrating this expression over the water column depth D and over one day yields the expression:

$$\overline{X_{RI}} = \frac{f}{K_e\,D}\,\ln\left(\frac{I_s + I_a}{I_a + I_a\exp(-K_e\,D)}\right) \qquad\qquad 5.13$$

The formulation by Smith (1936) for instantaneous light input is:

$$X_{RI} = \frac{I_o}{\sqrt{I_s^2 + I_o^2}} \qquad\qquad\qquad 5.14$$

where:

$\quad$ I_s $\quad = \quad$ the saturating photosynthetically available light intensity of phytoplankton, ly/day

Integrating this expression over the water column depth D and over one day of time yields the expression:

$$\overline{X_{RI}} = \frac{f}{K_e \, D} \ln \left(\frac{\dfrac{I_a}{I_s} + \sqrt{1 + \left(\dfrac{I_a}{I_s}\right)^2}}{\dfrac{I_a}{I_s}\exp(-K_e \, D) + \sqrt{1 + \left(\dfrac{I_a}{I_s}\exp(-K_e \, D)\right)^2}} \right)$$
$$\quad 5.15$$

Nutrients -- The effects of various nutrient concentrations on the growth of phytoplankton have been investigated and the results are quite complex. As a first approximation to the effect of nutrient concentration on the growth rate, it is assumed that the phytoplankton population in question follows Monod growth kinetics with respect to the important nutrients. That is, at an adequate level of substrate concentration, the growth rate proceeds at the saturated rate for the ambient temperature and light conditions present. At low substrate concentration, however, the growth rate becomes linearly proportional to substrate concentration. Thus, for a nutrient with concentration N_j in the jth segment, the factor by which the saturated growth rate is reduced is: $N_j/(K_m + N_j)$. The constant, K_m (called the Michaelis or half-saturation constant) is the nutrient concentration at which the growth rate is half the saturated growth rate. Because there are two nutrients, nitrogen and phosphorus, considered in this framework, the Michaelis-Menten expression is evaluated for the dissolved inorganic forms of both nutrients and the minimum value is chosen to reduce the saturated growth rate, as given by Equation 5.16.

$$X_{RN} = Min \left(\frac{DIN}{K_{mN} + DIN} \, , \, \frac{DIP}{K_{mP} + DIP} \right) \qquad 5.16$$

At the user's discretion, the multiplicative formulation for nutrient limitation may be selected. This formulation multiplies the two terms in 5.16. It is not generally recommended.

Figure 5.3 presents plots of G(N) versus DIN and DIP with $K_{mN} = 25$ g-N/L and $K_{mP} = 1$ g-P/L, respectively. The upper plot shows the standard Michaelis-Menten response curve to various concentrations of the inorganic nutrients. As can be seen, no significant reduction in growth rate is achieved until DIN is less than 200 g/L (0.2 mg/l) or until DIP is less than 8 g/L (0.008 mg/l).

EFFECTS OF NUTRIENT LIMITATION ON GROWTH
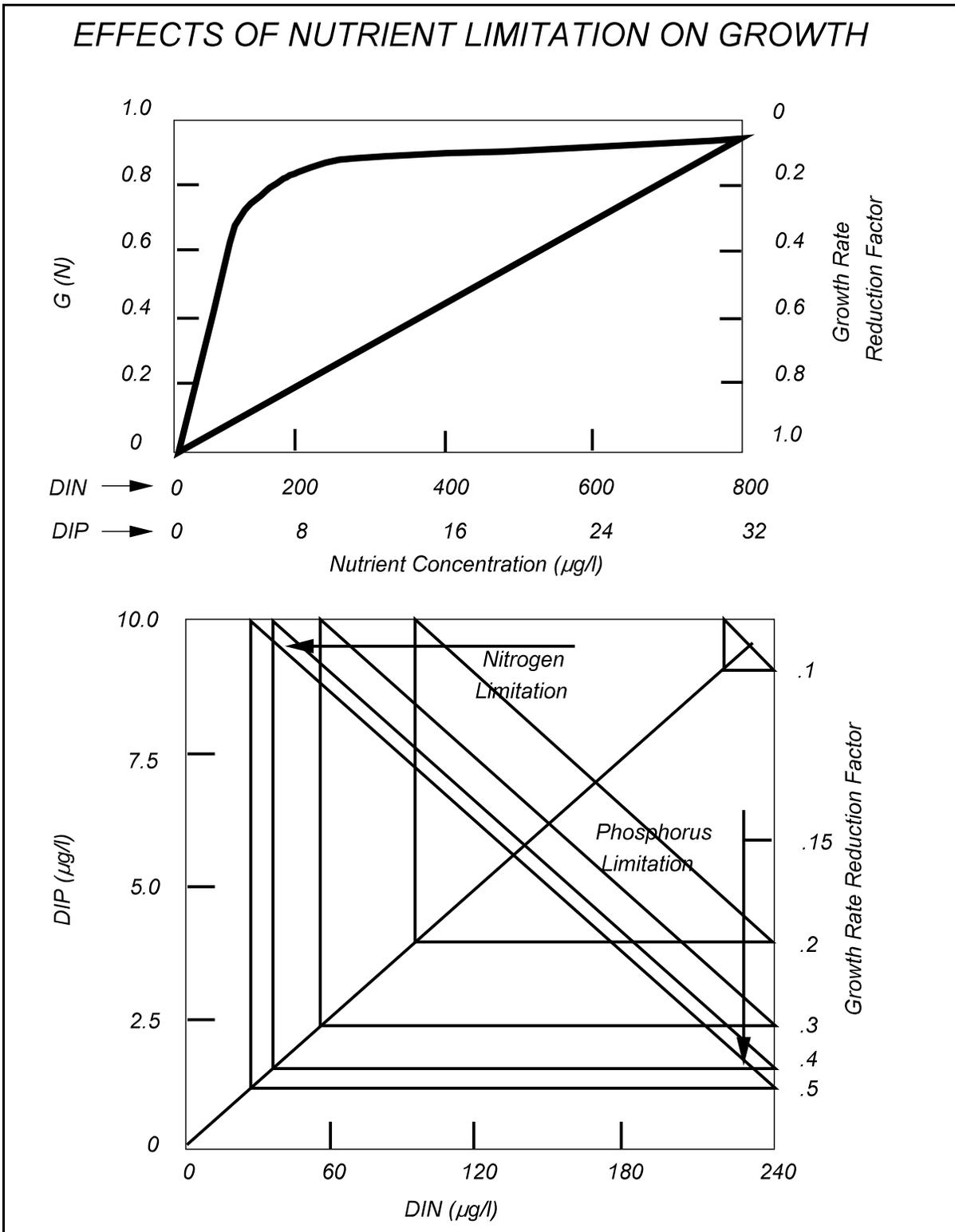
Figure 5.3   Effects of nutrient limitation on growth rate, assuming $K_{mn} = 25$ g-N/L, $K_{mn} = 1$ g-P/L.

The lower plot on Figure 5.3 uses an expanded nutrient scale and shows the Michaelis-Menten formulation in a slightly different format. Here the impact of the function may be evaluated quite readily. For example, a particular reach of the water body may have concentrations of DIN equal to 100 g/L. This corresponds to a 20% reduction in the growth rate (X_{RN} = 0.8). In order for phosphorus to become the limiting nutrient in the same reach, dissolved inorganic phosphorus must reach a level of 4 g/L or less. It should also be noted that if upstream nitrogen controls were instituted such that DIN was reduced to 60 g/L for that same reach, then a further reduction in DIP to 2.5 g/L would be required to keep phosphorus as the limiting nutrient. In other words, as water column concentrations of DIP begin to approach growth limiting levels due to continued reduction in point source phosphorus effluents, any nitrogen control strategies that might be instituted would require additional levels of phosphorus removal in order to keep phosphorus as the limiting nutrient.

Phytoplankton Death

Numerous mechanisms have been proposed that contribute to the biomass reduction rate of phytoplankton: endogenous respiration, grazing by herbivorous zooplankton, and parasitization. The first two mechanisms have been included in previous models for phytoplankton dynamics, and they have been shown to be of general importance.

The endogenous respiration rate of phytoplankton is the rate at which the phytoplankton oxidize their organic carbon to carbon dioxide per unit weight of phytoplankton organic carbon. Respiration is the reverse of the photosynthesis process and, as such, contributes to the reduction in the biomass of the phytoplankton population. If the respiration rate of the phytoplankton as a whole is greater than the growth rate, there is a net loss of phytoplankton carbon or biomass. The endogenous respiration rate is temperature dependent (Riley et at., 1949) and is determined via Equation 5.17:

$$k_{1R}(T) = k_{1R}(20°C)\ \Theta_{1R}^{(T-20)}$$ **5.17**

where:

$k_{1R}(20°C)$ = the endogenous respiration rate at 20°C, day^{-1}

$k_{1R}(T)$ = the temperature corrected rate, day^{-1}

$_{1R}$ = temperature coefficient, dimensionless

Reported values of endogenous respiration at 20° vary from 0.02 day^{-1} to 0.60 day^{-1}, with most values falling between 0.05 day^{-1} and 0.20 day^{-1} (Bowie et al., 1985). Di Toro and Matystik (1980) report a value of 1.045 for $_{1R}$. The total biomass reduction rate for the phytoplankton in the jth segment is expressed via Equation 5.18:

$$D_{1j} = k_{1R}(T) + k_{1D} + k_{1G} Z(t) \qquad \qquad \textbf{5.18}$$

where:

D_{1j} = biomass reduction rate, day^{-1}

k_{1D} = death rate, representing the effect of parasitization, i.e., the infection of algal cells by other microorganisms, and toxic materials, such as chlorine residual, day^{-1}

k_{1G} = grazing rate on phytoplankton per unit zooplankton population, L/mgC-day

$Z(t)$ = herbivorous zooplankton population grazing on phytoplankton, mgC/L

Note that the zooplankton population dynamics are described by the user, not simulated. If population fluctuations are important in controlling phytoplankton levels in a particular body of water, the user may want to simulate zooplankton and their grazing. On the other hand, many studies need only a constant first order grazing rate constant, where grazing rates are assumed proportional to phytoplankton levels. In that case, k_{1G} can be set to the first order constant with $Z(t)$ omitted (default value = 1). Reported grazing rates vary from 0.1 to 1.5 L/mgC-day (Bowie et al., 1985).

Phytoplankton Settling

The settling of phytoplankton is an important contribution to the overall mortality of the phytoplankton population, particularly in lakes and coastal oceanic waters. Published values of the settling velocity of phytoplankton, mostly under quiescent laboratory conditions, range from 0.07-18 m/day. In some instances, however, the settling velocity is zero or negative. Actual settling in natural waters is a complex phenomenon, affected by vertical turbulence, density gradients, and the physiological state of the different species of phytoplankton. Although the effective settling rate of phytoplankton is greatly reduced in a relatively shallow, well mixed river or estuary due to vertical turbulence, it still can contribute to the overall mortality of the algal population. In addition, the settling phytoplankton can be a significant source of nutrients to the sediments and can play an important role in the sediment oxygen demand. In EUTRO5, phytoplankton are equated to solid type 2. Time and segment-variable phytoplankton settling velocities can be input by the user, then, using transport field 4, so that:

$$k_{s4j} = \frac{v_{s4ij}}{D_j}$$
5.19

where:

$\quad k_{s4j} \quad = \quad$ the effective phytoplankton settling or loss rate, day^{-1}

$\quad v_{s4ij} = \quad$ the net settling velocity of phytoplankton from segment j to segment i, m/day

$\quad D_j \quad = \quad$ depth of segment j, equal to volume/surface area, m

Summary

This completes the specification of the growth and death rates of the phytoplankton population in terms of the physical variables: light, temperature, and the nutrient concentrations present. Table 5.3 summarizes the variables and parameters in the net growth equations. With these variables known as a function of time, it is possible to calculate the phytoplankton

Table 5.3 Phytoplankton Net Growth Terms

<u>Exogenous Variables</u>

<u>Description</u>	<u>Notation</u>	<u>Values</u>	<u>Units</u>
Extinction Coefficient	K_e	0.1-5	m^{-1}
Segment Depth	D	0.1-30	m
Water Temperature	T	0-35	°C
Fraction of day that is daylight	f	0.3-0.7	-
Average Daily Surface Solar Radiation	I_a	200-750	langleys/day
Zooplankton Population	Z	0	mg C/L

<u>Rate Constants</u>

<u>Description</u>	<u>Notation</u>	<u>Values</u>	<u>Units</u>
Maximum Growth Rate	k_{1c}	2.0	day^{-1}
Temperature Coefficient	θ_{1c}	1.068	none
Maximum Photosynthetic Quantum Yield	ϕ_{max}	720.0	mg C/mole photon
Phytoplankton Self-Light Attenuation	K_c	0.017	m^2/mg Chl <u>a</u>
Carbon-Chlorophyll Ratio	a_c	20-50	-
Saturating Light Intensity	I_s	200-500	langleys/day
Half-Saturation Constant for Nitrogen	K_{mN}	25.0	μg N/L
Half-Saturation Constant for Phosphorus	K_{mP}	1.0	μg P/L
Endogenous Respiration	k_{1R}	0.125	day^{-1}
Temperature Coefficient	θ_{1R}	1.045	none
Settling Velocity	v_{s4}	0.1	m/day
Death Rate	k_{1D}	0.02	day^{-1}

chlorophyll throughout the year. The nutrients are not known a priori, however, because they depend upon the phytoplankton population that develops. These systems are interdependent and cannot be analyzed separately. It is necessary to formulate a

mass balance for the nutrients as well as the phytoplankton in order to calculate the chlorophyll that would develop for a given set of environmental conditions.

Stoichiometry and Uptake Kinetics

A principal component in the mass-balance equations written for the nutrient systems included in the eutrophication framework is the nutrient uptake kinetics associated with phytoplankton growth. To specify the nutrient uptake kinetics associated with this growth, however, it is necessary to specify the population stoichiometry in units of nutrient uptake/mass of population synthesized. For carbon as the unit of population biomass, the relevant ratios are the mass of nitrogen and phosphorus per unit mass of carbon. A selection of these ratios presented by Di Toro et al. (1971) indicates that their variability is quite large. The use of constant ratios in the analysis, then, is questionable.

Upon further investigation, however, it is clear that the reason these ratios vary is the varying cellular content of nutrients, which is, in turn, a function of the external nutrient concentrations and the past history of the phytoplankton population. Large ratios of carbon to nitrogen or phosphorus correspond to that nutrient limiting growth; small ratios reflect excess nutrients. Thus, the choice of the relevant ratios can be made with the specific situation in mind.

The operational consequence of this choice is that the population stoichiometry under non-limiting conditions may be underestimated, but under limiting conditions should be estimated correctly. Hence the trade off is a probable lack of realism during a portion of the year versus a correct estimate of phytoplankton biomass during periods of possible nutrient limitations. Because this is usually the critical period and because most questions to be answered are usually sensitive to maximum summer populations, this choice is a practical expedient. A comparison of carbon-to-nitrogen and carbon-to-phosphorus ratios measured in the Potomac Estuary is provided in Table 5.4.

Once the stoichiometric ratios have been determined, the mass balance equations may be written for the nutrients in much the same way as is done for the phytoplankton biomass. The primary interaction between the nutrient systems and the phytoplankton system is the reduction or sink of nutrients associated with phytoplankton growth. A secondary interaction occurs wherein the phytoplankton system acts as a source of

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Table 5.4 Phosphorus-to-Carbon and Nitrogen-to-Carbon Ratios

Sampling Period	Phosphorus/Carbon mg P/mg C		Nitrogen/Carbon mg N/mg C	
	Observed Mean	Observed Range	Observed Mean	Observed Range
July 20-Oct. 6, 1970[1]	0.023	0.010-0.046	0.26	0.10-0.48
August 1-29, 1977[2]	0.024	0.012-0.028	0.24	0.15-0.36
Sept. 7-28, 1978[2]	0.030	0.017-0.047	0.26	0.18-0.35
Sept. 7-28, 1978[2]	0.031		0.26	
Model	0.025		0.25	

1. Elemental analysis of blue-green algae
2. Laboratory elemental analysis of overall phytoplankton population
3. Estimates of cell composition based upon field data

nutrients due to release of stored cellular nitrogen and phosphorus during algal respiration and death.

Periphyton/macrophyte Kinetics

Exisitng models of periphyton and macrophytes in aquatic systems share a common basic approach, namely that the growth of attached algae (periphyton) and macrophytes can be modeled as a mass balance in which growth is offset by death and respiration. The models share the formulation that the growth rate depends upon the availability of certain limiting resources. However, within these general bounds, there are large differences in approach.

The basic conceptual model shared by virtually all of the models is the following mass balance:

$$\frac{\partial B}{\partial t} = (G - R - P - M) B \qquad\qquad\qquad \textbf{5.20}$$

where, B is the periphyton/macrophyte biomass per unit area $[M/L^2]$;

   G is the growth rate $[T^{-1}]$;

   R is the respiration rate $[T^{-1}]$;

   P is the predation rate $[T^{-1}]$; and

   M is the non-predatory mortality rate $[T^{-1}]$.

   Significant differences in the models arise in the determination of the various rates. Growth rates for macrophytes are generally taken as a function of the availability of light, nutrients (from both the water column and sediment), and in some models substrate. Models of only periphyton often omit dependence on nutrients in the sediment, which considerably simplifies the model. Even in models that ostensibly account for the same factors, the functional dependence on those factors may differ. Virtually all models include respiration, but some models omit predation while other omit non-predatory mortality. Periphyton and macrophytes are generally modeled as non-motile and not subject to advection or dispersion. The following provides a brief review of alternative formulations found in the literature reviewed. A complete list of reviewed references is included at the end of this report.

   A number of models are quite simple in their approach, borrowing the formulation from similar formulations for phytoplankton. For example, QUAL-TX (TDWR, 1985) and LA-QUAL (Wiland and LeBlanc, 2000) model macrophytes identically with phytoplankton (algae). Indeed, if one uses the default parameter values for both macrophytes and algae, the two model compartments are indistinguishable. This similarity extends to the representation of macrophytes in terms of mass per unit volume rather than per unit of bottom area. We rejected this approach as too simple: macrophytes and attached algae are not simply a different form of phytoplankton. Rather, they experience different characteristics (such as growth limitation due to substrate availability, zero or limited advective transport, possible scouring during floods, and the ability to withdraw

nutrients from sediment as well as the water column) that distinguish them from algae in the water column.

The Chesapeake Bay model (Cerco and Seitzinger, 1997; Cerco and Meyers, 2000) employs a more complicated formulation after Madden and Kemp (1996) and Kemp et al. (1995). This model includes separate compartments for biomass in the macrophyte plant shoots and roots, and also distinguishes benthic algae (periphyton), algae attached to plant leaves (epiphyton), and floating algae (phytoplankton). This approach is initially appealing because the complexity presumably creates greater accuracy. However, it would necessitate a proliferation of difficult-to-define parameters and coefficients. In the final analysis, we rejected this very complicated approach as overkill.

Several of the models converged on a similar middle ground: Collins and Wlosinski (1989), Rutherford et al. (2000), Uehlinger et al. (1996), Wright and McDonnell (1986b), and Muhammetoglu and Soyupak (2000). These models follow the form of Equation 5.20; represent periphyton/macrophytes in terms of density per unit area; incorporate similar limitations as far as nutrients, light, and in some cases substrate; and include generally the same loss mechanisms. One aspect distinguishes models of macrophytes from those of periphyton. Generally, periphyton nutrient supply is presumed to come only from the water column while macrophytes are presumed to draw from both the water column and sediment. For simplicity, we assumed that nutrients are drawn only from the water column and in this sense, the modified model is most applicable to periphyton and not macrophytes.

With respect to loss mechanisms, some papers emphasize the significance of predation on periphyton (e.g., Rutherford et al., 2000). Since WASP does not include a model compartment for zooplankton, I opted not to include a separate representation of predatory loss, but to simply include a lumped loss term for both predatory and non-predatory loss. This is mathematically equivalent to assuming a constant predator population density.

The final macrophyte/periphyton (hereinafter simply called periphyton) model formulation follows the existing WASP formulations for phytoplankton as closely as possible with respect to nomenclature and structure. The model equations for periphyton are:

$$\frac{\partial C_9}{\partial t} = (G_{M1} - D_{M1})\,C_9$$

$$= (k_{2c}\,X_{2RTj}\,X_{2RIj}\,X_{2RNj}\,X_{2RDj} - [k_{2R}(T) + k_{2D}(T)])\,C_9$$

5.21

Table 5.5 Periphyton Net Growth Terms

Rate Constants

Description	Notation	Values	Units
Maximum Growth Rate	k_{2c}	0.42[*], 0.267[+]	day^{-1}
Temperature Coefficient	θ_{2c}	1.068[+]	none
Half-Saturation Constant for Nitrogen	K_{2mN}	0.01[*+]	mg N/L
Half-Saturation Constant for Phosphorus	K_{2mP}	0.005[*+]	mg P/L
Half-Saturation Constant for Density	K_{2mD}	300 to 900[#]	mg/m^2
Endogenous Respiration	k_{2R}	0.012[+], 0.05[+]	day^{-1}
Temperature Coefficient for Respiration	θ_{2R}	1.045[+]	none
Death and Grazing Rate	k_{2D}	0.03[*], 0.012[+]	day^{-1}
Temperature Coefficient for Death and Grazing	θ_{2D}	1.05[+]	none
Fraction of Bottom Available as Substrate	f_A	0 to 1	none
Fraction of dead periphyton recycled to the water column	f_{2WC}	0 to 1	none

* indicates values from Collins and Wlosinski (1989)
+ indicates values from Muhammetoglu and Soyupak (2000)
# indicates values from Brown (2002), but with a conversion from dependence on chlorophyll-a to dependence on carbon assuming carbon equals 30 times chlorophyll-a

where, C_9 is the periphyton biomass in mg/m^2. Other terms in the equation follow those for phytoplankton in WASP5 as shown in Table 5.5. The factor f_A in Table 5.5 is used to adjust the effect of periphyton on the DO and nutrient balances.

Computed terms in Equation 5.21 include the following:

$$X_{2RTj} = \Theta_{2c}^{T-20}$$

$$X_{2RNj} = Min\left(\frac{DIN_j}{K_{2mN}+DIN_j}, \frac{DIP_j}{K_{2mP}+DIP_j} \right)$$

    5.22

$$k_{2R}(T) = k_{2R}(20°C)\,\Theta_{2R}^{T-20}$$

$$k_{2D}(T) = k_{2D}(20°C)\,\Theta_{2D}^{T-20}$$

The light limitation term (X_{2RIj}) is calculated using the Smith (1980), DiToro/Steele, half-saturation, and Smith (1936) options, but with light computed at the full water depth, D_j, of the segment rather than integrated over the entire water column as for phytoplankton:

$$I_h = I_o \exp(-K_e D_j)$$

Light limitation was modeled with the following formula using the Smith (1980) formulation for instantaneous conditions:

$$X_{2RIj} = \frac{I_h}{I_s} \exp\left(-\frac{I_h}{I_s}+1 \right)$$

    5.23

The equation with the DiToro/Steele formulation for instantaneous conditions is identical. The equation for the half-saturation function for instantaneous conditions is:

$$X_{2RIj} = \frac{I_h}{I_s+I_h}$$

    5.24

For the Smith (1936) function, the equation for instantaneous conditions is:

$$X_{2RIj} = \frac{I_h}{\sqrt{I_s^2+I_h^2}}$$

    5.25

Equations 5.23, 5.24, and 5.25 are converted to their daily average forms by substituting the daily average light, $I_{h,ave} = I_a \exp(-K_e D_j)$, for I_h, and multiplying the right-hand side of the equation by the photoperiod fraction, f.

The growth of periphyton is also presumed to be limited by periphyton density, as captured in the density limitation term (X_{2RDj}):

$$X_{2RDj} = 1 - \frac{C_9}{K_{2mD} + C_9} \qquad \textbf{5.26}$$

Dead periphyton are presumed to partition between the water column and the sediment layer according to the fraction f_{2WC}. The fraction of dead periphyton that goes to the water column, f_{2WC}, is immediately broken down into its component constituents, CBOD, Organic and Inorganic P, and Organic N and ammonia. The remaining fraction ($1 - f_{2WC}$) of the dead periphyton is assumed to settle to the underlying sediment layer where it undergoes decomposition. Thus, either water column or sediment segments may have periphyton present, however the presumption is that periphyton in sediment segments is dead and undergoing decomposition, while that in the water column is alive and undergoing photosynthesis and respiration.

The Phosphorus Cycle

Four phosphorus variables are modeled: phytoplankton phosphorus, periphyton phosphorus, organic phosphorus, and inorganic (orthophosphate) phosphorus. Organic phosphorus is divided into particulate and dissolved concentrations by spatially variable dissolved fractions. Inorganic phosphorus also is divided into particulate and dissolved concentrations by spatially variable dissolved fractions, reflecting sorption. The phosphorus equations are summarized in Figure 5.4.

Table 5.6 presents the reaction rate terms used in the Potomac study.

4. PHYTOPLANKTON PHOSPHORUS

$$\frac{\partial (C_4 a_{pc})}{\partial t} = G_{P1} a_{pc} C_4 - D_{P1} a_{pc} C_4 - \frac{v_{s4}}{D} a_{pc} C_4$$

$$\text{growth} \qquad \text{death} \qquad \text{settling}$$

9. PERIPHYTON PHOSPHORUS

$$\frac{\partial (C_9 a_{2pc})}{\partial t} = G_{M1} a_{2pc} C_9 - D_{M1} a_{2pc} C_9$$

$$\text{growth} \qquad \text{death}$$

8. ORGANIC PHOSPHORUS

$$\frac{\partial C_8}{\partial t} = D_{P1} a_{pc} f_{op} C_4 - k_{83} \Theta_{83}^{T-20} \left(\frac{C_4}{K_{mPc} + C_4} \right) C_8 - \frac{v_{s3} (1 - f_{D8})}{D} C_8$$

$$\text{phytop. death} \qquad \text{mineralization} \qquad \text{settling}$$

$$+ f_{2WC} D_{M1} a_{2pc} f_{2op} f_A \frac{A}{V} C_9$$

$$\text{perip. death}$$

3. INORGANIC PHOSPHORUS

$$\frac{\partial C_3}{\partial t} = D_{P1} a_{pc} (1 - f_{op}) C_4 - G_{P1} a_{pc} C_4 + k_{83} \Theta_{83}^{T-20} \left(\frac{C_4}{K_{mPc} + C_4} \right) C_8$$

$$\text{phytop. death} \qquad \text{growth} \qquad \text{mineralization}$$

$$+ f_{2WC} D_{M1} a_{2pc} (1 - f_{2op}) f_A \frac{A}{V} C_9 - G_{M1} a_{2pc} f_A \frac{A}{V} C_9$$

$$\text{periphyton death} \qquad \text{growth}$$

$$- \frac{v_{s5} (1 - f_{D3})}{D} C_3 + \frac{f_{PO4}}{D}$$

$$\text{settling} \qquad \text{benthic flux}$$

Figure 5.4   Phosphorus cycle equations.

Table 5.6   Phosphorus Reaction Terms

Description	Notation	Value	Units
Phytoplankton biomass as carbon	P_c	–	mg C/L
Specific phytoplankton growth rate	G_{p1j}	(eq 5.2)	day^{-1}
Phytoplankton loss rate	D_{p1j}	(eq 5.14)	day^{-1}
Phosphorus to carbon ratio	a_{PC}	0.025	mg P/mg C
Dissolved organic phosphorus mineralization at 20°C	k_{83}	0.22	day^{-1}
Temperature coefficient	Θ_{83}	1.08	none
Half saturation constant for phytoplankton limitation of phosphorus recycle	K_{mPc}	1.0	mg C/L
Fraction of dead and respired phytoplankton recycled to the organic phosphorus pool	f_{op}	0.5	none
. . . recycled to the phosphate phosphorus pool	$(1-f_{op})$	0.5	none
Fraction dissolved inorganic phosphorus in the water column	f_{D3}	0.85, 0.70	none
Fraction dissolved organic phosphorus	f_{D8}	–	none
Organic matter settling velocity	v_{s3}	–	m/day
Inorganic sediment settling velocity	v_{s5}	–	m/day
Specific growth rate for periphyton	G_{M1}	computed	day^{-1}
Phosphorus to carbon ratio for periphyton	a_{2PC}	0.009[*]	mg P/mg C
Loss rate for periphyton	D_{M1}	computed	day^{-1}
Fraction of dead and respired periphyton recycled to the organic phosphorus pool	f_{2op}	0.7[+]	none
. . . recycled to the phosphate phosphorus pool	$(1-f_{2op})$	0.3[+]	none
Flux of inorganic P from the sediment	f_{PO4}		mg/m^2-day

 * indicates values from Collins and Wlosinski (1989)
 + indicates values from Muhammetoglu and Soyupak (2000)

Phytoplankton Growth

    As phytoplankton grow, dissolved inorganic phosphorus is
taken up, stored and incorporated into biomass. For every mg of
phytoplankton carbon produced, a_{PC} mg of inorganic phosphorus is
taken up.

Phytoplankton Death

     As phytoplankton respire and die, biomass is recycled to
nonliving organic and inorganic matter. For every mg of
phytoplankton carbon consumed or lost, a_{PC} mg of phosphorus is
released. A fraction f_{op} is organic, while $(1 - f_{op})$ is in the
inorganic form and readily available for uptake by other viable
algal cells. In work on the Great Lakes, f_{op} was assigned at 50%
(Di Toro and Matystik, 1980).

Mineralization

     Nonliving organic phosphorus must undergo mineralization or
bacterial decomposition into inorganic phosphorus before
utilization by phytoplankton. In their work on Lake Huron and
Saginaw Bay, Di Toro and Matystik (1980) proposed a nutrient
recycle formulation that was a function of the localized
phytoplankton population. This proposal was based on both an
analysis of available field data and the work of others (Hendry,
1977; Lowe, 1976; Henrici, 1938; Menon, 1972; and Rao, 1976) that
indicated bacterial biomass increased as phytoplankton biomass
increased. EUTRO5 uses a saturating recycle mechanism, a
compromise between conventional first-order kinetics and a second
order recycle mechanism wherein the recycle rate is directly
proportional to the phytoplankton biomass present, as had been
indicated in pure culture, bacteria-seeded, laboratory studies
(Jewell and McCarty, 1971).

     Saturating recycle permits second order dependency at low
phytoplankton concentrations, when $P_c << K_{mPc}$, where K_{mPc} is the
half-saturation constant for recycle, and permits first order
recycle when the phytoplankton greatly exceed the half-saturation
constant. Basically, this mechanism slows the recycle rate if
the phytoplankton population is small, but does not permit the
rate to increase continuously as phytoplankton increase. The
assumption is that at higher population levels, recycle kinetics
proceed at the maximum first order rate. The default value for
K_{mPc} is 0, which causes mineralization to proceed at its first
order rate at all phytoplankton levels.

Sorption

     There is an adsorption-desorption interaction between
dissolved inorganic phosphorus and suspended particulate matter
in the water column. The subsequent settling of the suspended
solids together with the sorbed inorganic phosphorus can act as a
significant loss mechanism in the water column and is a source of
phosphorus to the sediment. Because the rates of reaction for

adsorption-desorption are in the order of minutes versus reaction rates in the order of days for the biological kinetics, an equilibrium assumption can be made. This equilibrium reaction implies that the dissolved and particulate phosphorus phases "instantaneously" react to any discharge sources of phosphorus or runoff or shoreline erosion of solids so as to redistribute the phosphorus to its "equilibrium" dissolved and solids phase concentrations.

Consider C_{DIP} to be the concentration of dissolved inorganic phosphorus in the water column. It interacts with the particulate concentration, C_{PIP}. The interaction may be an adsorption-desorption process with the solids or an assimilation-depuration process with the phytoplankton. If the total suspended solids is considered, the particulate concentration can be defined as:

$$C_{PIP} = C'_{PIP}\, M \qquad\qquad\qquad\qquad \textcolor{red}{5.27}$$

where:

$\quad$ C_{PIP}' $\quad=\quad$ concentration of phosphorus sorbed to solids, mg P/kg M

$\quad$ M $\quad=\quad$ concentration of solids, kg/L

The total inorganic phosphorus is then the sum of dissolved inorganic and the particulate inorganic phosphorus:

$$C_3 = C_{DIP} + C_{PIP} \qquad\qquad\qquad\qquad \textcolor{red}{5.28}$$

The underlying assumption that is made, as mentioned previously, is "instantaneous equilibrium" between the adsorption-desorption processes. The equilibrium between the dissolved inorganic phosphorus in the water column and the mass concentration of inorganic phosphorus of the solids is usually expressed in terms of a partition coefficient:

$$K_{PIP} = \frac{C'_{PIP}}{C_{DIP}} \qquad\qquad\qquad\qquad \textcolor{red}{5.29}$$

where:

K_{PIP} =   partition coefficient for particulate phosphorus,
                (mg P/kg M) per (mg P/L), or (L/kg M)

Substituting equation 5.29 into 5.27 gives:

$$C_{PIP} = K_{PIP} \, M \, C_{DIP}$$ **5.30**

Equation 5.30 is the linear portion of the Langmuir isotherm. Although not always representative of actual conditions, it is a reasonable approximation when the sorbed phosphorus concentration is much less than the ultimate adsorbing capacity of the solids. Combining Equations 5.29 and 5.30, the total concentration may be expressed as:

$$C_3 = C_{DIP} + K_{PIP} \, M \, C_{DIP}$$ **5.31**

The dissolved and particulate fractions may be expressed, respectively, as:

$$f_{D3} = \frac{C_{DIP}}{C_3} = \frac{1}{1 + K_{PIP} \, M}$$ **5.32**

$$f_{p3} = \frac{C_{PIP}}{C_3} = \frac{K_{PIP} \, M}{1 + K_{PIP} \, M}$$ **5.33**

A wide range of partition coefficients is found in the literature. Thomann and Fitzpatrick (1982) report values between 1,000 and 16,000. Using a range in partition coefficients from 1,000 - 16,000 and a range of inorganic solids of from 10 to 30 mg/L in the water column leads to a range in the fraction particulate inorganic phosphorus of from 0.01 to 0.33. In EUTRO5, the dissolved and particulate phosphorus phases are assigned as spatially-variable, time-constant fractions of the total inorganic phosphorus:

$$C_{DIP,i} = f_{D3i}\ C_{3i} \qquad\qquad\qquad \text{5.34}$$

$$C_{PIP,i} = (1 - f_{D3i})\ C_{3i} \qquad\qquad\qquad \text{5.35}$$

where:

C_{3i} = the total inorganic phosphorus in segment i, mg/L

f_{D3i} = the fraction of the total inorganic phosphorus assigned to the dissolved phase in segment i

$C_{DIP,i}$ = the equilibrium dissolved inorganic phosphorus in segment i, available for algal uptake, mg/L

$C_{PIP,i}$ = the equilibrium sorbed inorganic phosphorus in segment i, which may then settle to the sediment layer from the water column, mg/L.

Settling

Particulate organic and inorganic phosphorus settle according to user-specified velocities and particulate fractions. Particulate organic phosphorus is equated to solid type 1, which represents organic matter. Time and segment-variable organic matter settling velocities, v_{s3}, can be input by the user using transport field 3. Segment-variable organic phosphorus dissolved fractions, f_{D8j}, are input with initial conditions.

Particulate inorganic phosphorus is equated to solid type 3, which represents inorganic sediment. Time and segment variable inorganic phosphorus settling velocities, v_{s5}, can be input by the user using transport field 5. Segment-variable inorganic phosphorus dissolved fractions, f_{D3}, are input with initial conditions.

Benthic Flux

Inorganic phosphorus may diffuse from the bottom sediments into the water column. In models without sediment segments, this flux may be specified as an input by the user. In models that include sediment segments, the flux between the water column and the sediment is computed based on the user-specified diffusion coefficient and the computed concentrations of inorganic phosphorus in the water column and the sediment. The user-

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The Nitrogen Cycle
<u></u>

Five nitrogen variables are modeled: phytoplankton
nitrogen, periphyton nitrogen, organic nitrogen, ammonia, and
nitrate. A summary is illustrated in Figure 5.5. Table 5.7
summarizes the terms used in the nitrogen system kinetics.

Phytoplankton Growth

As phytoplankton grow, dissolved inorganic nitrogen is taken
up and incorporated into biomass. For every mg of phytoplankton
carbon produced, a_{NC} mg of inorganic nitrogen is taken up. Both
ammonia and nitrate are available for uptake and use in cell
growth by phytoplankton; however, for physiological reasons, the
preferred form is ammonia nitrogen. The ammonia preference term
P_{NH3} is given in Figure 5.5. The behavior of this equation, for a
Michaelis value, K_{mN}, of 25 g N/L, is shown in Figure 5.6. The
behavior of this equation is most sensitive at low values of
ammonia or nitrate. For a given concentration of ammonia, as the
available nitrate increases above approximately the Michaelis
limitation, the preference for ammonia reaches an asymptote.
Also as the concentration of available ammonia increases, the
plateau levels off at values closer to unity, i.e., total
preference for ammonia.

Phytoplankton and Periphyton Death

As phytoplankton and periphyton respire and die, living
organic material is recycled to nonliving organic and inorganic
matter. For every mg of phytoplankton and periphyton carbon
consumed or lost, a_{NC} mg of nitrogen is released. During
phytoplankton and periphyton respiration and death, a fraction of
the cellular nitrogen f_{on} is organic, while $(1 - f_{on})$ is in the
inorganic form of ammonia nitrogen. The fraction recycled to the
inorganic pool for Great Lakes models has been assigned at 50%
(Di Toro and Matystik, 1980).

4. PHYTOPLANKTON NITROGEN

$$\frac{\partial (C_4 a_{nc})}{\partial t} = G_{P1} a_{nc} C_4 - D_{P1} a_{nc} C_4 - \frac{v_{s4}}{D} a_{nc} C_4$$

$$\quad\quad\quad\quad\quad\quad growth \quad\quad death \quad\quad settling$$

9. PERIPHYTON NITROGEN

$$\frac{\partial (C_9 a_{2nc})}{\partial t} = G_{M1} a_{2nc} C_9 - D_{M1} a_{2nc} C_9$$

$$\quad\quad\quad\quad\quad growth \quad\quad death$$

7. ORGANIC NITROGEN

$$\frac{\partial C_7}{\partial t} = D_{P1} a_{nc} f_{on} C_4 - k_{71} \Theta_{71}^{T-20} \left(\frac{C_4}{K_{mPc}+C_4} \right) C_7 - \frac{v_{s3}(1-f_{D7})}{D} C_7 - f_{2WC} D_{M1} a_{2nc} f_{2on} f_A \frac{A}{V} C_9$$

$$\quad\quad phytop.\ death \quad\quad mineralization \quad\quad settling \quad\quad perip.\ death$$

1. AMMONIA NITROGEN

$$\frac{\partial C_1}{\partial t} = D_{P1} a_{nc} (1-f_{on}) C_4 + k_{71} \Theta_{71}^{T-20} \left(\frac{C_4}{K_{mPc}+C_4} \right) C_7 - G_{P1} a_{nc} P_{NH3} C_4 - k_{12} \Theta_{12}^{T-20} \left(\frac{C_6}{K_{NIT}+C_6} \right) C_1$$

$$\quad phytop.\ death \quad\quad mineralization \quad\quad growth \quad\quad nitrification$$

$$+ f_{2WC} D_{M1} a_{2nc} (1 - f_{2on}) f_A \frac{A}{V} C_9 - G_{M1} a_{2nc} P_{2NH3} f_A \frac{A}{V} C_9 + \frac{f_{NH4}}{D}$$

$$\quad\quad perip.\ death \quad\quad\quad\quad growth \quad\quad\quad benthic\ flux$$

2. NITRATE NITROGEN

$$\frac{\partial C_2}{\partial t} = k_{12} \Theta_{12}^{T-20} \left(\frac{C_6}{K_{NIT}+C_6} \right) C_1 - G_{P1} a_{nc} (1-P_{NH3}) C_4 - k_{2D} \Theta_{2D}^{T-20} \left(\frac{K_{NO3}}{K_{NO3}+C_4} \right) C_2$$

$$\quad\quad nitrification \quad\quad\quad phytop.\ growth \quad\quad denitrification$$

$$- G_{M1} a_{2nc} (1 - P_{2NH3}) f_A \frac{A}{V} C_9$$

$$\quad\quad periphyton\ growth$$

$$where$$

$$P_{NH3} = C_1 \left(\frac{C_2}{(K_{mN}+C_1)(K_{mN}+C_2)} \right) + C_1 \left(\frac{K_{mN}}{(C_1+C_2)(K_{mN}+C_2)} \right)$$

$$\quad\quad ammonia\ preference\ factor\ for\ macrophytes$$

$$P_{2NH3} = C_1 \left(\frac{C_2}{(K_{2mN}+C_1)(K_{2mN}+C_2)} \right) + C_1 \left(\frac{K_{2mN}}{(C_1+C_2)(K_{2mN}+C_2)} \right)$$

$$\quad\quad ammonia\ preference\ factor\ for\ periphyton$$

Figure 5.5 Nitrogen cycle equations.

Table 5.7 Nitrogen Reaction Terms

Description	Notation	Value from Potomac Estuary Model	Units
Nitrogen to carbon ratio	a_{NC}	0.25	mg N/gm C
Organic nitrogen mineralization rate at 20°C	k_{71}	0.075	day^{-1}
Temperature coefficient	$_{71}$	1.08	-
Nitrification rate	k_{12}	0.09-0.13	day^{-1}
Temperature coefficient	$_{12}$	1.08	-
Half saturation constant for oxygen limitation of nitrification	K_{NIT}	2.0	mg O_2/L
Denitrification rate at 20°C	k_{2D}	0.09	day^{-1}
Temperature coefficient	$_{2D}$	1.045	-
Michaelis constant for denitrification	K_{NO3}	0.1	mg O_2/L
Fraction of dead and respired phytoplankton recycled ... to the organic nitrogen pool	f_{ON}	0.5	-
....to the ammonia nitrogen pool	$(1-f_{ON})$	0.5	-
Preference for ammonia uptake term	P_{NH3}	eq. 5.30	-
Fraction dissolved organic nitrogen	f_{D7}	1.0	-
Organic matter settling velocity	v_{s3}	-	m/day
Nitrogen to carbon ration for periphyton	a_{2NC}	0.17*	mg N/mg C
Fraction of dead and respired periphyton recycled ... to the organic nitrogen pool	f_{2ON}	0.65+	-
...to the ammonia nitrogen pool	$(1-f_{2ON})$	0.35+	-
Preference for ammonia uptake term for periphyton	P_{2NH3}	computed	-
Flux of ammonia from the sediment	f_{NH4}		mg/m^2-day

* indicates values from Collins and Wlosinski (1989)
+ indicates values from Muhammetoglu and Soyupak (2000)

Ammonia Preference Structure
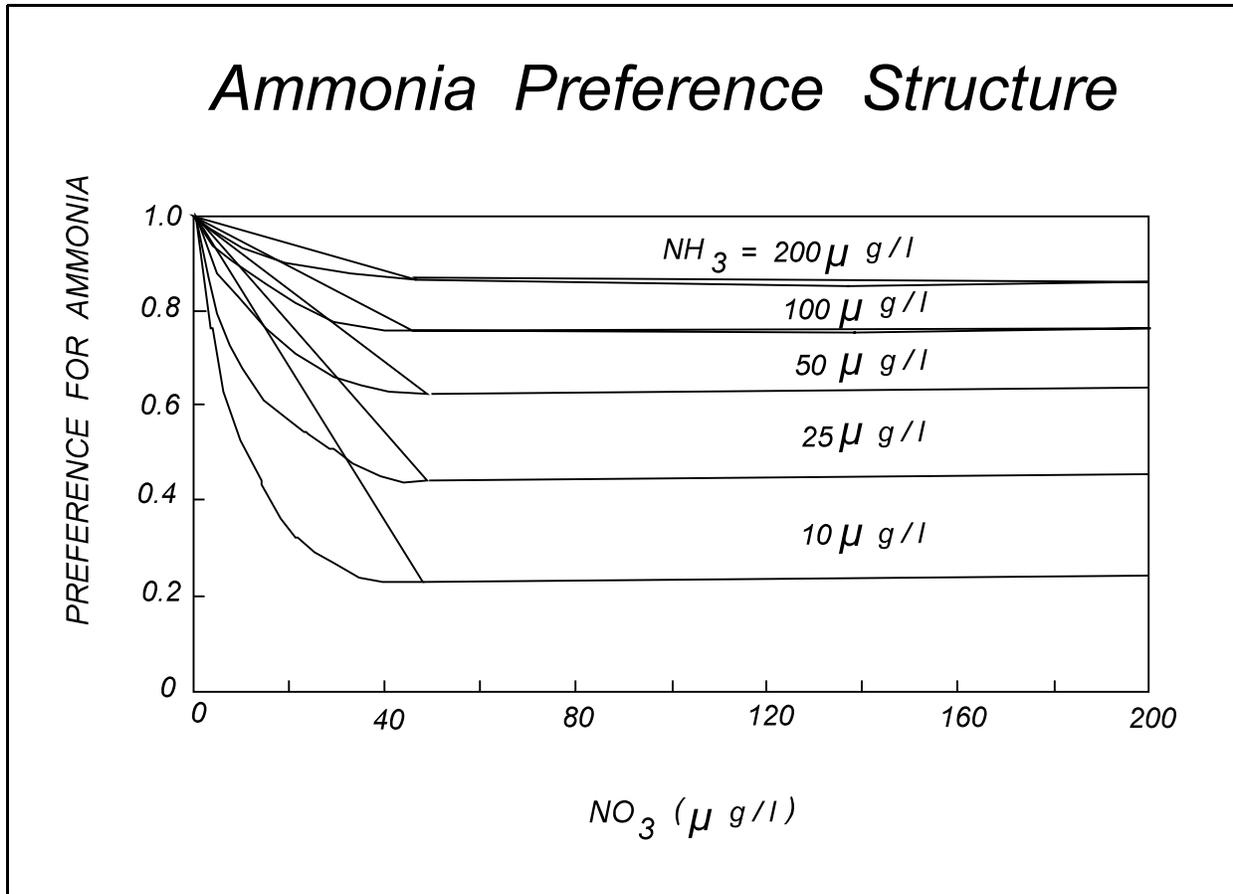
Figure 5.6   Ammonia preference structure (Thomann and Fitzpatrick, 1982).

Mineralization

Nonliving organic nitrogen must undergo mineralization or bacterial decomposition into ammonia nitrogen before utilization by phytoplankton. In EUTRO5, the first order, temperature-corrected rate constant is modified by a saturated recycle term, as explained in the phosphorus mineralization section. This mechanism slows the mineralization rate if the phytoplankton population is small, but does not permit the rate to increase continuously as phytoplankton increase. The default value for the half-saturation constant K_{mPc} is 0, which causes mineralization to proceed at its first order rate at all phytoplankton levels.

Settling

Particulate organic nitrogen settles according to user-specified velocities and particulate fractions. Particulate

organic nitrogen is equated to solid type 1, which represents
organic matter. Time and segment-variable organic matter
settling velocities, v_{s3}, can be input by the user using
transport field 3. Segment-variable organic nitrogen dissolved
fractions, f_{D7}, are input with initial conditions.

Nitrification

    Ammonia nitrogen, in the presence of nitrifying bacteria and
oxygen, is converted to nitrate nitrogen (nitrification). The
process of nitrification in natural waters is carried out by
aerobic autotrophs; Nitrosomonas and Nitrobacter predominate in
fresh waters. It is a two-step process with Nitrosomonas
bacteria responsible for the conversion of ammonia to nitrite and
Nitrobacter responsible for the conversion of nitrite to nitrate.

    Essential to this reaction process are aerobic conditions.
Also this process appears to be affected by high or low values of
pH that inhibit Nitrosomonas growth, particularly for pH below 7
and greater than 9. As with phytoplankton, the nitrifying
bacterial populations are sensitive to flow. During periods of
high flow or storm runoff, upstream bacteria may be advected
downstream, with some lag time after a flow transient before they
can build up to significant levels again.

    The process of nitrification in natural waters, then, is
complex, depending on dissolved oxygen, pH, and flow conditions,
which in turn leads to spatially and temporally varying rates of
nitrification. To properly account for this complex phenomenon
in the modeling framework would be difficult and would require a
data base that is usually unavailable.

    The kinetic expression for nitrification in EUTRO5 contains
three terms -- a first order rate constant, a temperature
correction term, and a low DO correction term. The first two
terms are standard. The third term represents the decline of the
nitrification rate as DO levels approach 0. The user may specify
the half-saturation constant K_{NIT}, which represents the DO level
at which the nitrification rate is reduced by half. The default
value is zero, which allows this reaction to proceed fully even
under anaerobic conditions.

Denitrification

    Denitrification refers to the reduction of NO_3 (or NO_2) to N_2
and other gaseous products such as N_2O and NO. This process is
carried out by a large number of heterotrophic, facultative
anaerobes. Under normal aerobic conditions found in the water

column, these organisms use oxygen to oxidize organic material. Under the anaerobic conditions found in the sediment bed or during extremely low oxygen conditions in the water column, however, these organisms are able to use NO_3 as the electron acceptor.

The process of denitrification is included in the modeling framework simply as a sink of nitrate. The kinetic expression for denitrification in EUTRO5 contains three terms -- a first order rate constant, a temperature correction term, and a DO correction term. The first two terms are standard. The third term represents the decline of the denitrification rate as DO levels rise above 0. The user may specify the half-saturation constant K_{NO3}, which represents the DO level at which the denitrification rate is reduced by half. The default value is zero, which prevents this reaction at all DO levels. Denitrification is assumed to always occur in the sediment layer where anaerobic conditions always exist.

Benthic Flux

Ammonia may diffuse from the bottom sediments into the water column. In models without sediment segments, this flux may be specified as an input by the user. In models that include sediment segments, the flux between the water column and the sediment is computed based on the user-specified diffusion coefficient and the computed concentrations of inorganic ammonia in the water column and the sediment. The user-specified benthic flux is bypassed in models that include sediment segments.

The Dissolved Oxygen Balance

Six state variables participate in the DO balance: phytoplankton carbon, periphyton carbon, ammonia, nitrate, carbonaceous biochemical oxygen demand, and dissolved oxygen. A summary is illustrated in Figure 4.2. The reduction of dissolved oxygen is a consequence of the aerobic respiratory processes in the water column and the anaerobic processes in the underlying sediments. Both these processes contribute significantly and, therefore, it is necessary to formulate their kinetics explicitly.

The dissolved oxygen processes in EUTRO5 are discussed in Chapter 4. The CBOD and DO reaction terms are summarized in Table 4.1.

<u>Benthic - Water Column Interactions</u>

The decomposition of organic material in benthic sediment can have profound effects on the concentrations of oxygen and nutrients in the overlying waters. The decomposition of organic material releases nutrients to the sediment interstitial waters and also results in the exertion of an oxygen demand at the sediment-water interface. As a result, the areal fluxes from the sediment can be substantial nutrient sources or oxygen sinks to the overlying water column. Additionally, the occurrence of anoxia, due in part to the sediment oxygen demand, may dramatically increase certain nutrient fluxes through a set of complex redox reactions that change the state and concentrations of various nutrients and metals thereby releasing bound nutrients. The relative importance of the sediment oxygen demand and nutrient fluxes vis-a-vis future nutrient control strategies requires the incorporation of a dynamic sediment layer and its associated interactions with the overlying water column in a framework that is consistent with that discussed in the previous sections.

EUTRO5 provides two options for nutrient and oxygen fluxes: descriptive input and predictive calculations (Fig. 5.7). The first option is used for networks composed of water column segments only. Spatially-variable observed fluxes must be specified for ammonia, phosphate, sediment oxygen demand, and CBOD. Time functions may be specified for ammonia, phosphate, and CBOD reflecting seasonal changes. Seasonal changes in water temperature can affect SOD through its temperature coefficient. The descriptive input option is implemented via the flux terms FNH4, FPO4, and FBOD specified in the Data Group G inputs.

Benthic Simulation

The calculational framework incorporated for benthic-water column exchange draws principally from a study of Lake Erie, which incorporated sediment-water column interactions, performed by Di Toro and Connolly (1980). For a surficial benthic layer with thickness D_j, the nitrogen and phosphorus mass balance equations are summarized in Figure 5.8 and Table 5.8. The benthic CBOD and DO equations were summarized in Figure 4.3 and Table 4.2 in the previous chapter.

WASP5 allows a more detailed parameterization of settling into the benthos that includes not only a downward settling velocity but an upward resuspension velocity as well. In this

SEDIMENT - WATER EXCHANGE

1. OBSERVED FLUXES

Water Column Segments

1 2 3

1. AMMONIA LOAD	$= +F_{NH_4} \cdot A_S \cdot TFNH$
2. PHOSPHATE LOAD	$= +F_{PO_4} \cdot A_S \cdot TFPO$
3. DISS OXYGEN LOAD	$= -SOD \cdot A_S$

Flux Surface Area   Time Function

2. CALCULATED FLUXES

Water Column Segment

Benthic Segment

1,2,3,6,7,8
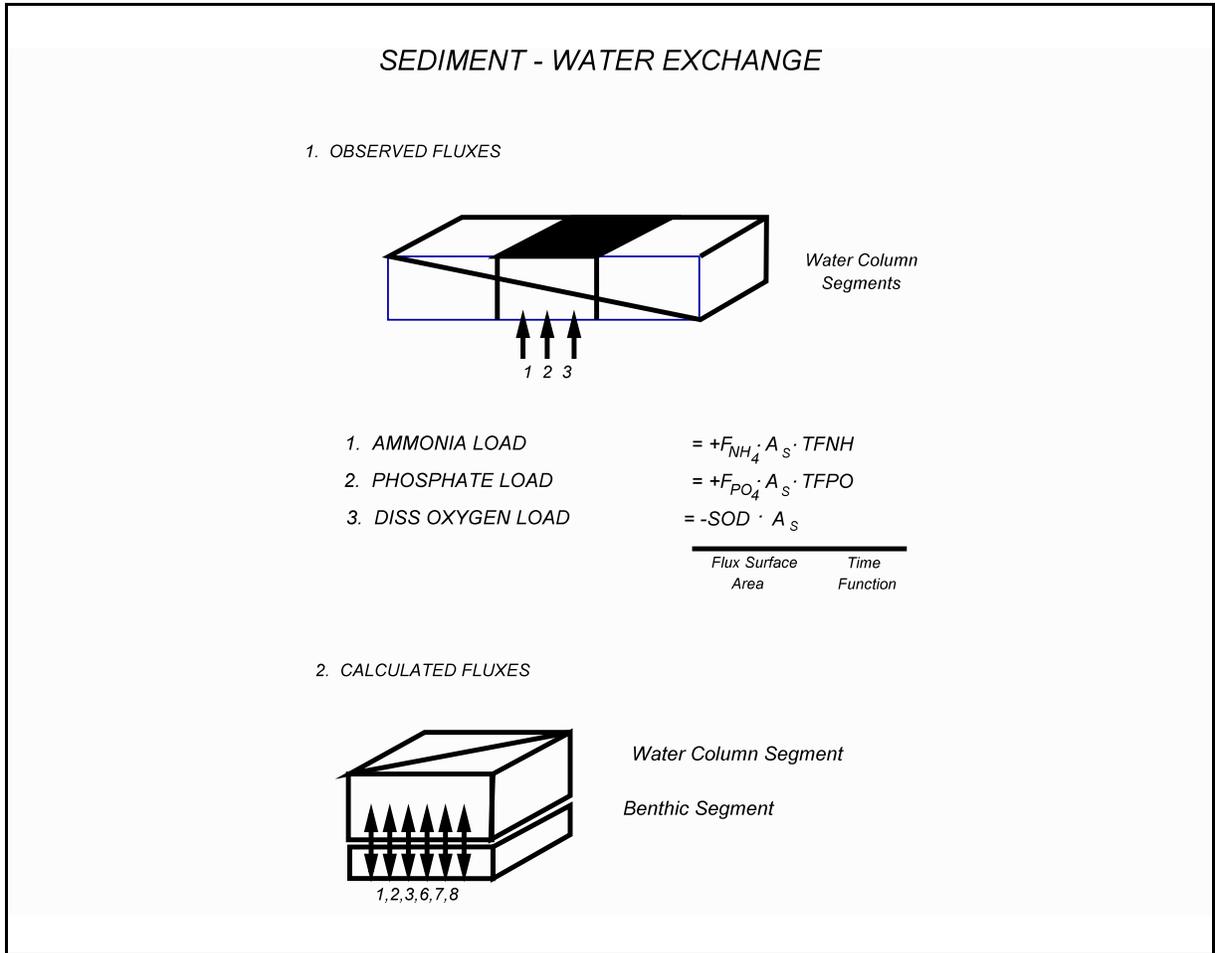
Figure 5.7   Sediment-water exchange.

context, then, the net particulate flux to the sediment is due to
the difference between the downward settling flux and the upward
resuspension flux.

Benthic Depth -- One of the first decisions to be made
regarding the benthic layer is to determine its depth. Two
factors influence this decision. The first is to adequately
reflect the thickness of the active layer, the depth to which the
sediment is influenced by exchange with the overlying water
column. Secondly one wishes the model to reflect a reasonable
time history or "memory" in the sediment layer. Too thin a
layer and the benthos will "remember" or be influenced by
deposition of material that would have occurred only within the
last year or two of the period being analyzed; too thick a layer
and the model will "average" too long a history, not reflecting,
as in the case of phosphorus, substantial reductions in

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<u>7. ORGANIC NITROGEN</u>

$$\frac{\partial C_7}{\partial t} = k_{PZD}\Theta_{PZD}^{T-20} a_{nc} f_{on} C_4 - k_{OND}\Theta_{OND}^{T-20} C_7 + k_{PZD2}\Theta_{PZD2}^{T-20} a_{2nc} f_{2on} f_A \frac{A}{V} C_9$$

phytop. decomposition   mineralization   perip. decomposition

<u>1. AMMONIA NITROGEN</u>

$$\frac{\partial C_1}{\partial t} = k_{PZD}\Theta_{PZD}^{T-20} a_{nc} (1-f_{on}) C_4 + k_{OND}\Theta_{OND}^{T-20} C_7 + k_{PZD2}\Theta_{PZD2}^{T-20} a_{2nc} (1-f_{2on}) f_A \frac{A}{V} C_9$$

phytop. decomposition   mineralization   perip. decomposition

<u>2. NITRATE NITROGEN</u>

$$\frac{\partial C_2}{\partial t} = - k_{2D}\Theta_{2D}^{T-20} C_2$$

denitrification

<u>8. ORGANIC PHOSPHORUS</u>

$$\frac{\partial C_8}{\partial t} = k_{PZD}\Theta_{PZD}^{T-20} a_{PC} f_{op} C_4 - k_{OPD}\Theta_{OPD}^{T-20} f_{D8} C_8 + k_{PZD2}\Theta_{PZD2}^{T-20} a_{2PC} f_{2op} f_A \frac{A}{V} C_9$$

phytop. decomposition   mineralization   perip. decomposition

<u>3. INORGANIC PHOSPHORUS</u>

$$\frac{\partial C_3}{\partial t} = k_{PZD}\Theta_{PZD}^{T-20} a_{pc} (1 - f_{op}) C_4 + k_{OPD}\Theta_{OPD}^{T-20} f_{D8} C_8 + k_{PZD2}\Theta_{PZD2}^{T-20} a_{2pc} (1 - f_{2op}) f_A \frac{A}{V} C_9$$

phytop. decomposition   mineralization   perip. decomposition

<u>Sediment Flux for Chemical k   (g/m^2-day)</u>

$$FLUX_k = \frac{E_{DIF}}{D_j} (C_{kj} f_{kj} - C_{ki} f_{ki})$$

(for benthic segment j, water segment i)

Figure 5.8   Benthic nutrient equations.

sedimentary phosphorus resulting from reduced phosphorus discharges from sewage treatment plants. The choice of sediment thickness is further complicated by spatially variable

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sedimentation rates. The benthic layer depths, together with the assigned sedimentation velocities, provide for a multi-year detention time or "memory", providing a reasonable approximation of the active layer in light of the observed pore water gradients.

Benthic Nitrogen -- The next consideration is the application of these mass balance equations to the nitrogen species in a reducing sediment (Berner, 1974). Particulate organic nitrogen is hydrolyzed to ammonia by bacterial action

Table 5.8 Benthic Nutrient Reaction Coefficients

Description	Notation	Value from Potomac Estuary Study	Units
Anaerobic algal decomposition rate	k_{PZD}	0.02	day^{-1}
Temperature coefficient	θ_{PZD}	1.08	none
Organic nitrogen decomposition rate	k_{OND}	0.0004	day^{-1}
Temperature coefficient	θ_{OND}	1.08	none
Organic phosphorus decomposition rate	k_{OPD}	0.0004	day^{-1}
Temperature coefficient	θ_{OPD}	1.08	none
Fraction inorganic phosphorus dissolved in benthic layer	f_{D3j}	0.045-0.001	none
Diffusive exchange coefficient	E_{DIF}	$2-2.5 \times 10^{-4}$	m^2/day
Benthic layer depth	D_j	0.1-0.3	m
Benthic layer	j		
Water column	i		
Decomposition rate for periphyton	k_{PZD2}	0.02	day^{-1}
Temperature coefficient for decomposition of periphyton	θ_{PZD2}	1.08	-

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within the benthos. In addition to the ammonia produced by the
hydrolysis of particulate organic nitrogen in the benthos,
ammonia is generated by the anaerobic decomposition of algae. In
a study of this reaction, Foree and McCarty (1970) showed that
the anaerobic rate of decay of algae is substantial (0.007-0.022
day^{-1}). However, the end product initially is not exclusively
ammonia. Rather, a fraction of the algal nitrogen becomes
particulate organic nitrogen, which must undergo hydrolysis
before becoming ammonia.

Ammonia produced by the hydrolysis of non-algal organic
nitrogen and the decomposition of detrital algal nitrogen may
then be exchanged with the overlying water column via diffusion.
No nitrification occurs in the sediment due to the anaerobic
conditions present in the sediment. Denitrification, the
conversion of nitrate to nitrogen gas, may occur, however.
Nitrate is present in the benthos due to diffusive exchange with
the overlying water column.

The analysis of the benthic nitrogen concentrations and the
resulting flux of ammonia is relatively straightforward because
of the simplicity of the kinetics: hydrolysis and anaerobic
algal decay produce a stable end product, ammonia, which does not
undergo further reactions in the anaerobic sediment. The
equations resulting from the above framework are presented in
Figure 5.9, and the coefficients are summarized in Table 5.8.

Benthic Phosphorus -- A complete analysis of the phosphorus
fluxes from sediments would require a rather complex and
elaborate computation of solute-precipitate chemistry and its
interaction with the mass transport of the dissolved species. The
reasons for this are twofold: first, it is well known (Nriagu,
1972) that for phosphorus the formation of precipitates affects
the interstitial water concentrations, thereby affecting the
interstitial water transport of the various phosphorus forms or
species; second, the dissolved concentrations are affected by the
redox reactions, which in turn, affect the phosphorus fluxes that
occur during aerobic and anaerobic conditions. (Phosphorus
fluxes are enhanced under anaerobic conditions.)

A computation of solute-precipitate chemistry was judged to
be outside the scope of this model. Instead, a simplified
approach was taken, which to a large degree relies on empiricism.
Anaerobic decomposition of detrital algal phosphorus is assumed
to occur using the same rate expressions and rate constants as
those for detrital algal nitrogen, yielding both organic and
inorganic phosphorus. Anaerobic decomposition of organic
phosphorus then proceeds. A spatially-variable fraction of the

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end product, dissolved inorganic phosphorus, remains in the interstitial water and is not involved in the formation of precipitates and is not sorbed onto the benthic solids. This spatial variation reflects the ionic chemical makeup of the benthos in various regions of the water body.

Using observed total and interstitial dissolved inorganic phosphorus values, the fraction dissolved inorganic phosphorus can be assigned to each segment, with the particulate and dissolved inorganic phosphorus computed for each time step in a manner similar to the overlying water column inorganic phosphorus (equations 5.30 through 5.32). Exchange of the dissolved phosphorus forms with the overlying water column is also similar to that of ammonia, nitrate, and dissolved oxygen. Mass flux equations are presented in Figure 5.9. The effects of anoxia upon sediment phosphorus flux were not included in the modeling framework. The approach used to generate sediment phosphorus flux, although not entirely satisfactory, is at least consistent with the framework within which the fluxes of other materials are being generated.

Benthic Carbon -- The reactions that convert algal and refractory carbon to their end products are complex. The initial step in which the algal and refractory carbon are converted to reactive intermediates appears to be similar to the refractory organic and algal nitrogen degradation, and in the subsequent calculations, the rates for carbon and nitrogen decomposition are assumed to be equal. The reactive intermediates, however, participate in further reactions: for example, volatile acids react to become methane, and the mechanisms that control these reactions are somewhat uncertain. In addition, few measurements of these intermediate species are available and a calculation that incorporates their concentrations explicitly would of necessity be speculative. Thus, one uses a simplified, yet realistic, formulation of these reactions.

The method proposed by Di Toro and Connolly (1980), and highlighted here, is based upon separating the initial reactions that convert sedimentary organic material into reactive intermediates and the remaining redox reactions that occur. Then using a transformation variable and an orthogonality relationship, Di Toro and Connolly derive mass balance equations that are independent of the details of the redox equations. Rather they are only functions of the component concentration, and it suffices to compute only the component concentrations, which can be treated in exactly the same way as any other variable in the mass transport calculation.

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The convenient choice of components for the calculation are those that parallel the aqueous variables -- carbonaceous BOD and dissolved oxygen. Restricting the calculation to these components, however, eliminates the possibility of explicitly including the effects of other reduced species such as iron, manganese, and sulfide, which play a role in overall redox reactions and may be involved in the generation of sediment oxygen demand. This simplification appears reasonable in light of the preliminary nature of the benthic calculation.

The decomposition reactions that drive the component mass balance equations are the anaerobic decomposition of the algal carbon, and the anaerobic breakdown of the benthic organic carbon. Both reactions are sinks of the oxygen and rapidly drive its concentration negative, indicating that the sediment is reduced rather than oxidized. The negative concentrations computed can be considered the oxygen equivalents of the reduced end products produced by the chains of redox reactions occurring in the sediment.

Because the calculated concentration of oxygen is positive in the overlying water, it is assumed that the reduced carbon species (negative oxygen equivalents) that are transported across the benthic water interface combine with the available oxygen and are oxidized to CO_2 and H_2O with a consequent reduction of oxygen in the overlying water column. The sediment mass balance equations for carbonaceous BOD and DO, together with the equation for sediment oxygen demand, are presented in Figure 4.3 and Table 4.2.

5.2 MODEL IMPLEMENTATION

To simulate eutrophication with WASP5, use the preprocessor to create a EUTRO5 input dataset. For the portions of the dataset describing environment, transport, and boundaries, EUTRO5 model input will be similar to that for the conservative tracer model as described in Chapter 2. To those basic parameters, the user will add combinations of transformation parameters and perhaps solids transport rates.

EUTRO5 kinetics can be implemented using some or all of the processes and kinetic terms described above to analyze eutrophication problems. For convenience, three levels of complexity are identified here: (1) simple eutrophication kinetics, (2) intermediate eutrophication kinetics, and (3) intermediate eutrophication kinetics with benthos. Please note

that the discrete levels of simulation identified here are among
a continuum of levels that the user could implement.

The three implementation levels are described briefly below,
along with the input parameters required to solve the
eutrophication equations in EUTRO5. Input parameters are
prepared for WASP5 in four major sections of the preprocessor --
environment, transport, boundaries, and transformation. Basic
model parameters are described in Chapter 2, and will not be
repeated here. The eight state variables, with abbreviations
used in this text, are listed in Table 5.9.

Table 5.9 Summary of EUTRO5 Variables

	Variable	Notation	Concentration	Units
1.	Ammonia Nitrogen	NH3	C_1	mg N/L
2.	Nitrate Nitrogen	NO3	C_2	mg N/L
3.	Inorganic Phosphorus	PO4	C_3	mg P/L
4.	Phytoplankton Carbon	PHYT	C_4	mg C/L
5.	Carbonaceous BOD	CBOD	C_5	mg O_2/L
6.	Dissolved Oxygen	DO	C_6	mg O_2/L
7.	Organic Nitrogen	ON	C_7	mg N/L
8.	Organic Phosphorus	OP	C_8	mg P/L
9.	Periphyton Carbon	CMAC	C_9	mg C/m^2
10.	Salinity	SAL	C_{10}	g/L

Simple Eutrophication Kinetics

Simple eutrophication kinetics simulate the growth and death of phytoplankton interacting with one of the nutrient cycles. Growth can be limited by the availability of inorganic nitrogen or inorganic phosphorus, and light. Equations include phytoplankton kinetics:

$$S_{k4} = \left(G_{P1} - D_{P1} - \frac{v_{s4}}{D} \right) C_4 \qquad\qquad \textbf{5.36}$$

and either the phosphorus cycle:

$$S_{k8} = +D_{P1} a_{PC} C_4 - k_{83} \Theta_{83}^{T-20} C_8 - \frac{v_{s3}}{D} (1 - f_{D8}) C_8 \qquad\qquad \textbf{5.37}$$

$$S_{k3} = +k_{83} \Theta_{83}^{T-20} C_8 - G_{P1} a_{PC} C_4 - \frac{v_{s5}}{D} (1 - f_{D3}) C_3 \qquad\qquad \textbf{5.38}$$

$$S_{k7} = +D_{P1} a_{NC} C_4 - k_{71} \Theta_{71}^{T-20} C_7 - \frac{v_{s3}}{D} (1 - f_{D7}) C_7 \qquad\qquad \textbf{5.39}$$

or the nitrogen cycle:

$$S_{k1} = +k_{71} \Theta_{71}^{T-20} C_7 - G_{P1} a_{PC} P_{NH_3} C_4 - k_{12} \Theta_{12}^{T-20} C_1 \qquad\qquad \textbf{5.40}$$

$$S_{k2} = +k_{12} \Theta_{12}^{T-20} C_1 - G_{P1} a_{NC} (1 - P_{NH_3}) C_4 \qquad\qquad \textbf{5.41}$$

where S_{ki} is the source/sink term for variable "i" in a segment, in mg/L-day. Kinetic rate constants and coefficients are as defined in Tables 5.3, 5.6, and 5.7.

Phytoplankton plus either three nitrogen variables or two phosphorus variables are used in simple eutrophication simulations. While phytoplankton are simulated internally as mg/L carbon, initial concentrations and boundary concentrations are input by the user as μg/L chlorophyll *a*. EUTRO5 converts these input concentrations to internal concentrations using a user-specified carbon to chlorophyll ratio. If the carbon to chlorophyll ratio is not input, then a default value of 30 is used. Internal concentrations of phytoplankton nitrogen and phytoplankton phosphorus are calculated from user-specified nitrogen to carbon and phosphorus to carbon ratios. If these ratios are not input, then default values of 0.25 and 0.025 are used.

Simple eutrophication kinetics assume that death returns phytoplankton nitrogen and phosphorus entirely to the organic nitrogen and organic phosphorus pools. Mineralization is a simple first order function that is unaffected by phytoplankton levels, and nitrification is a simple first order function unaffected by dissolved oxygen. Denitrification is not simulated.

Light limitation is described by the Di Toro formulation, equation 5.4, and the user must calibrate the saturating light intensity I_s.

The particulate fractions of ON and OP are associated with transport field 3, organic matter settling. Particulate PHYT is associated with transport field 4. The particulate fraction of PO4 is associated with transport field 5, inorganic settling.

Environment Parameters

These parameters define the basic model identity, including the segmentation, and control the simulation.

Systems-- Select "simulate" for PHYT and either ON, NH3, and NO3, or OP and PO4. Select "constant" for the nonsimulated nutrients and "bypass" for CBOD and DO. During calibration, the user may select "constant" or "bypass" for any selected variables. (Group A, Record 4, NOSYS; Record 9, SYSBY)

Segments-- Water column segments should be defined in the standard fashion. If settling is to be simulated (i.e., for ON, OP, PHYT, or PO4), the user should add a single benthic segment underlying all water column segments. This benthic segment will merely act as a convenient sink for settling organic matter. Model calculations within this benthic segment should be ignored.

(Group A, Record 4, NOSEG; Group C, Record 3, ISEG, IBOTSG, ITYPE, BVOL, DMULT)

Transport Parameters

     This group of parameters defines the advective and dispersive transport of model variables.

     <u>Number of Flow Fields</u>-- To simulate settling of ON and OP, the user should select solids 1 flow under advection. To simulate settling of PHYT, the user should select solids 2 flow. To simulate PO4 settling, the user should select solids 3 flow. The user should also select water column flow. (Group D, Record 1, NFIELD)

     <u>Particulate Transport, m^3/sec</u>-- Time variable settling and resuspension rates for solids 1, solids 2, and solids 3 can be input using the continuity array BQ and the time function QT. For each solids flow field, cross-sectional exchange areas (m^2) for adjacent segment pairs are input using the spatially-variable BQ. Time-variable settling velocities can be specified as a series of velocities, in m/sec, versus time. If the units conversion factor is set to 1.157e-5, then these velocities are input in units of m/day. These velocities are multiplied internally by cross-sectional areas and treated as flows that carry particulate organic matter out of the water column. (Group D, Record 4, BQ, JQ, IQ; Record 6, QT, TQ)

Boundary Parameters

     This group of parameters includes boundary concentrations, waste loads, and initial conditions. Boundary concentrations must be specified for any segment receiving flow inputs, outputs, or exchanges. Initial conditions include not only initial concentrations, but also the density and solids transport field for each solid, and the dissolved fraction in each segment.

     <u>Boundary Concentrations, mg/L</u>-- At each segment boundary, time variable concentrations must be specified for PHYT, expressed as µg/L chlorophyll *a*. Time variable concentrations must also be specified for either ON, NH3, and NO3, or OP and PO4. A boundary segment is characterized by water exchanges from outside the network, including tributary inflows, downstream outflows, and open water dispersive exchanges. (Group E, Record 4, BCT)

Waste Loads, kg/day-- For each point source discharge, time variable PHYT, ON, NH3, NO3, OP, and PO4 loads can be specified. These loads can represent municipal and industrial wastewater discharges, or urban and agricultural runoff. If any phytoplankton loads are specified, they should be in units of kg carbon/day. (Group F.1, Record 4, WKT)

Solids Transport Field-- The transport fields associated with particulate settling must be specified under initial conditions. Solids 1 (Field 3) is recommended for ON and OP. Solids 2 (Field 4) is recommended for PHYT. Solids 3 (Field 5) is recommended for PO4. (Group J, Record 1, IFIELD)

Solid Density, g/cm^3-- A value of 0 can be entered for the nominal density of PHYT, ON, NH3, NO3, OP, and PO4. This information is not used in EUTRO5. (Group J, Record 1, DSED)

Initial Concentrations, mg/L-- Concentrations of PHYT, expressed as μg/L chlorophyll a and either ON, NH3, and NO3, or OP and PO4 in each segment must be specified for the time at which the simulation begins. For the nonsimulated nutrients held constant, average concentrations must be specified. These nutrient concentrations will remain constant throughout the simulation and can affect PHYT through growth rate limitation (although nonsimulated nutrients should be in excess and therefore not affect growth). Concentrations of zero for bypassed variables -- CBOD and DO -- will be entered by the preprocessor. (Group J, Record 2, C)

Dissolved Fraction-- The dissolved fraction of PHYT, ON, NH3, NO3, OP, and PO4 in each segment must be specified. The dissolved fraction of PHYT should be set to 0. Only the particulate fractions of the nutrients will be subject to settling. (Group J, Record 2, DISSF)

Transformation Parameters

     This group of parameters includes spatially variable parameters, constants, and kinetic time functions for the water quality constituents being simulated. Parameter values are entered for each segment. Specified values for constants apply over the entire network for the whole simulation. Kinetic time functions are composed of a series of values versus time, in days.

     Water Temperature, C-- Time and segment variable water temperatures can be specified using the parameters TMPSG and

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TMPFN, and the time functions TEMP(1-4). If temperatures are to
remain constant in time, then the user should enter segment
temperatures using the parameter TMPSG. TMPFN and TEMP(1-4)
should be omitted.

If the user wants to enter time-variable temperatures, then
values for the parameter TMPSG should be set to 1.0. The
parameter TMPFN indicates which temperature function will be used
by the model for each segment. Values of 1.0, 2.0, 3.0, or 4.0
will call time functions TEMP(1), TEMP(2), TEMP(3), and TEMP(4),
respectively. Water temperatures should then be entered via
these time functions as a series of temperature versus time
values. The product of TMPSG and the selected TEMP function will
give the segment and time specific water temperatures used by
EUTRO5.

TMPSG and TMPFN are identified in EUTRO5 as parameters 3 and
4, respectively. TEMP(1-4) are identified in EUTRO5 as time
functions 1-4. (Group G, Record 4, PARAM(I,3), PARAM(I,4); Group
I, Record 2, VALT(1-4,K))

Solar Radiation, langleys/day-- Time-variable solar
radiation at the water surface can be described using time
functions ITOT and FDAY. Seasonally-varying values of solar
radiation at the surface can be entered using ITOT with a series
of radiation versus time values. The program assumes that ITOT
is the total solar radiation and not the visible-light portion of
solar radiation that is used in photosynthesis. FDAY gives the
seasonally-varying fraction of day that is daylight, entered as a
series of fraction versus time values. Internally, EUTRO5 uses
the quotient ITOT/FDAY for the average radiation intensity during
daylight hours. The fraction, TFACT, of solar radiation that is
photosynthetically active is used in the light limitation
calculations for phytoplankton and periphyton. (Group I, Record
2, VALT(5,K), VALT(6,K))

Light Extinction, m^{-1}-- Time and segment variable light
extinction coefficients can be specified using the parameters
KESG and KEFN, and the time functions KE(1-5). If extinction
coefficients are to remain constant in time, then the user should
enter segment coefficients using the parameter KESG. KEFN and
KE(1-4) should be omitted.

If the user wants to enter time-variable extinction
coefficients, then values for the parameter KESG should be set to
1.0. The parameter KEFN indicates which light extinction
function will be used by the model for each segment. Values of
1.0, 2.0, 3.0, 4.0, or 5.0 will call time functions KE(1), KE(2),

KE(3), KE(4), and KE(5), respectively. Light extinction coefficients should then be entered via these time functions as a series of coefficient versus time values. The product of KESG and the selected KE function will give the segment and time specific light extinction coefficients used by EUTRO5.

KESG and KEFN are identified in EUTRO5 as parameters 5 and 6, respectively. KE(1-4) are identified in EUTRO5 as time functions 8-12. (Group G, Record 4, ISC, PARAM(I,5), PARAM(I,6); Group I, Record 2, VALT(8-12,K))

<u>Growth Rate, day^{-1}</u>-- The maximum phytoplankton growth rate constant and temperature coefficient can be input using constants K1C and K1T, respectively. (Group H, Record 4, CONST(41), CONST(42))

<u>Carbon to Chlorophyll Ratio, mg C/mg Chl</u>-- The average carbon to chlorophyll weight ratio in phytoplankton can be specified using constant CCHL. A default value of 30 is provided for in EUTRO5. (Group H, Record 4, CONST(46))

<u>Light Limitation</u>-- Available light is specified using time functions describing seasonal light at the water surface and segment- and time-variable light extinction coefficents. These are described above.

The Steele/DiToro light limitation option can be specified using a value of 1.0 for LGHTSW. The Smith (1936) light limitation option can be specified using a value of 4.0 for LGHTSW. For these two functions, the saturating light intensity can then be specified using constants IS1 and IS2 for phytoplankton and periphyton, respectively. The half-saturation option is specified by using a value of 3.0 for LIGHTSW, in which case IS1 and IS2 represent the half-saturation constant for light limitation. Consistent with the literature on light limitation, the saturating light intensity refers only to the photosynthetically active portion of the solar radiation. Default values for LGHTSW and IS1 are 1 and 300, respectively. The default value for IS2 is IS1. (Group H, Record 4, CONST(43), CONST(47), CONST(113))

<u>Respiration Rate, day^{-1}</u>-- The average phytoplankton respiration rate constant and temperature coefficient can be input using constants K1RC and K1RT, respectively. (Group H, Record 4, CONST(50), CONST(51))

Death Rate, day^{-1}-- The non-predatory phytoplankton death rate constant can be input using constant K1D. No temperature dependance is assumed. (Group H, Record 4, CONST(52))

Phosphorus to Carbon Ratio, mg P/mg C-- The average phosphorus to carbon weight ratio in phytoplankton can be specified using constant PCRB. The EUTRO5 default value for PCRB is 0.025. (Group H, Record 4, CONST(57)

Phosphorus Mineralization Rate, day^{-1}-- The mineralization rate constant and temperature coefficient for dissolved organic phosphorus can be specified using constants K83C and K83T, respectively. (Group H, Record 4, CONST(100), CONST(101))

Phosphorus Half-Saturation Constant, mg P/L-- The phosphorus half-saturation constant for phytoplankton growth can be specified using constant KMPG1. When inorganic phosphorus concentrations are at this level, the phytoplankton growth rate is reduced by half. (Group H, Record 4, CONST(49))

Nitrogen to Carbon Ratio, mg N/mg C-- The average nitrogen to carbon weight ratio in phytoplankton can be specified using constant NCRB. The EUTRO5 default value for NCRB is 0.25. (Group H, Record 4, CONST(58)

Nitrogen Mineralization Rate, day^{-1}-- The mineralization rate constant and temperature coefficient for dissolved organic nitrogen can be specified using constants K71C and K71T, respectively. (Group H, Record 4, CONST(91), CONST(92))

Nitrification Rate, day^{-1}-- The nitrification rate constant and temperature coefficient for dissolved ammonia nitrogen can be specified using constants K12C and K12T, respectively. (Group H, Record 4, CONST(11), CONST(12))

Nitrogen Half-Saturation Constant, mg N/L-- The nitrogen half-saturation constant for phytoplankton growth can be specified using constant KMNG1. When inorganic nitrogen concentrations are at this level, the phytoplankton growth rate is reduced by half. This parameter also affects ammonia preference P_{NH3} as outlined in Figures 5.5 and 5.6. When KMNG1 = 0, P_{NH3} = 1.0. When KMNG1 becomes very large, P_{NH3} approaches a value of $C_1/(C_1 + C_2)$. (Group H, Record 4, CONST(48))

Intermediate Eutrophication Kinetics

Intermediate eutrophication kinetics simulate the growth and death of phytoplankton interacting with the nitrogen and phosphorus cycles and the dissolved oxygen balance. Growth can be limited by the availability of inorganic nitrogen, inorganic phosphorus, and light.

Intermediate eutrophication kinetics add CBOD and DO equations as well as certain nonlinear terms and functions to the simple eutrophication kinetics described above. The oxygen balance equations and kinetic parameters are summarized in Figure 4.2 and Table 4.1. The phosphorus cycle equations and kinetic parameters are summarized in Figure 5.4 and Table 5.6. The nitrogen cycle equations and parameters are summarized in Figure 5.5 and Table 5.7. Phytoplankton equations are presented throughout Section 5.2, with parameters summarized in Table 5.3.

Light limitation can be described by either the Di Toro or the Smith formulation. The Smith formulation implements equations 5.6 through 5.11. These equations predict the carbon to chlorophyll ratio based on the availability of light, then predict the saturating light intensity based on the carbon to chlorophyll ratio.

Other terms included in the intermediate kinetics equations are the phytoplankton effect on mineralization of organic phosphorus and nitrogen, the dissolved oxygen limitation on nitrification, the denitrification reaction, and zooplankton grazing. The nonlinear DO balance equations can become important in inhibiting nitrification and carbonaceous oxidation and in promoting denitrification where low DO concentrations occur.

All eight state variables are simulated in intermediate eutrophication simulations. During calibration of the model to observed data, however, the user may want to bypass certain variables or hold them constant. Nutrients can be held at observed concentrations, for instance, while phytoplankton growth and death rates are calibrated.

Environment Parameters

These parameters define the basic model identity, including the segmentation, and control the simulation.

Systems-- Select "simulate" for all variables. During calibration, the user may select "constant" or "bypass" for any selected variables. (Group A, Record 4, NOSYS; Record 9, SYSBY)

Segments-- Water column segments should be defined in the standard fashion. If settling is to be simulated (i.e., for ON, OP, PHYT, PO4, or CBOD), the user should add a single benthic segment underlying all water column segments. This benthic segment will merely act as a convenient sink for settling organic matter. Model calculations within this benthic segment should be ignored. (Group A, Record 4, NOSEG; Group C, Record 3, ISEG, IBOTSG, ITYPE, BVOL, DMULT)

Transport Parameters

This group of parameters defines the advective and dispersive transport of model variables.

Number of Flow Fields-- To simulate settling of ON, OP, and CBOD, the user should select solids 1 flow under advection. To simulate settling of PHYT, the user should select solids 2 flow. To simulate PO4 settling, the user should select solids 3 flow. The user should also select water column flow. (Group D, Record 1, NFIELD)

Particulate Transport, m^3/sec-- Time variable settling and resuspension velocities can be specified for particulate ON, OP, CBOD, PHYT, and PO4, as described in the simple eutrophication section above.

Boundary Parameters

This group of parameters includes boundary concentrations, waste loads, and initial conditions. Boundary concentrations must be specified for any segment receiving flow inputs, outputs, or exchanges. Initial conditions include not only initial concentrations, but also the density and solids transport field for each solid, and the dissolved fraction in each segment.

Boundary Concentrations, mg/L-- At each segment boundary, time variable concentrations must be specified for PHYT, expressed as g/L chlorophyll *a*. Time variable concentrations must also be specified for either ON, NH3, NO3, OP, PO4, CBOD, and DO. A boundary segment is characterized by water exchanges from outside the network, including tributary inflows, downstream

outflows, and open water dispersive exchanges. (Group E, Record 4, BCT)

Waste Loads, kg/day-- For each point source discharge, time variable PHYT, ON, NH3, NO3, OP, PO4, CBOD, and DO loads can be specified. These loads can represent municipal and industrial wastewater discharges, or urban and agricultural runoff. If any phytoplankton loads are specified, they should be in units of kg carbon/day. (Group F.1, Record 4, WKT)

Solids Transport Field-- The transport fields associated with particulate settling must be specified under initial conditions. Solids 1 (Field 3) is recommended for ON, OP, and CBOD. Solids 2 (Field 4) is recommended for PHYT. Solids 3 (Field 5) is recommended for PO4. (Group J, Record 1, IFIELD)

Solid Density, g/cm^3-- A value of 0 can be entered for the nominal density of PHYT, ON, NH3, NO3, OP, PO4, CBOD, and DO. This information is not used in EUTRO5. (Group J, Record 1, DSED)

Initial Concentrations, mg/L-- Concentrations of all variables in each segment must be specified for the time at which the simulation begins. Concentrations of PHYT are expressed as g/L chlorophyll a. (Group J, Record 2, C)

Dissolved Fraction-- The dissolved fraction of each variable in each segment must be specified. The dissolved fraction of PHYT should be set to 0, and the dissolved fraction of DO should be set to 1. Only the particulate fractions of CBOD and the nutrients will be subject to settling. (Group J, Record 2, DISSF)

Transformation Parameters

     This group of parameters includes spatially variable parameters, constants, and kinetic time functions for the water quality constituents being simulated. Parameter values are entered for each segment. Specified values for constants apply over the entire network for the whole simulation. Kinetic time functions are composed of a series of values versus time, in days.

     Water Temperature, C-- Time and segment variable water temperatures can be specified using the parameters TMPSG and TMPFN, and the time functions TEMP(1-4), as described in the simple eutrophication section above.

Solar Radiation, langleys/day-- Time-variable total solar radiation at the water surface can be described using time functions ITOT and FDAY, as described in the simple eutrophication section above.

Light Extinction, m^{-1}-- Time and segment variable light extinction coefficients can be specified using the parameters KESG and KEFN, and the time functions KE(1-5), as described in the simple eutrophication section above.

Growth Rate, day^{-1}-- The maximum phytoplankton growth rate constant and temperature coefficient can be input using constants K1C and K1T, respectively. (Group H, Record 4, CONST(41), CONST(42))

Carbon to Chlorophyll Ratio, mg C/mg Chl-- The average carbon to chlorophyll weight ratio in phytoplankton can be specified using constant CCHL. A default value of 30 is provided for in EUTRO5. If the Smith light limitation option is chosen, then CCHL will be variable, recalculated daily throughout the simulation. (Group H, Record 4, CONST(46))

Light Limitation-- Available light is specified using time functions describing seasonal light at the water surface and segment- and time-variable light extinction coefficents. These are described above.

The Steele/DiToro light limitation option can be specified using a value of 1.0 for LGHTS. The saturating light intensity, in langleys/day can then be specified using constants IS1 and IS2 for phytoplankton and periphyton respectively. Consistent with the literature on light limitation, the saturating light intensity refers only to the photosynthetically active portion of the solar radiation.

The Smith (1936) light limitation option can be specified using a value of 4.0 for LGHTSW. For this function, the saturating light intensity can then be specified using constants IS1 and IS2 for phytoplankton and periphyton, respectively. The half-saturation option is specified by using a value of 3.0 for LIGHTSW, in which case IS1 and IS2 represent the half-saturation constant for light limitation. Default values for LGHTSW and IS1 are 1 and 300, respectively. (Group H, Record 4, CONST(43), CONST(47), CONST(113))

The Smith (1980) light limitation option can be specified using a value of 2.0 for LGHTSW. Two other parameters must then be specified. The maximum quantum yield constant, in mg C/mole

photons, can be specified using constant PHIMX. The chlorophyll extinction coefficient, in (mg chl $\underline{a}$/m^3)$^{-1}$m^{-1}, can be specified using constant XKC. Default values for PHIMX and XKC are 720 and 0.017, respectively. (Group H, Record 4, CONST(43), CONST(44), CONST(45))

Nitrogen Half-Saturation Constant, mg N/L-- The nitrogen half-saturation constant for phytoplankton growth can be specified using constant KMNG1. When inorganic nitrogen concentrations are at this level, the phytoplankton growth rate is reduced by half. This parameter also affects ammonia preference P_{NH3} as outlined in Figures 5.5 and 5.6. When KMNG1 = 0, P_{NH3} = 1.0. When KMNG1 becomes very large, P_{NH3} approaches a value of $C_1/(C_1 + C_2)$. (Group H, Record 4, CONST(48))

Phosphorus Half-Saturation Constant, mg P/L-- The phosphorus half-saturation constant for phytoplankton growth can be specified using constant KMPG1. When inorganic phosphorus concentrations are at this level, the phytoplankton growth rate is reduced by half. (Group H, Record 4, CONST(49))

Nutrient Limitation Option-- The nutrient limitation formulation can be specified using constant NUTLIM. A value of 0 selects the minimum formulation, which is recommended. A value of 1.0 selects the multiplicative formulation. The default value is 0. (Group H, Record 4, CONST(54))

Respiration Rate, day^{-1}-- The average phytoplankton endogenous respiration rate constant and temperature coefficient can be input using constants K1RC and K1RT, respectively. (Group H, Record 4, CONST(50), CONST(51))

Death Rate, day^{-1}-- The non-predatory phytoplankton death rate constant can be input using constant K1D. No temperature dependance is assumed. (Group H, Record 4, CONST(52))

Grazing Rate, day^{-1}-- Zooplankton grazing can be specified using parameter ZOOSG, time function ZOO, and constant K1G. Time- and segment-variable herbivorous zooplankton populations are described as the product of the time variable population ZOO, in mg zooplankton C/L, and segment specific ratios ZOOSG. The grazing rate per unit zooplankton population, in L/mg zooplankton C-day, can be input using constant K1G. The resulting grazing rate constant for phytoplankton is the product of the variable zooplankton population and the unit grazing rate. (Note that ZOO can also be expressed as cells/L if K1G is expressed as L/cell-day). (Group G, Record 4, PARAM(I,15); Group H, Record 4, CONST(53); Group I, Record 2 VALT(19,K))

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Phosphorus to Carbon Ratio, mg P/mg C-- The average phosphorus to carbon weight ratio in phytoplankton can be specified using constant PCRB. The EUTRO5 default value for PCRB is 0.025. (Group H, Record 4, CONST(57)

Phytoplankton Phosphorus Recycle-- The fraction of dead and respired phytoplankton phosphorus that is recycled to the organic phosphorus pool can be specified using constant FOP. The default value is 1. The fraction of phytoplankton phosphorus recycled directly to inorganic phosphorus is 1 - FOP. (Group H, Record 4, CONST(104))

Phosphorus Mineralization Rate, day^{-1}-- The mineralization rate constant and temperature coefficient for dissolved organic phosphorus can be specified using constants K83C and K83T, respectively. Phytoplankton effects on mineralization can be described using constant KMPHY, the half-saturation constant for mineralization dependence on phytoplankton, in mg C/L. This causes mineralization rates to increase as phytoplankton levels increase. If KMPHY is zero, there is no phytoplankton effect on mineralization. If KMPHY is large, then large concentrations of phytoplankton are needed to drive mineralization, and thus relatively low phytoplankton levels can lead to low mineralization rates. (Group H, Record 4, CONST(100), CONST(101), CONST(59))

Benthic Phosphorus Flux, mg/m^2-day-- The segment- and time-variable benthic phosphorus flux can be specified using parameter FPO4 and time function TFPO4 in models without sediment segments. The product of the spatially- variable FPO4 and time-variable TFPO4 gives the segment and time specific benthic flux for PO4 used by EUTRO5. Flux versus time values can be entered using TFPO4, while unitless segment ratios can be entered using FPO4. Values should be entered for water column segments that are in contact with the bottom of the water body. (Group G, Record 4, PARAM(I,8); Group I, Record 2, VALT(14,K))

Nitrogen to Carbon Ratio, mg N/mg C-- The average nitrogen to carbon weight ratio in phytoplankton can be specified using constant NCRB. The EUTRO5 default value for NCRB is 0.25. (Group H, Record 4, CONST(58)

Phytoplankton Nitrogen Recycle-- The fraction of dead and respired phytoplankton nitrogen that is recycled to the organic nitrogen pool can be specified using constant FON. The default value is 1. The fraction of phytoplankton nitrogen recycled directly to ammonia is 1 - FON. (Group H, Record 4, CONST(95))

Nitrogen Mineralization Rate, day^{-1}-- The mineralization rate constant and temperature coefficient for dissolved organic nitrogen can be specified using constants K71C and K71T, respectively. Phytoplankton effects on mineralization can be described using constant KMPHY, the half-saturation constant for mineralization dependence on phytoplankton, as explained above in the phosphorus mineralization section. (Group H, Record 4, CONST(91), CONST(92), CONST(59))

Nitrification Rate, day^{-1}-- The nitrification rate constant and temperature coefficient for dissolved ammonia nitrogen can be specified using constants K12C and K12T, respectively. The half-saturation constant for oxygen limitation of nitrification can be specified using constant KNIT. The default value for KNIT is 0.0, indicating no oxygen limitation. (Group H, Record 4, CONST(11), CONST(12), CONST(13))

Denitrification Rate, day^{-1}-- The denitrification rate constant and temperature coefficient for dissolved nitrate nitrogen can be specified using constants K20C and K20T, respectively. The half-saturation constant for oxygen limitation of denitrification can be specified using constant KNO3. The default value for KNO3 is 0.0, indicating no denitrification at oxygen concentrations above 0.0. (Group H, Record 4, CONST(21), CONST(22), CONST(23))

Benthic Nitrogen Flux, mg/m^2-day-- The segment- and time-variable benthic nitrogen flux can be specified using parameter FNH4 and time function TFNH4 in models without sediment segments. The product of the spatially- variable FNH4 and time-variable TFNH4 gives the segment and time specific benthic flux for NH3 used by EUTRO5. Flux versus time values can be entered using TFNH4, while unitless segment ratios can be entered using FNH4. Values should be entered for water column segments that are in contact with the bottom of the water body. (Group G, Record 4, PARAM(I,7); Group I, Record 2, VALT(13,K))

Sediment Oxygen Demand, g/m^2-day-- Segment variable sediment oxygen demand fluxes and temperature coefficients can be specified using the parameters SOD1D and SODTA, respectively. Values should be entered for water column segments that are in contact with the bottom of the water body. (Group G, Record 4, PARAM(I,9), PARAM(I,12))

Reaeration Rate, day^{-1}-- There are three basic options for specifying reaeration -- a single rate constant, segment and time variable rate constants, and flow and wind calculated rate

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constants. These options are described in Section 4.2, under the Streeter-Phelps transformation parameters.

   CBOD Deoxygenation Rate, day^{-1}-- The CBOD deoxygenation rate constant and temperature coefficient can be specified using constants KDC and KDT, respectively. The half-saturation constant for oxygen limitation of carbonaceous deoxygenation can be specified using constant KBOD. The default value for KBOD is 0.0, indicating no oxygen limitation. (Group H, Record 4, CONST(72), CONST(73), CONST(75))

Intermediate Eutrophication Kinetics with Benthos

   Simulating benthic interactions requires the addition of benthic segments to the model network. All state variables are simulated in the benthic segments. Dissolved fractions of NH3, NO3, PO4, CBOD, DO, ON, and OP may exchange with the water column by diffusion. Particulate fractions of PHYT, PO4, CBOD, ON, and OP may deposit to or be scoured from the benthic segments. Benthic layer decomposition rates for OP, ON, PHYT, and CBOD must be specified. The equations used are those presented in Figures 4.3 and 5.9. Rate parameters are summarized in Tables 4.2 and 5.7.

   Many of the environment, transport, boundary, and transformation parameters required to implement this option are the same as those in the intermediate eutrophication option presented above. The benthic nitrogen and phosphorus flux functions should be omitted, and the following should be modified or added.

   Segments-- Water column segments should be defined in the standard fashion. In addition, the user should add a benthic segment underlying each water column segment (or stack of water column segments). These benthic segments will receive settling organic and inorganic matter from the water column above, and can return material to the water column via resuspension or by pore water diffusion. (Group A, Record 4, NOSEG; Group C, Record 3, ISEG, IBOTSG, ITYPE, BVOL, DMULT)

   Phytoplankton Decomposition, day^{-1}-- The user may specify the rate constant and temperature coefficient for phytoplankton

decomposition in benthic segments using constants KPZDC and KPZDT. (Group H, Record 4, CONST(55), CONST(56))

     Carbonaceous BOD Decomposition, day^{-1}-- The user may specify the rate constant and temperature coefficient for CBOD decomposition in benthic segments using constants KDSC and KDST. (Group H, Record 4, CONST(73), CONST(74))

     Organic Nitrogen Decomposition, day^{-1}-- The user may specify the rate constant and temperature coefficient for organic nitrogen decomposition in benthic segments using constants KONDC and KONDT. (Group H, Record 4, CONST(93), CONST(94))

     Organic Phosphorus Decomposition, day^{-1}-- The user may specify the rate constant and temperature coefficient for organic phosphorus decomposition in benthic segments using constants KOPDC and KOPDT. (Group H, Record 4, CONST(102), CONST(103))

Diurnal Light Variation

The MDEP Version of WASP includes algorithms to compute solar radiation as a function of the time of day using algorithms similar to those in QUAL2E (Brown and Barnwell, 1987). The user selects the diurnally varying solar radiation option by setting the LGHTSW constant in Data Group H (ISC=43) to a negative value. As with the preexisting WASP code, the absolute value of LGHTSW is used to designate whether the Smith or DiToro algorithm is used to determine the impact of light on phytoplankton growth. The LGHTSW constant is therefore used as shown in Table 5.10.

The *heatex* routine from QUAL2E was adapted for use in WASP. As described in Section 4.3 of the QUAL2E user's manual (Brown and Barnell, 1987), that routine estimates the total solar

Table 5.10 Summary of Light Calculation Options

| | Value of LGHTSW | | | |
Option	DiToro/ Steele	Smith (1980)	Half- Saturation	Smith (1936)
Input daily-average light intensity	1	2	3	4
Calculated diurnally- varying light intensity	-1	-2	-3	-4

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radiation, *H*, as:

$$H = 0.271 \, H_0 \, a_t \, (1-R_s) \, (1-0.65 \, C_L^2)$$

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where:

H_o = amount of solar radiation flux reaching the earth's atmosphere, Langley/day

a_t = atmospheric transmission term

R_s = albedo or reflection coefficient

C_L = cloudiness, fraction of sky covered

Cloudiness is entered as a time varying function in the climate data file as described below. The remainder of the terms are computed as functions of the site latitude, longitude and elevation, the dust attenuation factor, the wet-bulb and dry-bulb temperatures and the local barometric pressure. The temperature and pressure terms are time-varying functions, while the others are constants entered as part of Data Group H. The new constants entered with Data Group H, their ISC numbers and references to their use in the QUAL2 User's Manual are in Table 5.11.

Table 5.11 Summary of Light Calculation Variables and Time Functions

Variable	Definition and Units	Reference in QUAL2E User's Manual
LAT	Site latitude, degrees	Eq. IV-8 on pg. 61
LLM	Longitude of local meridian, degrees	Eq. IV-14 on pg. 63
LSM	Longitude of standard meridian, degrees	Eq. IV-14 on pg. 63
ELEV	Site elevation, feet, MSL	Eq. IV-21 on pg. 64
DAT	Dust attenuation coefficient	Eq. IV-19 on pg. 63 and pg. 65
CLOUD	Cloudiness, decimal fraction	Eq. IV-26 on pg. 65
WETBLB	Wet bulb temperature, °F	Eq. IV-34 on pg. 68
DRYBLB	Dry bulb temperature, °F	Eq. IV-34 on pg. 68
ATMPR	Local barometric pressure, inches Hg	Eq. IV-34 on pg. 68

Each record in the file *climate.dat* contains a single value of each of these time functions at a specified date and hour. The record format used in QUAL2 has been preserved, so as to make use of available QUAL2 input files. The records are read free format, so that strict columnar formatting is not necessary. The record contains a year field; however WASP does not make use of this field. Multi-year simulations therefore cannot be run. The climate data functions will not repeat once the simulation has gone beyond the time range over which the function was defined.

The following is sample data from the *climate.dat* file:

```
07 01 90   1.              0.57    63.0    54.4    27.46
07 01 90   4.              0.70    59.7    54.3    27.46
07 01 90   7.              0.80    66.0    56.4    27.49
```

The fields are, from left to right, the month, day, year, hour, cloudiness, wet bulb temperature, dry bulb temperature, and local barometric pressure in units as designated above.

The photosynthetically available solar radiation is computed in MDEPWASP as a fraction of the total solar radiation:

$$I_0 = TFACT \ H \qquad\qquad\qquad 5.39$$

where

I_o =   instantaneous incident photosynthetically available solar radiation, langleys/day

$TFACT$ =   the fraction of the total solar radiation that is photosynthetically available. *TFACT* typically has a value of 0.43 to 0.45 according to Brown and Barnwell (1987).

Differences between the DiToro/Steele, half-saturation, and Smith (1936) functions and the Smith (1980) growth reduction function affect the calculation procedure for diurnally varying light. In the first three schemes, the value of I_s, the saturating light intensity or light half-saturation constant, is a constant set within Data Group H in the WASP input data. In the Smith (1980) scheme, the value of I_s is calculated as a function of the carbon-to-chlorophyll ratio which in turn is a

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function of the average daily photosynthetically active solar radiation. In the MDEP version of WASP, it is necessary to calculate this based on the prior day's light intensity, since the current day's light intensity is not available. (In the EPA version of WASP 5, the average light intensity for the current simulation day is available as an input and is used for this calculation.) For the first day of any simulated period, the average light intensity of the prior day is not available, so a default value of 30 is used for the carbon to chlorophyll ratio in order to calculate I_s.

If the option to calculate the solar heating is selected (LGHTSW<0) then the output solar radiation values are instantaneous rather than daily averages. Three solar radiation values are reported in the *edf* file. The data field names in the *edf* file and their definition for both the calculated solar radiation and input solar radiation modes are given in Table 5.12. All values of total radiation are also adjusted by the factor TFACT to convert to photosynthetically active radiation for the light limitation calculations for phytoplankton and periphyton.

Table 5.12   Output Total Solar Radiation Values

Data Field	Data Value	
	Input Radiation (langleys/day)	**Calculated Radiation (langleys/day)**
Total Light or Total Daily Light for input radiation	Total radiation received in a day reduced by local shading	Instantaneous radiation reduced by local shading
Light Top Seg	9/10 of Total Daily Light reduced by attenuation through water (if not top segment) averaged over daylight duration as indicated by time function	Total Daily Light reduced by attenuation through water (if not top segment)
Light Bot Seg	Light Top Seg reduced by attenuation through segment depth	Light Top Seg reduced by attenuation through segment depth

Data Group Descriptions

Input datasets to simulate eutrophication in a lake are given with the model software. A comprehensive listing of the WASP5 data groups, records, and variables is given in Part B of this report.

CHAPTER 6

SIMPLE TOXICANTS

6.1. MODEL DESCRIPTION

Introduction

Some organic and inorganic chemicals can cause toxicity to aquatic organisms, or bioconcentrate through the food chain. Humans may be affected by ingesting contaminated water or fish. Criteria for protecting human health and indiginous aquatic communities have been promulgated for specific chemicals and for general toxicity.

The simulation of toxicants has become common only in the past decade. Near-field mixing zone models simulate the dilution and dispersal of waste plumes, along with associated toxicants. Far-field models, such as WASP5, simulate the transport and ultimate fate of chemicals throughout a water body. At a minimum, these models simulate the water column and a bed layer, and include both chemical degradation and sorption to solids. The simpler models use first-order decay constants and equilibrium partition coefficients. More complex models may employ second-order decay mechanisms and either nonlinear sorption isotherms or first-order sorption and desorption rate constants.

Several physical-chemical processes can affect the transport and fate of toxic chemicals in the aquatic environment. Some chemicals undergo a complex set of reactions, while others behave in a more simplified manner. WASP5 allows the simulation of a variety of processes that may affect toxic chemicals. The model is designed to provide a broad framework applicable to many environmental problems and to allow the user to match the model complexity with the requirements of the problem.

Although the potential amount and variety of data used by WASP5 is large, data requirements for any particular simulation

can be quite small. For example, it is possible to simulate a
chemical using no reactions, or using only sorption and one or
two transformation reactions that significantly affect a
particular chemical. Indeed, for empirical studies, all
chemical constants, time functions, and environmental
parameters can be ignored and a simple user-specified
transformation rate constant used. Thus, WASP5 can be used as a
first-order water pollutant model to conduct simulations of dye
tracers, salinity intrusion, or coliform die-off.

Overview of Simple WASP5 Toxicants

Simple toxicants and
associated solids are
simulated using the TOXI5
program. TOXI5 simulates the
transport and transformation
of one to three chemicals and
one to three types of
particulate material (solids
classes, Table 6.1). The
three chemicals may be
independent or they may be
linked with reaction yields,
such as a parent
compound-daughter product
sequence. The simulation of
solids is described in Chapter
3. The simulation of simple
toxicants is described below.
The simulation of more complex
organic chemicals is described
in Chapter 7.

Table 6.1 WASP5 State Variables
for Toxicants.

SYSTEM	VARIABLE
1	CHEMICAL 1
2	SOLIDS 1
3	SOLIDS 2
4	SOLIDS 3
5	CHEMICAL 2
6	CHEMICAL 3

In an aquatic environment, toxic chemicals may be
transferred between phases and may be degraded by any of a
number of chemical and biological processes. Simplified
transfer processes defined in the model include sorption and
volatilization. Transformation processes include
biodegradation, hydrolysis, photolysis, and oxidation. Sorption
is treated as an equilibrium reaction. The simplified
transformation processes are described by first-order rate
equations.

WASP5 uses a mass balance equation to calculate sediment
and chemical mass and concentrations for every segment in a

specialized network that may include surface water, underlying
water, surface bed, and underlying bed. In a simulation,
sediment is advected and dispersed among water segments, settled
to and eroded from benthic segments, and moved between benthic
segments through net sedimentation, erosion, or bed load as
detailed in Chapter 3.

    Simulated chemicals undergo several physical or chemical
reactions as specified by the user in the input dataset.
Chemicals are advected and dispersed among water segments, and
exchanged with surficial benthic segments by dispersive mixing.
Sorbed chemicals settle through water column segments and
deposit to or erode from surficial benthic segments. Within the
bed, dissolved chemicals migrate downward or upward through
percolation and pore water diffusion. Sorbed chemicals migrate
downward or upward through net sedimentation or erosion. Rate
constants and equilibrium coefficients must be estimated from
field or literature data in simplified toxic chemical studies.
Their calculation from laboratory and field data is described in
Chapter 7.

    Some limitations should be kept in mind when applying
TOXI5. First, chemical concentrations should be near trace
levels, i.e., below half the solubility or 10^{-5} molar. At higher
concentrations, the assumptions of linear partitioning and
transformation begin to break down. Chemical density may become
important, particularly near the source, such as in a spill.
Large concentrations can affect key environmental
characteristics, such as pH or bacterial populations, thus
altering transformation rates.

    In TOXI5, it is convenient to define concentration related
symbols as in Table 6.2. Please note that in the general
development of the equations below, subscripts "i" and "j" are
sometimese omitted for convenience.

Simple Transformation Kinetics

    TOXI5 allows the user to specify simple first-order
reaction rates for the transformation reactions of each of the
chemicals simulated. First order rates may be applied to the
total chemical and varied by segment. Alternatively, constant

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Table 6.2 Concentration Related Symbols Used in Mathematical Equations.

Symbol	Definition	Units
C_{ij}	Concentration of total chemical i in segment j.	mg_c/L
C_{wij}	Concentration of dissolved chemical i in segment j.	mg_c/L
C'_{wij}	Concentration of dissolved chemical i in water in segment j. $C'_{wij} = C_{wij}/n_j$	mg_c/L_w
C_{sij}	Concentration of sorbed chemical i on sediment type "s" in segment j.	mg_c/L
C'_{sij}	Concentration of sorbed chemical i on sediment type "s" in segment j. $C'_{sij} = C_{sij}/M_{sij}$	mg_c/kg_s
m_{sj}	Concentration of sediment type "s" in segment j.	mg_s/L
M_{sj}	Concentration of sediment type "s" in segment j. $M_j = m_j \times 10^{-6}$	kg_s/L
M'_{sj}	Concentration of sediment type "s" in water in segment j.	kg_s/L_w
n_j	Porosity or volume water per volume segment j.	L_w/L
K_{psij}	Partition coefficient of chemical i on sediment type "s" in segment j.	L_w/kg_s
f_{Dij}	Fraction of chemical i in segment j in dissolved phase	-
f_{sij}	Fraction of chemical i in segment j in solid phase "s"	-

first order rates may be specified for particular processes, including biodegradation, hydrolysis, photolysis, volatilization, and oxidation. These constant rates may be used exclusively or in combination with model computed rates as described in Chapter 7. For example, the user may specify a first-order rate for biodegradation and have TOXI5 compute a loss rate for volatilization.

Option 1: Total Lumped First Order Decay

The simplest rate expression allowed by TOXI5 is lumped, first-order decay. This option allows the user to specify spatially-variable first order decay rate constants (day^{-1}) for each of the chemicals simulated. Because these are lumped decay reactions, chemical transformations to daughter products are not simulated.

$$\frac{\partial C_{ij}}{\partial t}\bigg|_{reaction} = K_{ij}\ C_{ij} \qquad\qquad\qquad \textbf{6.1}$$

where:

K_{ij} = lumped first order decay constants (day^{-1}) for chemical i in segment j.

The lumped decay rate constant is a model parameter that may be varied between model segments. If a lumped decay rate constant is specified, the chemical will react at that rate regardless of other model input.

Option 2: Individual First Order Transformation

This option allows the user to input a global first-order reaction rate constant separately for each of the following processes: volatilization, water column biodegradation, benthic biodegradation, alkaline hydrolysis, neutral hydrolysis, acid hydrolysis, oxidation, photolysis, and an extra reaction. The total reaction is then based on the sum of each of the individual reactions as given by

$$\frac{\partial C_{ij}}{\partial t}\bigg|_{reaction} = \sum_{k=1}^{N} K_{ki}\ C_{ij} \qquad\qquad\qquad \textbf{6.2}$$

where:

$$K_{ki} \quad = \quad \text{first order transformation constants for reaction k of chemical i, day}^{-1}$$

The user may input half-lives rather than first-order decay rate constants. If half-lives are provided for the transformation reactions, they will be converted internally to first order rate constants and used as above:

$$K_{ki} = 0.693/T_{Hki} \qquad\qquad\qquad\qquad \textbf{6.3}$$

where:

$$T_{Hki} \quad = \quad \text{half-life of reaction k for chemical i, days.}$$

Equilibrium Sorption

Sorption is the bonding of dissolved chemicals onto solid phases, such as benthic and suspended sediment, biological material, and sometime dissolved or colloidal organic material. Sorption can be important in controlling both the environmental fate and the toxicity of chemicals. Sorption may cause the chemical to accumulate in bed sediment or bioconcentrate in fish. Sorption may retard such reactions as volatilization and base hydrolysis, or enhance other reactions including photolysis and acid-catalyzed hydrolysis.

Sorption reactions are usually fast relative to other environmental processes, and equilibrium may be assumed. For environmentally relevant concentrations (less than 10^{-5} M or one-half water solubility), equilibrium sorption is linear with dissolved chemical concentration (Karickhoff, 1984) or:

$$C_s' = K_{ps} \cdot C_w' \qquad\qquad\qquad\qquad \textbf{(6.4)}$$

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At equilibrium, then, the distribution among the phases is
controlled by the partition coefficients K_{ps}. As developed in
Chapter 7, the total mass of chemical in each phase is
controlled by K_{ps} and the amount of solid phase present (ignoring
here any DOC phase), so that

$$f_D = \frac{n}{n + \sum\limits_{s} K_{ps} \cdot M_s} \qquad (6.5)$$

and

$$f_s = \frac{K_{ps} \cdot M_s}{n + \sum\limits_{s} K_{ps} \cdot M_s} \qquad (6.5)$$

These fractions are determined in time and space throughout
a simulation from the partition coefficients, internally
calculated porosities, and simulated sediment concentrations.
Given the total concentration and the phase fractions of
chemical i in segment j, the dissolved and sorbed concentrations
are uniquely determined:

$$C_{wij} = C_{ij} \cdot f_{Dij} \qquad (6.7)$$

$$C_{sij} = C_{ij} \cdot f_{sij} \qquad (6.8)$$

In addition to the assumption of instantaneous equilibrium,
implicit in the use of these equations is the assumption of
reversibility. Laboratory data for very hydrophobic chemicals
suggest, however, that a hysteresis exists, with desorption
being a much slower process than adsorption. Karickhoff
suggests that this effect may be the result of intraparticle
kinetics in which the chemical is slowly incorporated into
components of the sorbant. This phenomenon is not well

understood and no quantitative modeling framework is available to characterize it.

Values for the partition coefficients can be obtained from laboratory experiments or field data. TOXI5 allows the input of either a single constant partition coefficient, or a set of spatially-variable partition coefficients. These options are described under "Model Implementation" below. The calculation of partition coefficients for organic chemicals is described in Chapter 7.

Transformations and Daughter Products

The three chemicals that may be simulated by TOXI5 may be independent, or they may be linked with reaction yields, such as a parent compound-daughter product sequence. Linked transformations may be implemented by simulating two or three chemicals and by specifying appropriate yield coefficients for each process:

$$S_{kc1} = \sum_c \sum_k K_{kc} \, C_c \, Y_{kc1} \, , \qquad c = 2, 3 \tag{6.9}$$

$$S_{kc2} = \sum_c \sum_k K_{kc} \, C_c \, Y_{kc2} \, , \qquad c = 1, 3 \tag{6.10}$$

$$S_{kc3} = \sum_c \sum_k K_{kc} \, C_c \, Y_{kc3} \, , \qquad c = 1, 2 \tag{6.11}$$

where:

S_{kci} = production of chemical "i" from chemical "c" undergoing reaction "k," mg_i/L-day

K_{kc} = effective rate coefficient for chemical "c," reaction "k," day^{-1}

Y_{kci} = yield coefficients for production of chemical "i" from chemical "c" undergoing reaction "k," mg_i/mg_c
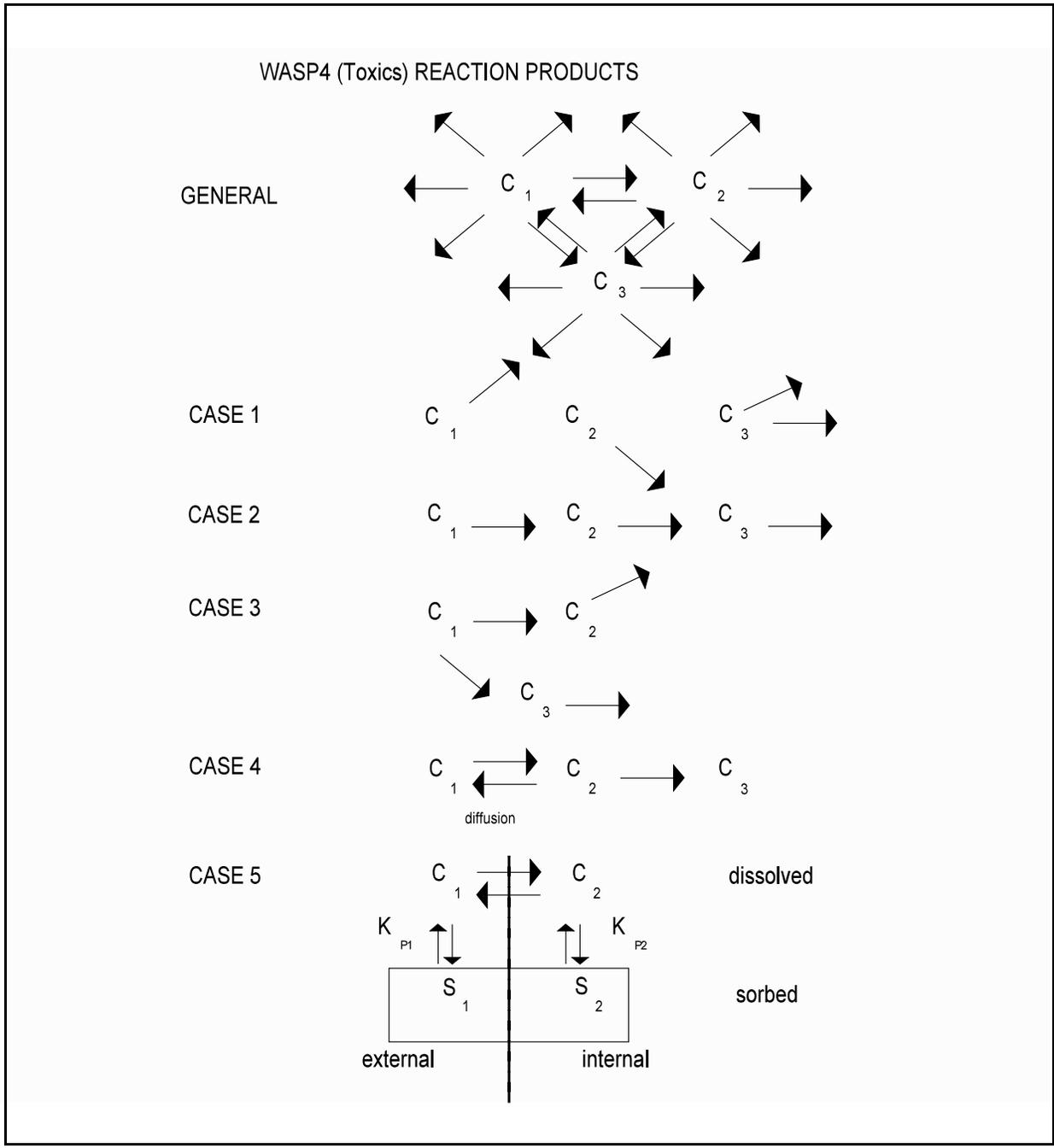
Figure 6.1. Potential Reaction Products in WASP5

Figure 6.1 illustrates some of the linked reactions that can be simulated by specifying appropriate yield coefficients.

6.2 MODEL IMPLEMENTATION

Introduction

To simulate simple toxicants with WASP5, use the preprocessor to create a TOXI5 input file. The model input dataset and the input parameters will be similar to those for the conservative tracer model as described in Chapter 2. To those basic parameters, the user will add benthic segments, solids transport rates, and transformation parameters. During the simulation, solids and toxicants will be transported both by the water column advection and dispersion rates and by these solids transport rates.

In WASP5, solids transport rates in the water column and the bed are input via up to three solids transport fields, as described in Chapter 3. The transport of the particulate fraction of toxicants follows the solids flows. The user must specify the dissolved fraction (i.e. 0.0) and the solids transport field for each simulated solid under initial conditions. To simulate total solids, solids 1 must be used.

Model Input Parameters

This section summarizes the input parameters that must be specified in order to solve the simple toxicant equations in TOXI5. The user is referred to Chapter 3 for a summary of input parameters for the sediment balance equations. Input parameters are prepared for WASP5 in four major sections of the preprocessor -- environment, transport, boundaries, and transformation. Basic model parameters are described in Chapter 2, and will not be repeated here.

Environment Parameters

These parameters define the basic model identity, including the segmentation, and control the simulation.

Systems-- To simulate a toxicant, select "simulate" for chemical 1 and "bypass" for chemical 2 and chemical 3. To simulate total solids along with the toxicant, select "simulate"

for solids 1 and "bypass" for solids 2 and solids 3. To
simulate two or more toxicants or solids, select "simulate" for
the appropriate variable. (Group A, Record 4, NOSYS; Record 9,
SYSBY)

    Bed Volume Option-- The user must determine whether bed
volumes are to be held constant or allowed to vary. Volumes may
be held constant by specifying 0, in which case sediment
concentrations and porosities in the bed segments will vary.
Alternatively, sediment concentrations and porosities may be
held constant by specifying 1, in which case surficial bed
segment volumes will vary. (Group C, Record 1, IBEDV)

    Bed Time Step-- While mass transport calculations are
repeated every model time step, certain benthic calculations are
repeated only at this benthic time step, in days. If the
constant bed volume option is chosen, sediment concentrations
are updated every model time step, but porosities are
recalculated every benthic time step. If the variable bed
volume is chosen, upper benthic segment volumes are updated
every time step, with compaction occurring every benthic time
step. (Group C, Record 1, TDINTS)

Transport Parameters

    Number of Flow Fields-- Under advection, the user has a
choice of up to six flow fields. To simulate surface water
toxicant and solids transport, select water column flow. When
simulating total solids, the user should also select solids 1
flow. To simulate three sediment types, the user should select
solids 1 flow, solids 2 flow, and solids 3 flow. (Group D,
Record 1, NFIELD)

    Water Column Flows, m^3/sec-- Time variable water column
flows can be specified, as detailed in Chapter 2. (Group D,
Record 6, QT, TQ; Record 4, BQ, JQ, IQ)

    Sediment Transport Velocities, m/sec-- Time variable
settling, deposition, scour, and sedimentation velocities can be
specified for each type of solid. If the units conversion
factor is set to 1.157e-5, then these velocities are input in
units of m/day. These velocities are multiplied internally by
cross-sectional areas and treated as flows that carry solids and
sorbed chemical between segments. Settling velocities are
important components of suspended sediment transport in the
water column. Scour and deposition velocities determine the

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transfer of solids and sorbed chemical between the water column and the sediment bed. Sedimentation velocities represent the rate at which the bed is rising in response to net deposition. (Group D, Record 6, QT, TQ)

Cross-Sectional Areas, m^2-- The interfacial surface area must be specified for adjoining segments where sediment transport occurs. These surface areas are multiplied internally by sediment transport velocities to obtain sediment transport flows.
(Group D, Record 4, BQ, JQ, IQ)

Number of Exchange Fields-- Under dispersion, the user has a choice of up to two exchange fields. To simulate surface water toxicant and solids dispersion, select water column dispersion. To simulate exchange of dissolved toxicants with the bed, the user should also select pore water diffusion. (Group B, Record 1, NRFLD)

Water Column Dispersion, m^3/sec-- Time variable water column dispersion can be specified, as detailed in Chapter 2. (Group B, Record 6, RT, TR; Record 4, A, EL)

Pore Water Diffusion Coefficients, m^2/sec-- Time variable pore water diffusion coefficients can be specified for dissolved toxicant exchange within the bed or between the bed and the water column. If the units conversion factor is set to 1.157e-5, then these coefficients are input in units of m^2/day. Diffusion coefficients are multiplied internally by cross-sectional areas divided by characteristic mixing lengths, and are treated as flows that carry dissolved toxicants between benthic segments and the water column. (Group B, Record 6, RT, TR)

Cross-Sectional Areas, m^2-- The interfacial surface area must be specified for adjoining segments where pore water diffusion occurs. These surface areas are multiplied internally by diffusion coefficients and divided by characteristic mixing lengths to obtain pore water exchange flows. (Group B, Record 4, A)

Characteristic Mixing Lengths, m-- The characteristic mixing length must be specified for adjoining segments where pore water diffusion occurs. The value for a mixing length is typically equal to the average depth of the pore water segments involved in the exchange. These mixing lengths are divided into the product of the diffusion coefficients and cross-sectional areas to obtain pore water exchange flows. (Group B, Record 4, EL)

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Boundary Parameters

This group of parameters includes boundary concentrations, waste loads, and initial conditions. Boundary concentrations must be specified for any segment receiving flow inputs, outputs, or exchanges. Initial conditions includes not only initial concentrations, but also the density and solids transport field for each solid, and the dissolved fraction in each segment.

Boundary Concentrations, mg/L-- At each segment boundary, time variable concentrations must be specified for each toxicant and for each solids type simulated. A boundary segment is characterized by water exchanges from outside the network, including tributary inflows, downstream outflows, and open water dispersive exchanges. (Group E, Record 4, BCT)

Waste Loads, kg/day-- For each point source discharge, time variable toxicant and solids loads can be specified. These loads can represent municipal and industrial wastewater discharges, or urban and agricultural runoff. (Group F.1, Record 4, WKT)

Solids Transport Field-- The transport field associated with total solids or each solids type must be specified under initial conditions. (Group J, Record 1, IFIELD)

Solid Density, g/cm^3-- The average density of the total sediment, or the density of each solids type must be specified. This information is used to compute the porosity of benthic segments. Porosity is a function of sediment concentration and the density of each solids type. (Group J, Record 1, DSED)

Initial Concentrations, mg/L-- Concentrations of toxicant and each solids type in each segment must be specified for the time at which the simulation begins. If the variable benthic volume option is used, the benthic sediment concentrations specified here will remain constant for the entire simulation. (Group J, Record 2, C)

Dissolved Fraction-- The dissolved fraction of each solid in each segment should be set to 0. The dissolved fraction of toxicant will be controlled by the partition coefficient and solids concentrations. (Group J, Record 2, DISSF)

Transformation Parameters

This group of parameters includes spatially variable parameters, constants, and kinetic time functions for the water quality constituents being simulated. None are necessary for sediment transport.

First-Order Degradation-- There are two options to input first-order toxicant degradation:

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Option 1: Total Lumped First Order Decay

    The use of the simple lumped first-order decay rate requires the user to input a decay rate constant for the chemical for each model segment. If a simple lumped first order rate is specified for a particular chemical, the chemical will decay at that rate regardless of other input. For example, if both a lumped decay rate and either a simple first order or second order transformation rate are specified, the simple first or second order rates will only be used if the lumped rate is zero. (Group G, Record 4, PARAM(ISEG, 16), PARAM(ISEG, 17), PARAM(ISEG, 18)

Option 2: Individual First Order Transformation

    The use of the simple first-order transformation rate requires the user to input a global rate constant (day^{-1}) or half-life (day) for each particular processes simulated. If a simple first-order transformation rate is specified, it will take priority over other input for that particular processes. For example, if both a first order and a second order transformation rate constant is specified, the second order rate will only be used if the first-order rate constant is zero. First-order transformation rate constant numbers are given in Table 6.3. (Group H, Record 4, CONST(i))

    Partition Coefficients-- TOXI5 allows the input of either a single constant partition coefficient, or a set of spatially-variable partition coefficients:

Option 1: Constant Partition Coefficient.

    This option allows the user to directly input constant partition coefficients that apply over the entire model network. These partition coefficients are input using the set of constants PIXC, in units of L_w/kg_s (**not** in log units). If only one chemical and one solids type is being simulated, then the partition coefficient can be input by specifying a value for Constant 111 -- PIXC(1,1). All other partitioning information should be omitted (i.e. - LKOW, LKOC, and FOC).

    If three chemicals are being simulated, the user may specify values for their partition coefficients to solids 1 using three separate PIXC values -- Constants 111, 711, and

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Table 6.3. TOXI5 Rate Coefficients for Simple Reactions.

Constant	C_1	C_2	C_3	REACTION
KV, day^{-1}	140	740	1340	Volatilization
THV, day	145?	745?	1345?	
KBW, day^{-1}	141	741	1341	Water Column Biodegradation
THBW, day	143	743	1343	
KBS, day^{-1}	142	742	1342	Benthic Biodegradation
THBS, day	144	744	1344	
KHOH, day^{-1}	181	781	1381	Alkaline Hydrolysis
THHOH, day	252	852	1452	
KHN, day^{-1}	182	782	1382	Neutral Hydrolysis
THHN, day	253	853	1453	
KHH, day^{-1}	183	783	1383	Acid Hydrolysis
THHH, day	254	854	1454	
KO, day^{-1}	256	856	1456	Oxidation
THO, day	257	857	1457	
KF, day^{-1}	287	887	1482	Photolysis
THF, day	289	889	1489	
KE, day^{-1}	571	1171	1771	Extra Reaction
THE, day	572	1172	1772	

1311, respectively.

If multiple solids types are being simulated, then separate partition coefficients may be input for each of the three solids types. The constant partition coefficients for chemical 1 to solids type 2 and 3 can be input by specifying appropriate PIXC values for Constants 116 and 121, respectively.

Constant numbers for partitioning of chemical i to solid j are summarized in Table 6.4.

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Table 6.4 Constant Partition
Coefficients PIXC

	C_1	C_2	C_3
Solids 1	111	711	1311
Solids 2	116	716	1316
Solids 3	121	721	1321

Option 2: Spatially-Variable Partition Coefficients.

This option allows the user to directly input spatially-variable partition coefficients for chemical 1. These partition coefficients are input using the parameter FOC, in units of L_w/kg_s (**not** in log units). If only one chemical and one solids type is being simulated, then the partition coefficients can be input by specifying segment-variable values for Parameter 7 -- FOC(ISEG,1). Constant 101, LKOC, should be given a small nonzero value, such as 1.0e-20.

If multiple solids types are being simulated, then separate sets of partition coefficients may be input for each of the three solids types. The constant partition coefficients for chemical 1 to solids type 2 and 3 can be input by specifying segment-variable values for FOC(ISEG,2) and FOC(ISEG,3) -- Parameters 8 and 9, respectively.

Reaction Yields-- The input yield constants that may be specified are $YHOH_{ci}$, YHN_{ci}, YHH_{ci}, YBW_{ci}, YBS_{ci}, YF_{ci}, YOX_{ci}, and YE_{ci} where c is the chemical reactant (1, 2, or 3) and i is the chemical product (1, 2, or 3) in units of mg_c/mg_i. Yield coefficients may be provided for all possible combinations of chemicals and for the reactions, as listed in Table 6.5.

Table 6.5 TOXI5 Yield Constants for Chemical Reactions.

FROM	to C_1	to C_2	to C_3	REACTION
C_1		176	177	Water Column Biodegradation YBW_{ci}
C_2	776		777	
C_3	1376	1377		
C_1		178	179	Benthic Biodegradation YBS_{ci}
C_2	778		779	
C_3	1378	1379		
C_1		246	247	Alkaline Hydrolysis $YHOH_{ci}$
C_2	846		847	
C_3	1446	1447		
C_1		248	249	Neutral Hydrolysis YHN_{ci}
C_2	848		849	
C_3	1448	1449		
C_1		250	251	Acid Hydrolysis YHH_{ci}
C_2	850		851	
C_3	1450	1451		
C_1		281	282	Oxidation YOX_{ci}
C_2	881		882	
C_3	1481	1482		
C_1		566	567	Photolysis YF_{ci}
C_2	1166		1167	
C_3	1766	1767		
C_1		596	597	Extra Reaction YE_{ci}
C_2	1196		1197	
C_3	1796	1797		

CHAPTER 7
ORGANIC CHEMICALS

7.1 MODEL DESCRIPTION

Introduction

In modern technological societies, synthetic organic chemicals have been manufactured, used, and disposed of in large quantities. The large number and variety of organic compounds include such major classes as pesticides, polychlorinated biphenyls, halogenated aliphatic hydrocarbons, halogenated ethers, monocyclic aromatics, phthalate esters, polycyclic aromatic hydrocarbons, and nitrosamines. Organic chemicals can enter the aquatic environment by various pathways, including point source waste discharges and nonpoint source runoff. Some of these organic chemicals can cause toxicity to aquatic organisms, or bioconcentrate through the food chain. Humans may be affected by ingesting contaminated water or fish. Criteria for protecting human health and indiginous aquatic communities have been promulgated for some organic chemicals.

Several environmental processes can affect the transport and fate of organic chemicals in the aquatic environment. The most important include physical processes such as hydrophobic sorption, volatilization, and sedimentation; chemical processes such as ionization, precipitation, dissolution, hydrolysis, photolysis, oxidation and reduction; and biological processes such as biodegradation and bioconcentration. WASP5 explicitly handles most of these, excluding only reduction and precipitation-dissolution. If the kinetics of these reactions are described by the user, they also can be included as an extra reaction.

WASP5 allows the simulation of a variety of processes that may affect toxic chemicals. However, WASP5 makes relatively few assumptions concerning the particular processes affecting the transport, transformations, and kinetic reactions. The model is designed to provide a broad framework applicable to many environmental problems and to allow the user to match the model complexity with the requirements of the problem.

Although the potential amount and variety of data used by WASP5 is large, data requirements for any particular simulation can be quite small. Most often, organic chemical simulations use only sorption and one or two transformation processes that significantly affect a particular chemical. What is gained by the second-order process functions and resulting input data

burden is the ability to extrapolate more confidently to future conditions. The user must determine the optimum amount of empirical calibration and process specification for each application.

Overview of WASP5 Organic Chemicals

Organic chemicals and associated solids are simulated using the TOXI5 program. TOXI5 simulates the transport and transformation of one to three chemicals and one to three types of particulate material (solids classes, Table 7.1). The three chemicals may be independent or they may be linked with reaction yields, such as a parent compound-daughter product sequence. The simulation of solids is described in Chapter 3. The simulation of organic chemicals is described below. Organic chemical process routines are closely derived from the Exposure Analysis Modeling System EXAMS (Burns, et al., 1982; Burns and Cline, 1985).

Table 7.1 TOXI5 State Variables for Toxicants

SYSTEM	VARIABLE
1	CHEMICAL 1
2	SOLIDS 1
3	SOLIDS 2
4	SOLIDS 3
5	CHEMICAL 2
6	CHEMICAL 3

Each organic chemical may exist as a neutral compound and up to four ionic species. The neutral and ionic species can exist in five phases: dissolved, sorbed to dissolved organic carbon (DOC), and sorbed to each of the up to three types of solids (Figure 7.1). Local equilibrium is assumed so that the distribution of the chemical between each of the species and phases is defined by distribution or partition coefficients. In this fashion, the concentration of any specie in any phase can be calculated from the total chemical concentration. Therefore, only a single state variable (WASP system) representing total concentration is required for each chemical. The model, then, is composed of up to six systems -- three chemicals and three solids -- for which the general WASP5 mass balance equation is solved.

There are often other factors that may influence the transport and transformations of the chemicals simulated. For example, water temperature affects reaction kinetics, sorption may also occur onto dissolved organic carbon, and pH can affect ionization and hydrolysis reactions. These concentrations or

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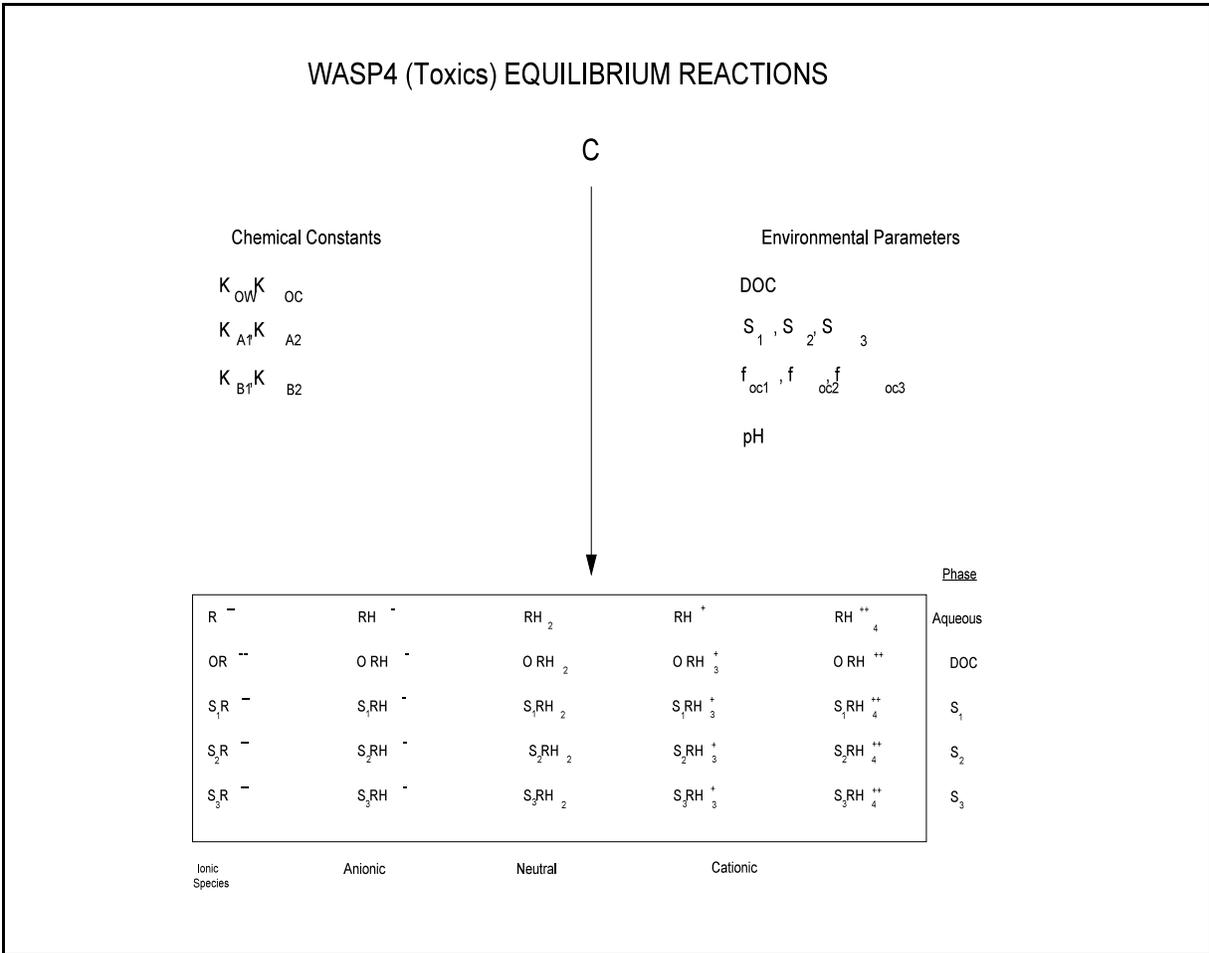
Figure 7.1   Equilibrium speciation.

properties are included in TOXI5 through the use of model
parameters and time functions. They are specified to the model
(described) rather than simulated. They may be varied over
space (e.g. between model segments) and/or over time.   Examples
of the concentrations or properties that are described to the
model are provided in Table 7.2.

TOXI5 Reactions and Transformations

In an aquatic environment, an organic chemical may be
transferred between phases and may be degraded by any of a

Table 7.2 Examples of TOXI5 Parameters and Time Functions.

Parameter or Time Function	Units	Time Variable	Affected Kinetic Processes
Water Temperature	°C	Y	All
Dissolved Organic Carbon	mg/L	N	Sorption, Photolysis
Fraction Organic Carbon	none	N	Sorption
pH	–	Y	Hydrolysis
Oxidant Concentration	moles/L	N	Oxidation
Bacterial Concentration	variable	Y	Biodegradation
Extra Property	variable	N	Extra 2nd Order Reaction
Wind Velocity	m/sec	Y	Volatilization
Air Temperature	°C	Y	Volatilization
Chlorophyll *a* Concentration	mg/L	Y	Photolysis
Normalized Light Intensity	None	Y	Photolysis (Option 2 Only)

number of chemical and biological processes. Ionization may speciate the chemical into multiple forms. Transfer processes defined in the model include sorption and volatilization. Defined transformation processes include biodegradation, hydrolysis, photolysis, and chemical oxidation. Sorption and ionization are treated as equilibrium reactions. All other

processes are described by rate equations. Rate equations may
be quantified by first-order constants or by second-order
chemical specific constants and environment-specific parameters
that may vary in space and time.

WASP5 uses a mass balance equation to calculate sediment
and chemical mass and concentrations for every segment in a
specialized network that may include surface water, underlying
water, surface bed, and underlying bed. In a simulation,
sediment is advected and dispersed among water segments, settles
to and erodes from benthic segments, and moves between benthic
segments through net sedimentation, erosion, or bed load.
Chapter 3 details the TOXI5 sediment transport processes.

In a simulation, the chemical can undergo several physical
or chemical transformations. It is convenient to group these
into fast and slow reactions. Fast reactions have
characteristic reaction times that are much faster than, or on
the same order as the model time step, and are handled with the
assumption of local equilibrium. Slow reactions have
characteristic reaction times much longer than the model time
step. These are handled with the assumption of local first
order kinetics using a lumped rate constant specified by the
user, or calculated internally, based on summation of several
process rates, some of which are second-order. Thus, the
effective first order decay rate can vary with time, and space,
and is recalculated as often as necessary throughout a
simulation.

The chemical is advected and dispersed among water
segments, and exchanged with surficial benthic segments by
dispersive mixing. Sorbed chemical settles through water column
segments and deposits to or erodes from surficial benthic
segments. Within the bed, dissolved chemical migrates downward
or upward through percolation and pore water diffusion. Sorbed
chemical migrates downward or upward through net sedimentation
or erosion. Both rate constants and equilibrium coefficients
must be estimated in most toxic chemical studies. Although
these can be calculated internally from chemical properties and
local environmental characteristics, site-specific calibration
or testing is desirable.

Some limitations should be kept in mind when applying
TOXI5. First, chemical concentrations should be near trace
levels, i.e., below half the solubility or 10^{-5} molar. At higher
concentrations, the assumptions of linear partitioning and
transformation begin to break down. Chemical density may become
important, particularly near the source, such as in a spill.
Large concentrations can affect key environmental
characteristics, such as pH or bacterial populations, thus

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altering transformation rates. TOXI5 does not include such feedback phenomena.

7.2 MODEL IMPLEMENTATION

<u>Introduction</u>

To simulate organic chemicals with WASP5, use the preprocessor or text editor to create a TOXI5 input file. The model input dataset and the input parameters will be similar to those for the conservative tracer model as described in Chapter 2. To those basic parameters, the user will add benthic segments, solids transport rates, and transformation parameters. During the simulation, solids and organic chemicals will be transported both by the water column advection and dispersion rates and by these solids transport rates.

In WASP5, solids transport rates in the water column and the bed are input via up to three solids transport fields, as described in Chapter 3. The transport of the particulate fraction of organic chemicals follows the solids flows. The user must specify the dissolved fraction (i.e. 0.0) and the solids transport field for each simulated solid under initial conditions. To simulate total solids, solids 1 must be used.

<u>Model Input Parameters</u>

Input parameters are prepared for WASP5 in four major sections of the preprocessor -- environment, transport, boundaries, and transformation. The organic chemical input parameters comprising the first three sections are identical to those in the simple toxicant model. The user is referred to Section 6.2 for a summary of these input parameters. This section, and the rest of this chapter, describes the organic chemical reaction parameters.

Transformation Parameters

This group of parameters includes spatially variable parameters, constants, and kinetic time functions for the water quality constituents being simulated. The organic chemical reactions and model input parameters are described in individual sections below. Because water temperature can affect every chemical reaction, it is described here.

<u>Water Temperature, °C</u>-- Water temperature can vary in space and time, affecting the rates of all chemical reactions. Time and segment variable water temperatures can be specified using the parameters TEMP and TMPFN, and the time functions TEMPN(1-4). If temperatures are to remain constant in time, then the user should enter segment temperatures using the parameter TEMP. TMPFN and TEMPN(1-4) should be omitted.

If the user wants to enter time-variable temperatures, then values for the parameter TEMP should be set to 1.0. The parameter TMPFN indicates which temperature function will be used by the model for each segment. Values of 1.0, 2.0, 3.0, or 4.0 will call time functions TEMPN(1), TEMPN(2), TEMPN(3), and TEMPN(4), respectively. Water temperatures should then be entered via these time functions as a series of temperature versus time values. The product of TEMP and the selected TEMPN function will give the segment and time specific water temperatures used by TOXI5.

TEMP and TMPFN are identified in TOXI5 as parameters 3 and 2, respectively. TEMPN(1-4) are identified in TOXI5 as time functions 1-4. (Group G, Record 4, PARAM(I,3), PARAM(I,2); Group I, Record 2, VALT(1-4,K))

Notation

In TOXI5, it is convenient to define concentration related symbols as in Table 7.3. Please note that in the general development of the equations in the sections below, subscripts "i" and "j" are sometimes omitted for convenience.

7.3 IONIZATION

Introduction

Ionization is the dissociation of a chemical into multiple charged species. In an aquatic environment some chemicals may occur only in their neutral form while others may react with water molecules to form positively (cationic) or negatively (anionic) charged ions. These reactions are rapid and are generally assumed to be at (local) equilibrium. At equilibrium, the distribution of chemicals between the neutral and the ionized species is controlled by the pH and temperature of the water and the ionization constants.

Ionization can be important because of the different toxicological and chemical properties of the neutral and ionized species. For example, in some cases only the neutral form of the chemical may react or be transported through biotic membranes resulting in toxicity. As a result, it is often necessary to compute the distribution of chemicals among ionic forms as well as to allow them to react or transform at different rates. For example, in TOXI5 different sorption and

Table 7.3 Concentration Related Symbols Used in Mathematical Equations.

Symbol	Definition	Units
C_{ij}	Concentration of total chemical i in segment j.	mg_c/L
C_{wij}	Concentration of dissolved chemical i in segment j.	mg_c/L
C'_{wij}	Concentration of dissolved chemical i in water in segment j; C_{wij}/n_j	mg_c/L_w
C_{sij}	Concentration of sorbed chemical i on sediment type "s" in segment j.	mg_c/L
C'_{sij}	Concentration of sorbed chemical i on sediment type "s" in segment j; C_{sij}/M_{sij}	mg_c/kg_s
C_{Bj}	Concentration of DOC-sorbed chemical i in segment j.	mg_c/L
C'_{Bj}	Concentration of DOC-sorbed chemical i in segment j; C_{Bj}/B_j	mg_c/kg_B
m_{sj}	Concentration of sediment type "s" in segment j.	mg_s/L
M_{sj}	Concentration of sediment type "s" in segment j; $m_j \cdot 10^{-6}$	kg_s/L
M'_{sj}	Concentration of sediment type "s" in water in segment j; M_{sj}/n	kg_s/L_w
B_j	Concentration of DOC in segment j.	kg_B/L
B'_j	Concentration of DOC in water in segment j; B_j/n	kg_B/L_w
n_j	Porosity or volume water per volume segment j.	L_w/L
K_{psij}	Partition coefficient of chemical i on sediment type "s" in segment j.	L_w/kg_s
K_{pBij}	Partition coefficient of chemical i on DOC in segment j.	L_w/kg_B

reaction constants (e.g. for hydrolysis, biodegradation, photolysis, etc.) may be specified for each ionic form of the chemical.

Overview of TOXI5 Ionization Reactions

In TOXI5, each of the three possible chemicals being simulated may occur in up to five forms, including 1) the

neutral molecule, 2) singly charged cations, 3) doubly charged cations, 4) singly charged anions, and 5) doubly charged anions. Each of the neutral or ionic species may also occur in the dissolved phase or sorbed to dissolved organic carbon (DOC) or the three solids types. A total of 25 forms of each chemical may occur. Each chemical form may have different reactivities as reflected by different degradation or transformation rates. TOXI5 makes no direct assumptions as to the formation of the ionic species or their reactivity. The formation is controlled by the user by specification of model input.

A chemical being modeled by TOXI5 is presumed to exist as neutral molecules that may, or may not, react with water molecules to form singly and, possibly, doubly charged cations and anions. To illustrate, an organic acid (A^{--}) may react with water as described by:

$$AH_2 + H_2O \rightleftharpoons AH_3^+ + OH^- \qquad\qquad\qquad 7.1$$

$$AH_3^+ + H_2O \rightleftharpoons AH_4^{++} + OH^- \qquad\qquad\qquad 7.2$$

$$AH_2 + H_2O \rightleftharpoons AH^- + H_3O^+ \qquad\qquad\qquad 7.3$$

$$AH^- + H_2O \rightleftharpoons A^{--} + H_3O^+ \qquad\qquad\qquad 7.4$$
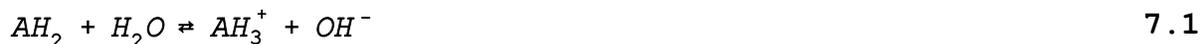
so that the chemical may exist in from one to a maximum of five species simultaneously (A^{--}, AH^-, AH_2, AH_3^+, AH_4^{++}). The law of mass action can be used to describe local chemical equilibrium for each of these reactions:

$$K_{b_1} = \frac{[AH_3^+][OH^-]}{[AH_2]} \qquad\qquad\qquad 7.5$$

$$K_{b_2} = \frac{[AH_4^{++}][OH^-]}{[AH_3^+]} \qquad\qquad\qquad 7.6$$

$$K_{a_1} = \frac{[AH^-][H^+]}{[AH_2]} \qquad\qquad\qquad 7.7$$

$$K_{a_2} = \frac{[A^{--}][H^+]}{[AH^-]} \qquad\qquad\qquad 7.8$$

where K is the equilibrium constant for the formation of the acid (K_{ai}), or anionic species, or the base (K_{bi}) or cationic species.

The total concentration of the particular chemical is the sum of the concentration of each of these forms, as given by

$$C = AH_2 + AH_3^+ + AH_4^{++} + AH^- + A^{--} \qquad\qquad 7.9$$

which may be combined with the law of mass action to form

$$C = AH_2 \left[\frac{K_{b1}}{[OH^-]} + \frac{K_{b1}K_{b2}}{[OH^-]^2} + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} \right] \qquad 7.10$$

By definition, $[H^+] = 10^{-pH}$ and $[OH^-] = 10^{14-pH}$; the bracketed term in equation 7.10, denoted D, can be written

$$D = \left[\frac{K_{b1}}{10^{pH-14}} + \frac{K_{b1}K_{b2}}{(10^{pH-14})^2} + \frac{K_{a1}}{10^{-pH}} + \frac{K_{a1}K_{a2}}{(10^{-pH})^2} \right] \qquad 7.11$$

Equations 7.10 and 7.11 may be combined with equations 7.5 – 7.8 and solved for the fraction of the total chemical f^k occurring in each of the chemical species k, given the total chemical concentration, the pH, and the equilibrium constants:

$$f^0 = \frac{1}{D} \qquad\qquad\qquad 7.12$$

$$f^+ = \frac{K_{b1}/10^{pH-14}}{D} \qquad\qquad\qquad 7.13$$

$$f^{++} = \frac{K_{b1}K_{b2}/(10^{pH-14})^2}{D}$$

7.14

$$f^{-} = \frac{K_{a1}/10^{-pH}}{D}$$

7.15

$$f^{--} = \frac{K_{a1}K_{a2}/(10^{-pH})^2}{D}$$

7.16

The rates of chemical reactions may also vary with temperature so that the equilibrium constants are a function of temperature. The functional dependence of these constants on temperature may be described by the Van't Hoff equation:

$$\frac{d\ln K_i}{dT_K} = \frac{E_{ai}}{RT_K^2}$$

7.17

or in its integrated form:

$$\log K_i(T_K) = \log K_i(T_{Ri}) + \frac{E_{ai}}{2.303\ R}\cdot\left[\frac{T_K - T_{Ri}}{T_K T_{Ri}}\right]$$

7.18

$$= -pK_{ai} + \frac{E_{ai}}{2.303\ R}\cdot\left[\frac{T_K - T_{Ri}}{T_k T_{Ri}}\right]$$

here

K_i	=	equilibrium constant
A_i	=	frequency factor
E_{ai}	=	standard enthalpy change for reaction, kcal/mole
R	=	the universal gas constant, kcal/mole °K
T_K	=	water temperature, °K.
T_{Ri}	=	reference temperature at which input ionization reaction constant was observed, °K.

<u>Implementation</u>

The data required for the implementation of ionization in TOXI5 are summarized in Table 7.4. They include first identifying whether or not a particular ionic specie is to be included in the simulation and then, if a particular specie is selected, the information necessary to compute its formation. For example, to compute a particular ionic specie, it is necessary to input the pK (negative log) of the equilibrium constant for the formation of the acid and/or base, and the activation energy used in the Van't Hoff Equation to adjust the equilibrium constant with temperature. If the activation energy is not input, then no temperature correction will occur. If no data are input for ionization, none will occur and the reactions and transformations will be applied to the total or dissolved form of the chemical, as appropriate.

In addition to the constants for the formation of the ionic species, the pH and temperature (if the rate is to be temperature corrected) are required. The pH and temperature are model parameters, which are specified for each model segment. They may be constant or time variable.

Table 7.4 TOXI5 Ionization Data.

Description	Notation	Common Range	S.I. Units
Negative log of hydrogen ion activity [H^+]	pH	5-9	-
Negative log of ionization constants for acid	pK_{ai}	-	-
Negative log of ionization constants for base	pK_{bi}	-	-
Enthalpy change for ionization reactions	E_{ai}	4-8	kcal/mole
Water temperature	T	4-30	°C
Reference temperature	T_{Ri}	20-25	°C

If ionization is specified in input, separate transformation and reaction rates may be specified for each ionic specie. For example, where necessary, different sorption, biodegradation, hydrolysis, oxidation, and photolysis constants may be specified for each ionic specie, providing considerable flexibility in the model application.

The transformation input parameters for ionization are summarized below. Constant numbers are given in Table 7.5.

<u>Ionization Switches</u>-- The user may choose to simulate ionic species by specifying values of 1.0 for constant SFLG.

<u>Ionization Constants</u>-- For each ionic specie being simulated, the user should provide a value for the negative log of the frequency factor in the Van't Hoff equation using

Table 7.5   TOXI5 Constants for Ionization Reactions.

IONIC SPECIE "i"	C_1	C_2	C_3	INPUT VARIABLE
+	85	685	1285	Species Flag, $SFLG_i$
++	86	686	1286	
–	87	687	1287	
––	88	688	1288	
+	91	691	1291	Negative Log of Ionization Constant, PKA_i
++	92	692	1292	
–	93	693	1293	
––	94	694	1294	
+	95	695	1295	Ionization Reaction Enthalpy, $EPKA_i$, kcal/mole
++	96	696	1296	
–	97	697	1297	
––	98	698	1298	
All	99	699	1299	Reference Temp TREFI, °C

constant PKA. If the activation energy is 0, then this is
equivalent to the pK_a or pK_b.

    <u>Reaction Enthalpy, kcal/mole</u>-- To simulate temperature
dependence for ionization, the user can specify the standard
enthalpy change of the dissociation reaction using constant
EPKA. Higher reaction enthalpies cause more temperature
dependence.

    <u>pH</u>-- The user may specify segment and time variable
bacterial concentrations using parameter 11, PH, and time
funcions 10 and 11, PHNW and PHNS. If pH is to remain constant
in time, the user should enter segment mean values using
parameter PH. PHNW and PHNS should be omitted.

    The user may enter time-variable water column and benthic
pH values via time functions PHNW and PHNS, respectively, as a
series of concentration versus time values. Parameter PH will
then represent the ratio of each segment pH to the time function
values. The product of PH and the PHNW or PHNS function gives
the segment and time specific pH values used by TOXI5. (Group
G, Record 4, PARAM(I,11); Group I, Record 2, VALT(10,K),
VALT(11,K))

7.4   EQUILIBRIUM SORPTION

<u>Introduction</u>

    Sorption is the bonding of dissolved chemicals onto solid
phases, such as benthic and suspended sediment, biological
material, and sometime dissolved or colloidal organic material.
Sorption can be important in controlling both the environmental
fate and the toxicity of chemicals. Sorption may cause the
chemical to accumulate in bed sediment or bioconcentrate in
fish. Sorption may retard such reactions as volatilization and
base hydrolysis, or enhance other reactions including photolysis
and acid-catalyzed hydrolysis.

    Sorption reactions are usually fast relative to other
environmental processes, and equilibrium may be assumed. For
environmentally relevant concentrations (less than 10^{-5} M or one-
half water solubility), equilibrium sorption is linear with
dissolved chemical concentration (Karickhoff, 1984) or:

$$C'_s = K_{ps} \cdot C'_w \qquad\qquad\qquad 7.19$$

At equilibrium, then, the distribution among the phases is controlled by the partition coefficients K_{ps}. The total mass of chemical in each phase is controlled by K_{ps} and the amount of solid phase present (including any DOC phase).

In addition to the assumption of instantaneous equilibrium, implicit in the use of equation 7.19 is the assumption of reversibility. Laboratory data for very hydrophobic chemicals suggest, however, that a hysteresis exists, with desorption being a much slower process than adsorption. Karickhoff suggests that this effect may be the result of intraparticle kinetics in which the chemical is slowly incorporated into components of the sorbant. This phenomenon is not well understood and no quantitative modeling framework is available to characterize it.

Overview of TOXI5 Sorption Reactions

Dissolved chemical in water column and benthic segments interacts with sediment particles and dissolved organic carbon to form five phases-- dissolved, DOC-sorbed, and sediment-sorbed (three sediment types "s"). The reactions can be written with respect to unit volume of water:

$$M'_s + C'_w \leftrightarrow C_s/n \qquad\qquad\qquad 7.20$$

$$B' + C'_w \leftrightarrow C_B/n \qquad\qquad\qquad 7.21$$

where n is the porosity (volume of water divided by total volume),

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The forward reaction is sorption and the backward reaction is desorption. These reactions are usually fast in comparison with the model time step, and can be considered in local equilibrium. The phase concentrations C_w, C_s, and C_B are governed by the equilibrium partition coefficients K_{ps0} and K_{pB} (L/kg):

$$K_{ps0} = \frac{C_s/n}{M_s'\ C_w'} = \frac{C_s'}{C_w'} \qquad\qquad 7.22$$

$$K_{pB} = \frac{C_B/n}{B'\ C_w'} = \frac{C_B'}{C_w'} \qquad\qquad 7.23$$

These equations give the linear form of the Freundlich isotherm, applicable when sorption sites on sediment and DOC are plentiful:

$$C_s' = K_{ps}\ C_w' \qquad\qquad 7.24$$

$$C_B' = K_{pB}\ C_w' \qquad\qquad 7.25$$

The total chemical concentration is the sum of the five phase concentrations

$$C = C_w'\ n + \sum_s C_s'\ M_s + C_B'\ B \qquad\qquad 7.26$$

Substituting in equations 7.24 and 7.25, factoring, and rearranging terms gives the dissolved fraction f_D:

$$f_D = \frac{C'_w \, n}{C} = \frac{n}{n + K_{pB} \cdot B + \sum\limits_{s} K_{ps} \cdot M_s}$$ **7.27**

Similarly, the sediment-sorbed and DOC-sorbed fractions are

$$f_s = \frac{C'_s \, M_s}{C} = \frac{K_{ps} \cdot M_s}{n + K_{pB} \cdot B + \sum\limits_{s} K_{ps} \cdot M_s}$$ **7.28**

$$f_B = \frac{C'_B \, B}{C} = \frac{K_{pB} \cdot B}{n + K_{pB} \cdot B + \sum\limits_{s} K_{ps} \cdot M_s}$$ **7.29**

These fractions are determined in time and space throughout a simulation from the partition coefficients, internally calculated porosities, simulated sediment concentrations, and specified DOC concentrations. Given the total concentration and the five phase fractions, the dissolved, sorbed, and biosorbed concentrations are uniquely determined:

$$C_w = C \cdot f_D$$ **7.30**

$$C_s = C \cdot f_s$$ **7.31**

$$C_B = C \cdot f_B$$ **7.32**

These five concentrations have units of mg/L, and can be expressed as concentrations within each phase:

$$C'_w = C_w/n \qquad\qquad\qquad\qquad\qquad \textbf{7.33}$$

$$C'_s = C_s/M_s \qquad\qquad\qquad\qquad\qquad \textbf{7.34}$$

$$C'_B = C_B/B \qquad\qquad\qquad\qquad\qquad \textbf{7.35}$$

These concentrations have units of mg/L_w, mg/kg_s, and mg/kg_B, respectively.

In some cases, such as near discharges, the user may have to alter input partition coefficients to describe the effect of incomplete sorption. As guidance, Karickhoff and Morris (1985) found that typical sorption reaction times are related to the partition coefficient:

$$k_d^{-1} = 0.03 \; k_{ps} \qquad\qquad\qquad\qquad\qquad \textbf{7.36}$$

where k_d^{-1} is the desorption rate constant, hr^{-1}.

Thus, compounds with high, medium, and low K_{ow}'s of 10^5, 10^3, and 10 sorbing onto 2% organic sediment should have reaction times of a day, a half hour, and seconds. Given that time to equilibrium is roughly three times the reaction time, the three compounds should reach equilibrium within 3 days, 1 hour, and 30 minutes.

Computation of Partition Coefficients

Values for the partition coefficients can be obtained from laboratory experiments. For organic chemicals, lab studies have shown that the partition coefficient is related to the hydrophobicity of the chemical and the organic matter content of

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the sediment. TOXI5 provides several optional methods for the
description or computation of the partition coefficients. These
options are identified by the data input, as described below.

Option 1. Measured Partition Coefficients.

     This option allows the user to directly input a partition
coefficient. Separate partition coefficients may be input for
each of the three solids types. The partition coefficient is
input in units of L_w/kg_s (**not** in log units).

Option 2. Input of Organic Carbon Partition Coefficient.

     Normalization of the partition coefficient by the organic-
carbon content of the sediment has been shown to yield a
coefficient, K_{oc} (the organic carbon partition coefficient), that
is relatively independent of other sediment characteristics or
geographic origin. Many organic pollutants of current interest
are non-polar, hydrophobic compounds whose partition
coefficients correlate quite well with the organic fraction of
the sediment. Rao and Davidson (1980) and Karickhoff et al.
(1979) have developed empirical expressions relating equilibrium
coefficients to laboratory measurements leading to fairly
reliable means of estimating appropriate values. The
correlations used in TOXI5 are

$$K_{ps0} = f_{ocs} \ K_{oc} \qquad\qquad\qquad\qquad 7.37$$

$$K_{pB} = 1.0 \ K_{oc} \qquad\qquad\qquad\qquad 7.38$$

where:

     K_{oc} =   organic carbon partition coefficient, L_w/kg_{oc}

     f_{ocs} =   organic carbon fraction of sediment

1.0   =   organic carbon fraction of DOC

Option 3.   Computation of the Organic Carbon Partition
Coefficient.

     Correlation of K_{oc} with the water solubility of the chemical
or the octonal/water partition coefficient of the chemical has
yielded successful predictive tools for incorporating the
hydrophobicity of the chemical in an estimate of its
partitioning. If no log K_{oc} values are available, one is
generated internally using the following correlation with the
octanol-water partition coefficient K_{ow} (L_w/L_{oct}):

  $$\log K_{oc} = a_o + a_1 \log K_{ow} \hspace{4cm} 7.39$$

where a_o and a_1 are typically considered to be log 0.6 and 1.0,
respectively. Once the value of K_{oc} is determined, the
computation of the partition coefficient proceeds as in Option
2.

Option 4.   Computation of Solids Dependant Partitioning.

     The value of the partition coefficient is dependent on
numerous factors in addition to the fraction organic carbon of
the sorbing particles. Of these, perhaps the most potentially
significant and the most controversial is the effect of particle
concentration, which was first presented by O'Connor and
Connolly (1980). Based on empirical evidence, O'Connor and
Connolly   concluded that the partition coefficient was
inversely related to the solids concentration. Much research
has been conducted to prove or disprove this finding. At
present, the issue remains contentious. A particle interaction
model has been proposed (Di Toro, 1985) which describes the
effects of particle concentration. This model was shown to be
in conformity with observations for a large set of
adsorption-desorption data. At present, this should be
considered an empirical relationship. The equation defining
partition coefficient is:

$$K_{ps} = \frac{K_{ps0}}{1 + M_s \, K_{ps0}/\nu_x}$$

7.40

where:

K_{ps0} = limiting partition coefficient with no particle interaction ($f_{ocs} \, K_{oc}$ for neutral organic chemicals)

M_s = solids concentration, kg/L

ν_x = ratio of adsorption to particle-induced desorption rate

Di Toro found that ν_x was of order 1 over a broad range of chemical and solids types. This formulation has been included in TOXI5. If ν_x is specified to be 1.0, then TOXI5 will predict a maximum particulate fraction in the water column of 0.5 for all hydrophobic chemicals ($K_{ps0}M_s > 10$).

Implementation

TOXI5 data specifications for sorption are summarized in Table 7.6. For each chemical modeled, up to 20 partition coefficients are defined representing the five species of chemical (neutral plus four ionic) and the four sorbants (DOC and three types of solids). Normally, only a subset of these would be used, as defined by those species and solids being modeled. Sorption of the neutral chemical to DOC and the solids is defined by the f_{oc} of the sorbant (assumed to be 1 for DOC), the octanol-water partition coefficient of the chemical (K_{ow}), the user defined relationship between K_{ow} and K_{oc}, and the particle interaction parameter ν_x values for each species. The input ionic species partition coefficients are used as the limiting partition coefficients in equation 7.40. Constant numbers for the different coefficient options are given in Table 7.7.

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Option 1: Measured Partition Coefficients.

    For each chemical simulated, separate partition coefficients may be entered for sorption of the neutral molecule and up to 4 ionic species onto each of the three possible solids types and DOC. The partition coefficient is input in units of L_w/kg_s (**not** in log units). If a partition coefficient is

Table 7.6 TOXI5 Sorption Data.

Description	Notation	Common Range	S.I. Units
Suspended sediment concentration	m_s	10-100	mg/L
Benthic sediment concentration	M_B	0.5-2	kg/L
Dissolved organic carbon	DOC, B	0-10	mg/L
Partition coefficient, phase i	K_{pi}	$10^{-1}-10^5$	L/kg
Lumped metal distribution coefficient	K_D	10^0-10^5	L/kg
Octanol-water partition coefficient	K_{ow}	10^0-10^6	-
Organic carbon fraction, phase i	f_{oci}	0.005-0.5	-
Particle interaction parameter	x	$1-10^{12}$	-

specified it will be used regardless. The user is referred to Chapter 6 for details on directly specifying partition coefficients.

    <u>Solids Partition Coefficient, L/kg</u>-- The user may directly specify partition coefficients to solids using constant PIXC. Constant numbers for sorption of the neutral molecule are given in Table 7.7. Constant numbers for sorption of ionic species are given in Part B of this document.

DOC Partition Coefficient-- The user may specify partition coefficients for sorption of ionic species to DOC using constant PIDOC. Constant numbers are given in Part B of this document. For sorption of the neutral molecule, the organic carbon partition coefficient is used.

Table 7.7 TOXI5 Constants for Sorption Reactions

VARIABLE	C_1	C_2	C_3	DEFINITION
LKOW	**84**	**684**	**1284**	Log_{10} octanol-water partition coefficient
LKOC	**101**	**701**	**1301**	Log_{10} organic carbon partition coefficient
A0	**102**	**702**	**1302**	Intercept in the K_{ow} - K_{oc} correlation
A1	**103**	**703**	**1303**	Slope in the K_{ow} - K_{oc} correlation
NUX_1	**106**	**706**	**1306**	Solids dependent partitioning parameter
$PIXC_{1,1}$	**111**	**711**	**1311**	Solids independent (limiting) partition coefficient to solids 1
$PIXC_{2,1}$	**116**	**716**	**1316**	Solids independent (limiting) partition coefficient to solids 2
$PIXC_{3,1}$	**121**	**721**	**1321**	Solids independent (limiting) partition coefficient to solids 3

Option 2: Input of Organic Carbon Partition Coefficient.

Under this option the user inputs the **log** (base 10) of the organic carbon partition coefficient (K_{oc}). In addition, the user should also input the fraction organic carbon for each of the solids types simulated. The fraction organic carbon for dissolved organic carbon is assumed to be 1.0. The fraction

organic carbon and dissolved organic carbon concentration are
model parameters, which may be specified for each model segment.
If a value for the partition coefficient (K_p, Option 1) is
input, then K_{oc} will not be used.

Organic Carbon Partition Coefficient, L/kg-- The user may
specify the $\log_{10}$ of the organic carbon partition coefficient
using constant LKOC. Constant numbers are given in Table 7.7.

Fraction Organic Carbon-- The user should specify the
segment variable fraction organic carbon for each solids type
simulated using parameters FOC(I,1), FOC(I,2), and FOC(I,3).
Parameter numbers for solids 1, 2, and 3 are 7, 8, and 9,
respectively.

Dissolved Organic Carbon, mg/L-- The user may specify
segment variable dissolved organic carbon concentrations using
parameter 6, DOC.

Option 3: Computation of the Organic Carbon Partition
Coefficient.

Under this option, the user allows the model to compute the
K_{oc} from a specified octanol water partition coefficient (K_{ow}).
The model then computes the K_{oc} using equation 7.39. This option
will not be used if values for the log (K_{oc}) are input.

Octanol-Water Partition Coefficient, L_w/L_o-- The user may
specify the **$\log_{10}$** of the octanol-water partition coefficient
using constant LKOC. Constant numbers are given in Table 7.7.

Correlation Coefficients-- The user should specify
correlation coefficients relating K_{ow} with K_{oc} using constants A0
and A1. A0 and A1 are the intercept and the slope in the
correlation described by equation 7.39. Default values are log
0.6 and 1.0, respectively. If these constants are not entered,
then, the correlation becomes $K_{oc} = 0.6 \, K_{ow}$. Constant numbers
are given in Table 7.7.

Fraction Organic Carbon-- The user should specify the
segment variable fraction organic carbon for each solids type
simulated using parameters FOC(I,1), FOC(I,2), and FOC(I,3).

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Parameter numbers for solids 1, 2, and 3 are 7, 8, and 9, respectively.

Dissolved Organic Carbon, mg/L-- The user may specify segment variable dissolved organic carbon concentrations using parameter 6, DOC.

Option 4: Solids Dependant Partitioning.

The user may include the effect of solids concentration on adsorption by using a value of ν_x of order 1 (see Di Toro, 1985 for more detail). If the user does not provide an input value for ν_x, the default value will eliminate any solids effect on the partition coefficient. Since collision induced desorption is only expected to occur in the water column, solids dependant partitioning is only computed for water column segments (where porosity is greater that 0.99). In addition to the partical interaction parameter, the user must provide for a partition coefficient following option 1, 2, or 3 described above.

Particle Interaction Parameter-- The user may implement solids dependent partitioning by specifying an appropriate value for constant NUX. A value of order 1 will cause the input partition coefficient to decrease with increasing suspended solids, following equation 7.40. Larger values of NUX will reduce the solids effect on partitioning. The default value of 10^{12} effectively eliminates this behavior. Constant numbers for the solids effect on the neutral molecule are given in Table 7.7. Constant numbers for the solids effect on sorption of ionic species are given in Part B of this documentation.

7.5 VOLATILIZATION

Introduction

Volatilization is the movement of chemical across the air-water interface as the dissolved neutral concentration attempts to equilibrate with the gas phase concentration. Equilibrium occurs when the partial pressure exerted by the chemical in solution equals the partial pressure of the chemical in the overlying atmosphere. The rate of exchange is proportional to the gradient between the dissolved concentration and the concentration in the overlying atmosphere and the conductivity across the interface of the two fluids. The conductivity is influenced by both chemical properties (molecular weight, Henry's Law constant) and environmental conditions at the air-water interface (turbulence-controlled by wind speed, current velocity, and water depth).

Overview of TOXI5 Volatilization

The dissolved concentration attempts to equilibrate with the gas phase concentration, as illustrated in Figure 7.2 and given by

$$\frac{\partial C}{\partial t}\Big|_{volat} = \frac{K_v}{D}\left(f_d C - \frac{C_a}{\dfrac{H}{RT_K}}\right) \qquad \textbf{7.41}$$

where

K_v	=	the transfer rate, m/day
D	=	segment depth, m
f_d	=	fraction of the total chemical that is dissolved,
C_a	=	atmospheric concentration, ug/L
R	=	universal gas constant, 8.206×10^{-5} atm-m^3/mole °K
T_K	=	water temperature, °K
H	=	Henry's law coefficient for the air-water partitioning of the chemical, atm-m^3/mole.

$$C_a$$

$$\frac{\partial C_W}{\partial t} = -\frac{k_V}{D}\left(C_W - \frac{C_a}{H/RT}\right)$$

C_W = Dissolved Concentration In Water, $\mu g/L$

C_a = Concentration In Air, $\mu g/L$

H = Henry's Law Constant, atm/M

R = Gas Constant (8.206×10^{-5}), atm/M-K

T = Water Temperature, K

D = Depth, m

k_V = Rate Constant, m/day (conductivity)
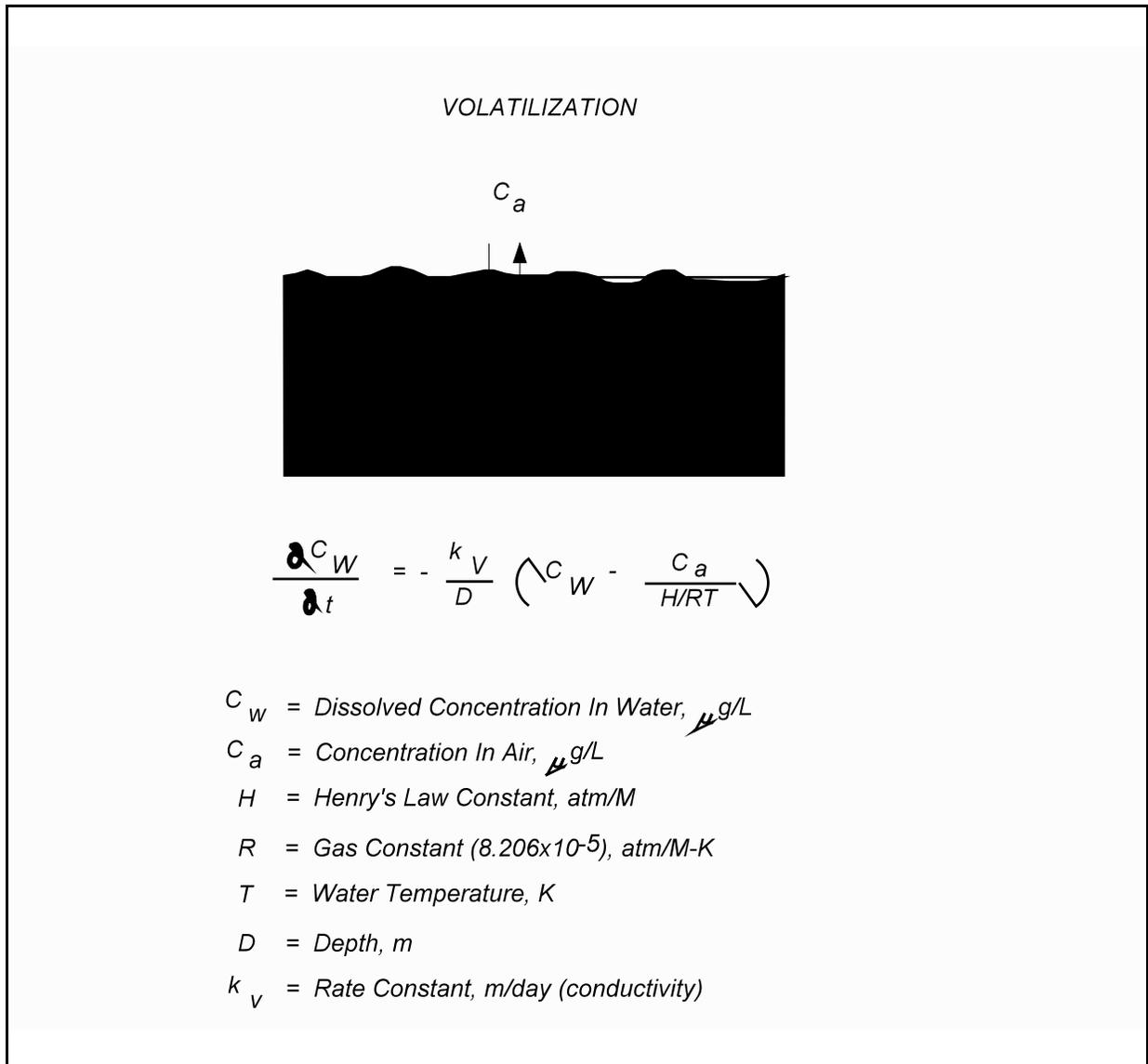
Figure 7.2 Volatilization reaction.

Equilibrium occurs when the dissolved concentration equals the partial pressure divided by Henry's Law Constant.

In TOXI5, the dissolved concentration of a chemical in a surface water column segment can volatilize at a rate determined by the two-layer resistance model (Whitman, 1923). The two-resistance method assumes that two "stagnant films" are bounded on either side by well mixed compartments. Concentration differences serve as the driving force for the water layer diffusion. Pressure differences drive the diffusion for the air layer. From mass balance considerations, it is

obvious that the same mass must pass through both films, thus the two resistances combine in series, so that the conductivity is the reciprocal of the total resistance:

$$K_v = (R_L + R_G)^{-1} = \left[K_L^{-1} + \left(K_G \ \frac{H}{R T_K} \right)^{-1} \right]^{-1} \qquad\qquad \textbf{7.42}$$

where

      R_L =   liquid phase resistance, day/m
      K_L =   liquid phase transfer coefficient, m/day
      R_G =   gas phase resistance, day/m
      K_G =   gas phase transfer coefficient, m/day.

There is actually yet another resistance involved, the transport resistance between the two interfaces, but it is assumed to be negligible. This may not be true in two cases: very turbulent conditions and in the presence of surface active contaminants. Although this two-resistance method, the Whitman model, is rather simplified in its assumption of uniform layers, it has been shown to be as accurate as more complex models.

The value of K_v, the conductivity, depends on the intensity of turbulence in a water body and in the overlying atmosphere. Mackay and Leinonen (1975) have discussed conditions under which the value of K_v is primarily determined by the intensity of turbulence in the water. As the Henry's Law coefficient increases, the conductivity tends to be increasingly influenced by the intensity of turbulence in water. As the Henry's Law coefficient decreases, the value of the conductivity tends to be increasingly influenced by the intensity of atmospheric turbulence.

Because Henry's Law coefficient generally increases with increasing vapor pressure of a compound and generally decreases with increasing solubility of a compound, highly volatile low solubility compounds are most likely to exhibit mass transfer limitations in water and relatively nonvolatile high solubility compounds are more likely to exhibit mass transfer limitations in the air. Volatilization is usually of relatively less magnitude in lakes and reservoirs than in rivers and streams.

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In cases where it is likely that the volatilization rate is regulated by turbulence level in the water phase, estimates of volatilization can be obtained from results of laboratory experiments. As discussed by Mill et al. (1982), small flasks containing a solution of a pesticide dissolved in water that have been stripped of oxygen can be shaken for specified periods of time. The amount of pollutant lost and oxygen gained through volatilization can be measured and the ratio of conductivities (KVOG) for pollutants and oxygen can be calculated. As shown by Tsivoglou and Wallace (1972), this ratio should be constant irrespective of the turbulence in a water body. Thus, if the reaeration coefficient for a receiving water body is known or can be estimated and the ratio of the conductivity for the pollutant to reaeration coefficient has been measured, the pollutant conductivity can be estimated.

The input computed volatilization rate constant is for a temperature of 20°C. It is adjusted for segment temperature using the equation:

$$K_{v,T} = K_{20} \, \Theta^{T-20} \qquad\qquad\qquad\qquad \textbf{7.43}$$

where

Θ_v = temperature correction factor

T = water temperature, °C.

Directly input volatilization rates are not temperature adjusted.

Computation of the Transfer Rates

There have been a variety of methods proposed to compute the liquid (K_L) and gas phase (K_G) transfer coefficients, several of which are included in TOXI5. The particular method to be employed is identified by the model through the user's selection of one of six volatilization options, each of which is briefly described below.

Volatilization Option 1.

This option allows the use of measured volatilization rates. The rates (K_v, m/day) are input as a parameter (which may be varied by segments) and may be time variable.

Volatilization Option 2.

This option allows the user to input an oxygen reaeration constant which is then adjusted to represent the liquid film transfer constant for the particular chemical. The adjustment is made in one of two ways. First, the user may input a measured ratio of oxygen to chemical exchange so that the rate (K_L) is computed from

$$K_L = K_a \cdot K_{vo}$$ 7.44

where

K_a = reaeration velocity, m/day
K_{vo} = ratio of volatilization rate to reaeration rate.

If K_{vo} is not provided, TOXI5 will compute the ratio based on the molecular weights of O_2 and the that of the chemical as shown below

$$K_L = K_a \sqrt{32/M_w}$$ 7.45

where M_w = molecular weight of the chemical, g/mole.

Under this option, the gas transfer rate (K_G) is calculated using O'Conner's method (see Option 4).

Volatilization Option 3.

If this option is specified, the liquid film transfer coefficient will be computed as in Option 2. However, the gas

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film transfer coefficient will be computed using Mackay's method (see Option 5).

Volatilization Option 4.

The liquid and gas film transfer coefficients computed under this option vary with the type of waterbody. The type of waterbody is specified as one of the volatilization constants and can either be a flowing stream, river or estuary or a stagnant pond or lake. The primary difference is that in a flowing waterbody the turbulence is primarily a function of the stream velocity, while for stagnant waterbodies wind shear may dominate. The formulations used to compute the transfer coefficients vary with the waterbody type as shown below.

    a) Flowing Stream, River or Estuary: For a flowing system (type 0) the transfer coefficients are controlled by flow induced turbulence. For flowing systems, the liquid film transfer coefficient (K_L) is computed using the Covar method (Covar, 1976) in which the equation used varies with the velocity and depth of the segment. First the transfer coefficient for dissolved oxygen is computed using the formulations provided below and then K_L calculated from equation 7.44 or 7.45.

For segments with depths less than 0.61 m the Owens formula is used to calculate the oxygen reaeration rate:

$$K_a = 5.349 \; \frac{u^{0.67}}{D^{0.85}} \qquad\qquad\qquad \textbf{7.46}$$

where

        u   =   velocity of the water, m/s
        D   =   segment depth, m

For segments with a velocity less than 0.518 m/s or a depth (m) greater than $13.584 \, u^{2.9135}$, the O'Connor-Dobbins formula is used:

$$K_L = \left(\frac{D_w u}{D}\right)^{0.5} 8.64 \cdot 10^4 \qquad\qquad \textbf{7.47}$$

where D_w is the diffusivity of the chemical in water (m^2/s), computed from

$$D_w = \frac{22 \cdot 10^{-9}}{M_w^{2/3}} \qquad\qquad \textbf{7.48}$$

In all other cases, the Churchill formula is used to calculate reaeration rate:

$$K_a = 5.049 \frac{u^{0.969}}{D^{0.673}} \qquad\qquad \textbf{7.49}$$

The gas transfer coefficient (K_G) is assumed constant at 100 m/day for flowing systems.

b) Stagnant Lake or Pond: For a stagnant system (type 1) the transfer coefficients are controlled by wind induced turbulence. For stagnant systems, the liquid film transfer coefficient (K_L) is computed using the O'Connor equations:

$$K_L = u^* \left(\frac{\rho_a}{\rho_w}\right)^{0.5} \frac{\kappa^{0.33}}{\lambda_2} S_{cw}^{-0.67} \qquad\qquad \textbf{7.50}$$

$$K_G = u^* \ \frac{\kappa^{0.33}}{\lambda_2} \ Sc_a^{-0.67} \qquad\qquad \textbf{7.51}$$

where u^* is the shear velocity (m/s) computed from

$$u^* = C_d^{0.5} \ W_{10} \qquad\qquad \textbf{7.52}$$

where

C_d	=	drag coefficient (0.0011)
W_{10}	=	wind velocity 10 m above water surface, m/sec
ρ_a	=	density of air, internally calculated from air temperature, kg/m^3
ρ_w	=	density of water, internally calculated from water temperature, kg/m^3
κ	=	von Karmen's constant (0.74)
λ_2	=	dimensionless viscous sublayer thickness (4)

S_{ca} and S_{cw} are air and water Schmidt Numbers, computed from

$$S_{ca} = \frac{\mu_a}{\rho_a \ D_a} \qquad\qquad \textbf{7.53}$$

$$S_{cw} = \frac{\mu_w}{\rho_w \ D_w} \qquad\qquad \textbf{7.54}$$

where

$$D_a = \text{diffusivity of chemical in air, } m^2/\text{sec}$$

D_a	=	diffusivity of chemical in air, m^2/sec
D_w	=	diffusivity of chemical in water, m^2/sec
$_a$	=	viscosity of air, internally calculated from air temperature, kg/m-sec
$_w$	=	viscosity of water, internally calculated from water temperature, kg/m-sec

The diffusivity of the chemical in water is computed using Equation 7.48 while the diffusivity of the chemical in air (D_a, m^2/sec) is computed from

$$D_a = \frac{1.9 \cdot 10^{-4}}{M_w^{2/3}} \qquad\qquad \textbf{7.55}$$

Thus K_G is proportional to wind and inversely proportional to molecular weight to the 4/9 power.

Volatilization Option 5.

As with Option 4, the liquid and gas film transfer coefficients computed under this option vary with the type of waterbody. The type of waterbody is specified to the water as one of the volatilization constants and can either be a flowing stream, river or estuary or a stagnant pond or lake. The primary difference is that in a flowing waterbody the turbulence is primarily a function of the stream velocity, while for stagnant waterbodies wind shear may dominate. The formulations used to compute the transfer coefficients vary with the waterbody type as shown below.

a. Flowing Stream, River or Estuary. The liquid and gas film transfer coefficients for flowing waterbodies are computed identically to those described under Option 4.

b) Stagnant Pond or Lake. Under this option, the liquid and gas film transfer coefficients are computed using formulations described by Mackay and Yeun (1983). The Mackay equations are:

$$K_L = 10^{-6} + 0.00341 \ u^* \ Sc_w^{-0.5} \qquad u^* > .3 \ m/s \qquad\qquad \textbf{7.56}$$

$$K_L = 10^{-6} + 0.0144 \ u^{*2.2} \ Sc_w^{-0.5} \qquad u^* < .3 \ m/s \qquad\qquad \textbf{7.57}$$

$$K_G = 10^{-3} + 0.0462 \ u^* \ Sc_a^{-0.67} \qquad\qquad\qquad\qquad\qquad \textbf{7.58}$$

Implementation

Although there are many calculations involved in determining volatilization, most are performed internally using a small set of data. TOXI5 volatilization data specifications are summarized in Table 7.8. Not all of the constants are required. If Henry's Law constant is unknown, it will be calculated internally from vapor pressure and solubility (provided in input). If K_{vo} is not measured, it will be calculated internally from molecular weight and specified or computed liquid film transfer coefficients. Volatilization is only allowed for surficial water column segments as identified by the segment type specified in input. The segment types are: 1) Surface water segments (Type 1), 2) Subsurface water segments (Type 2), Surficial sediment segments (Type 3), and 4) subsurface sediment segments (Type 4).

Transformation input parameters that must be specified by the user are given below for each volatilization option. Constant numbers are listed in Table 7.9. Three constants should be input for all volatilization options: the volatilization option number, Henry's Law Constant, and the atmospheric chemical concentration. Segment depths (from Data Group C) must be specified.

Table 7.8 TOXI5 Volatilization Input.

Description	Notation	Range	Units
Measured or calibrated conductance	K_v	0.6-25	m/day
Henry's Law Constant	H	$10^{-7}-10^{-1}$	atm-m^3/mole
Concentration of chemical in atmosphere	C_a	0-1000	g/L
Molecular weight	M_w	$10-10^3$	g/mole
Reaeration coefficient (conductance of oxygen)	K_a	0.6-25	m/day
Experimentally measured ratio of volatilization to reaeration	k_{vo}	0-1	
Current velocity	u_x	0-2	m/sec
Water depth	D	0.1-10	m
Water temperature	T	4-30	°C
Wind speed 10 m above surface	W_{10}	0-20	m/sec

Volatilization Option-- The user should chose the volatilization option using constant XV. Specifying a value of 0 will prevent volatilization from occuring. Values of 1 - 5 will invoke volatilization options 1 - 5 as outlined in the text above: (1) volatilization rates are input directly; (2) volatilization is computed from input reaeration rate constants and O'Connor's equation for gas transfer; (3) volatilization is computed from input reaeration rate constants and MacKay's equation for gas transfer; (4) in flowing systems, volatilization is computed using reaeration rates calculated from Covar's method and a gas transfer rate of 100 m/day; in quiescent systems, volatilization is computed from O'Connor's equations for liquid and gas transfer; (5) in flowing systems, volatilization is computed using reaeration rates calculated from Covar's method and a gas transfer rate of 100 m/day; in

Table 7.9 TOXI5 Constants for Volatilization Reactions.

VARIABLE	C_1	C_2	C_3	DEFINITION
WTYPE	**2**	**2**	**2**	Water body type (0 = flowing; 1 = quiescent)
AIRTMP	**5**	**5**	**5**	Multiplier for air temperature time function
ATMOS	**8**	**608**	**1208**	Atmospheric concentration of chemical, $\mu g/L$
MOLWT	**81**	**681**	**1281**	Molecular weight of chemical
SOLG	**82**	**682**	**1282**	Solubility of chemical in water, mg/L
VAPRG	**83**	**683**	**1283**	Vapor pressure of chemical, torr
XV	**136**	**736**	**1336**	Volatilization option: 0 = none; 1 = measured; 2 = measured reaeration + O'Connor; 3 = measured reaeration + MacKay; 4 = calculated by O'Connor; 5 = calculated by MacKay
HENRY	**137**	**737**	**1337**	Henry's Law constant, atm-m^3/mole
KLT	**138**	**738**	**1338**	Volatilization temperature correction factor
KVOG	**139**	**739**	**1339**	Measured ratio of volatilization to reaeration rate

quiescent systems, volatilization is computed from MacKay's equations for liquid and gas transfer.

Henry's Law Constant, atm-m^3/mole-- The user should specify Henry's Law constant for air-water partitioning of the chemical using constant HENRY.

Atmospheric Concentration, ug/L-- The user should specify the mean atmospheric concentration of chemical using constant ATMOS. If this concentration is 0, then volatilization will always cause a loss of chemical from the water body.

Volatilization Option 1

In this option, variable volatilization rate constants can be input directly.

Volatilization Rates, m/day-- When XV is set to 1, the user may then input segment and time variable volatilization rates using parameter 5, REAR, and time function 12, REARN. The product of spatially-variable REAR and time-variable REARN gives the segment and time specific volatilization rate constants used by TOXI5. These volatilization values are not modified by a temperature function.

Volatilization Option 2

In this option, volatilization rates are calculated from user-input reaeration rate constants and O'Connor's method for gas transfer. Input data required for option 2 are listed below. For flowing systems, wind speed and air temperature are not used and may be omitted.

Water Body Type-- The user should specify the water body type using constant WTYPE. A value of 0 indicates a flowing water body, such as a stream, river, or estuary. A value of 1 indicates a quiescent water body, such as a pond, reservoir, or lake.

Reaeration Rates, m/day-- When XV is set to 2, the user may then input segment and time variable reaeration rates using parameter 5, REAR, and time function 12, REARN. The product of spatially-variable REAR and time-variable REARN gives the segment and time specific reaeration rate constants used by TOXI5. These reaeration values are not modified by a temperature function.

Ratio of Volatilization to Reaeration-- The user may specify an experimentally-measured ratio of volatilization to reaeration using constant KVOG. If this constant is not given, the ratio will be calculated from molecular weight.

Molecular Weight g/mole-- The user may specify the molecular weight using constant MOLWT. This constant is used to calculate the ratio of volatilization to reaeration if an experimentally-measured value is not provided. It is also used in the calculation of diffusivities.

Wind Speed, m/sec-- The user may specify the segment and time variable wind speed using parameter 4, WVEL, and time function 9, WINDN. The product of spatially-variable WVEL and time-variable WINDN gives the segment and time specific reaeration rate constants used by TOXI5. Wind speed should be measured at 10 m height above the water surface.

Air Temperature, °C-- The user may specify time-variable air temperature using constant AIRTMP and time function 13, AIRTMPN. The ambient air temperature is calculated as the product of AIRTMP and AIRTMPN. For a constant air temperature, AIRTMPN can be omitted. For variable air temperatures, the user should set AIRTMP to 1.0 and input a series of air temperature versus time values via AIRTMPN.

Volatilization Option 3

In this option, volatilization rates are calculated from user-input reaeration rate constants and MacKay's method for gas transfer. Input data required for the same as for option 2, listed above. For flowing systems, wind speed and air temperature are not used and may be omitted.

Volatilization Option 4

In this option, volatilization rates in flowing systems are calculated using reaeration rates calculated from Covar's method and a gas transfer rate of 100 m/day. In quiescent systems, volatilization is computed from O'Connor's equations for liquid and gas transfer. Input data required for option 4 are listed below. For flowing systems, wind speed and air temperature are not used and may be omitted. For quiescent systems, water velocity may be omitted.

Water Velocity, m/sec-- Variable current velocities are calculated from flow using hydraulic geometry coefficients as described in Chapter 2. For most situations, no further input is required from the user. If an estuary is being simulated under tidal-average conditions, however, the net flows do not provide realistic ambient water velocities for use in volatilization calculations. In this case, the user should enter time and segment variable water velocities using parameter 1, VELFN and time functions 5-8, VELN(1-4).

The parameter VELFN indicates which velocity function will be used by the model for each segment. Values of 1.0, 2.0, 3.0, or 4.0 will call time functions VELN(1), VELN(2), VELN(3), and VELN(4), respectively. Water velocities should then be entered via these time functions as a series of velocity versus time values.

Water Body Type-- see Option 2 above.

Ratio of Volatilization to Reaeration-- see Option 2 above.

Molecular Weight g/mole-- see Option 2 above.

Wind Speed, m/sec-- see Option 2 above.

Air Temperature, C-- see Option 2 above.

Volatilization Option 5

In this option, volatilization rates in flowing systems are calculated using reaeration rates calculated from Covar's method and a gas transfer rate of 100 m/day. In quiescent systems, volatilization is computed from MacKay's equations for liquid and gas transfer. Input data required for option 5 are the same as for option 4 above. For flowing systems, wind speed and air temperature are not used and may be omitted. For quiescent systems, water velocity may be omitted.

7.6 HYDROLYSIS

Introduction

Hydrolysis, or reaction of the chemical with water, is
known to be a major pathway for degradation of many toxic
organics. Hydrolysis is a reaction in which cleavage of a
molecular bond of the chemical and formation of a new bond with
either the hydrogen or the hydroxyl component of a water
molecule occurs. Hydrolytic reactions are usually catalyzed by
acid and/or base and the overriding factor affecting hydrolysis
rates at a given temperature is generally hydrogen or hydroxide
ion concentration (Wolfe, 1980). An example reaction is shown
in Figure 7.3. The reaction can be catalyzed by hydrogen ions
or proceed by consuming hydroxide ions. Figure 7.4 illustrates
the effects of base hydrolysis on carbaryl, neutral hydrolysis
on chloromethane, and acid and base hydrolysis on 2,4-D.
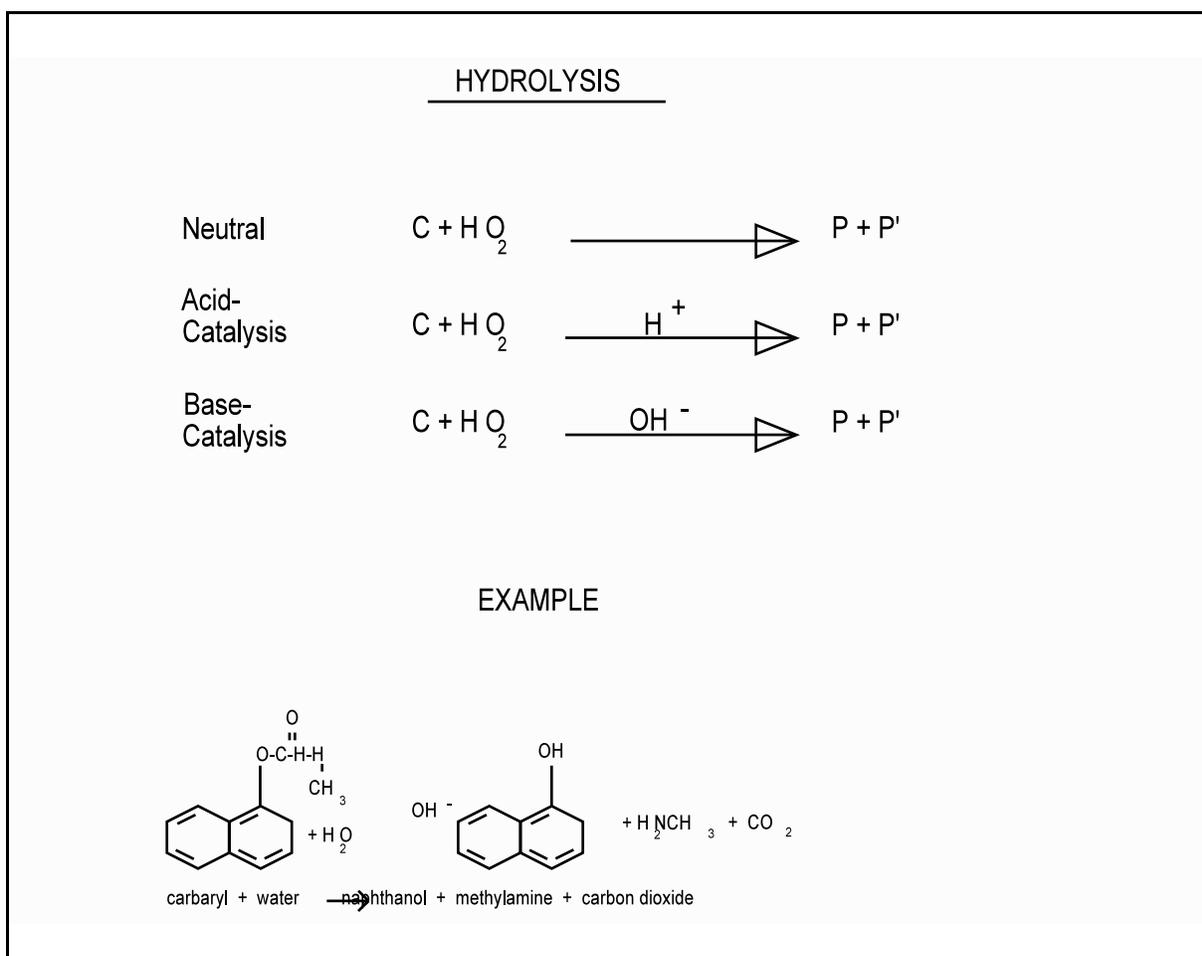
Figure 7.3   Hydrolysis reactions.
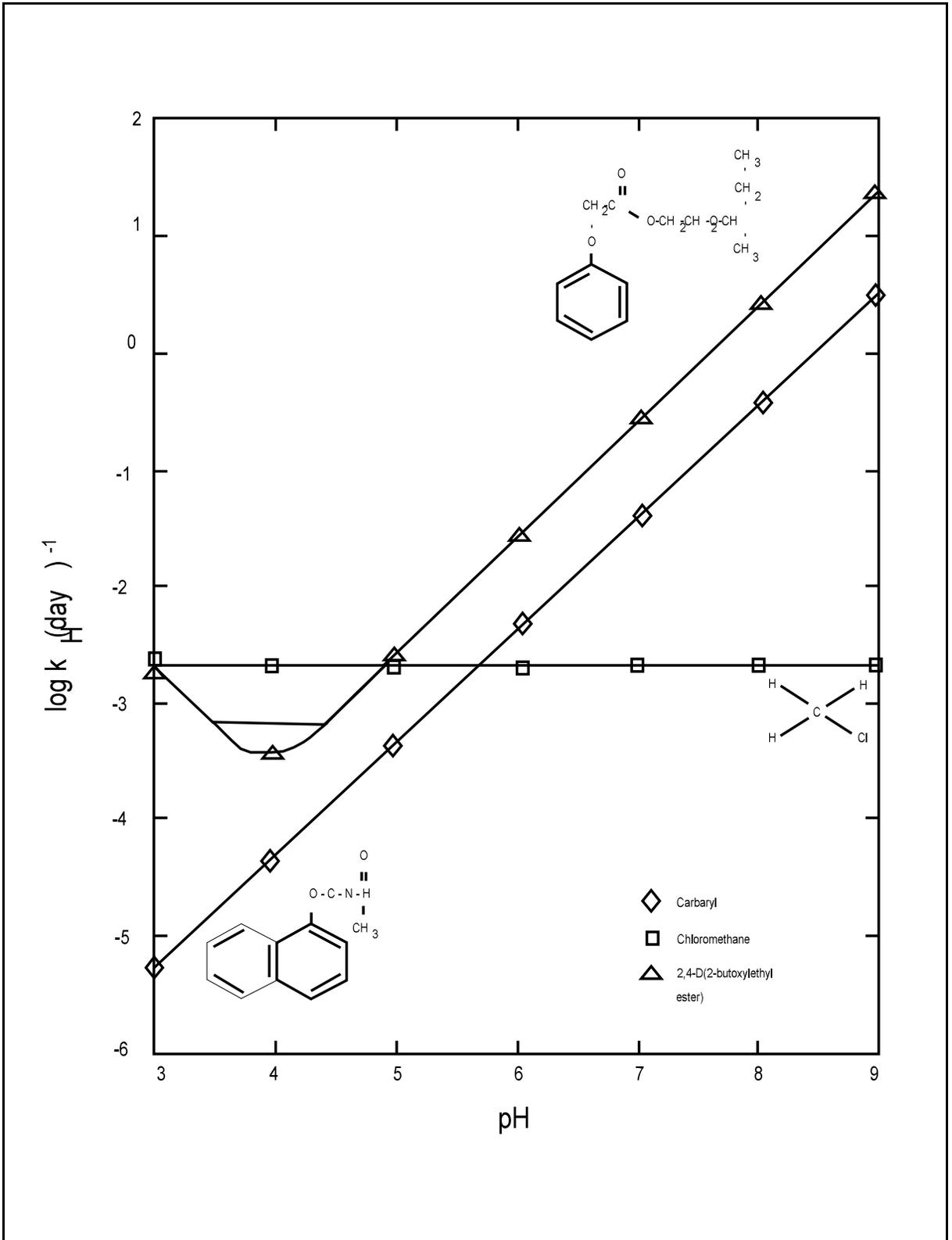
Figure 7.4 pH dependence of hydrolysis rate constants.

<u>Overview of TOXI5 Hydrolysis Reactions</u>

Hydrolysis may be simulated by TOXI5 using simple decay. Alternatively, hydrolysis can be simulated using rates that are first order for the neutral chemical and second order for its ionic forms. The second order rates are pH and temperature dependant.

Option 1. First Order Hydrolysis.

Under this option, the user inputs a first order rate constant for either neutral, alkaline, or acid hydrolysis. The first order rate term constant is then applied to the total chemical concentration (see Section 6.3).

Option 2. Second Order Hydrolysis.

Under this option, hydrolysis by specific-acid-catalyzed, neutral, or base pathways is considered for the various species and phases of each chemical. The reactions are first order for the neutral chemical and second order for the acidic or basic forms of the chemical:

$$K_{HN} = \sum_i \sum_j k_{nij} \; f_{ij} \qquad\qquad\qquad \textbf{7.59}$$

$$K_{HH} = \sum_i \sum_j k_{aij} \; [H^+] \; f_{ij} \qquad\qquad\qquad \textbf{7.60}$$

$$K_{HOH} = \sum_i \sum_j k_{bij} \; [OH^-] \; f_{ij} \qquad\qquad\qquad \textbf{7.61}$$

where:

K_{HN} =   net neutral hydrolysis rate constant, day^{-1}

K_{HH} = net acid catalyzed hydrolysis rate constant, day^{-1}

K_{HOH} = net base catalyzed hydrolysis rate constant, day^{-1}

k_{aij}, k_{bij} = specific acid catalyzed and base rate constants for ionic specie i in phase j, respectively, $molar^{-1} \, day^{-1}$

k_{nij} = neutral rate constant for ionic specie i in phase j, day^{-1}

f_{ij} = fraction of chemical as ionic specie i in phase j

The rates are also affected by temperature. TOXI5 adjusts the rates using the temperature-based Arrhenius function

$$k(T_k) = k(T_R) \, \exp[1000 \, E_{aH}(T_K - T_R)/(RT_k \, T_R)]$$ **7.62**

where:

T_K = water temperature, °K

T_R = reference temperature for which reaction rate is reported, °K

E_{aH} = Arrhenius activation energy for hydrolysis reaction, kcal/mole °K

R = 1.99 cal/mole °K

1000 = cal/kcal

<u>Implementation</u>

TOXI5 hydrolysis data specifications are summarized in Table 7.10. In addition, the simple first order rates may be specified as described under Option 1 and the section on simple TOXI5 reactions. If no hydrolysis data are input, then the effect of hydrolysis will not be included in simulations.

Table 7.10   TOXI5 Hydrolysis Data.

Description	Notation	Range	Units
Negative log of hydrogen ion activity [H^+]	pH	5-9	–
Acid hydrolysis rate constant for specie i, phase j	k_{HAij}	$0-10^7$	
Neutral hydrolysis rate constant for specie i, phase j	k_{HNij}	$0-10^2$	day^{-1}
Base hydrolysis rate constant for specie i, phase j	k_{HBij}	$0-10^7$	
Water temperature	T	4-30	°C
Activation energy for hydrolysis reaction for specie i	E_{aHi}	15-25	

Option 1.

Under this option, the user inputs one or more of the following: an acid, neutral, and base hydrolysis rate constant.

<u>First-Order Hydrolysis Rate Constants, day^{-1}</u>-- The user may input overall base, neutral, and acid hydrolysis rate constants using constants 181, 182, and 183 for chemical 1, constants 781, 782, and 783 for chemical 2, and constants 1381, 1382, and 1383

for chemical 3. The rates are first order, and are applied to the total chemical. If any one of these first order rates are specified in input they will be used regardless of whether other hydrolysis constants are specified.

Option 2.

     Under this option, the reaction coefficients can be specified as constants. If the chemical simulated does not ionize (as controlled by input of the ionization constants), then acid, base and neutral hydrolysis constants may be input for the dissolved, DOC sorbed and sediment sorbed phases of the

Table 7.11   TOXI5 Constants for Hydrolysis Reactions.

PHASE "i" or REACTION "k"	C_1	C_2	C_3	INPUT VARIABLE
all	**184**	**784**	**1384**	Reference Temperature TREFH, °C
aqueous	**186**	**786**	**1386**	Alkaline Hydrolysis $KH2O_{1,i,1}$ $M^{-1}day^{-1}$
DOC	**191**	**791**	**1391**	
sediment	**196**	**796**	**1396**	
aqueous	**201**	**801**	**1401**	Neutral Hydrolysis $KH2O_{2,i,1}$ day^{-1}
DOC	**206**	**806**	**1406**	
sediment	**211**	**811**	**1411**	
aqueous	**216**	**816**	**1416**	Acid Hydrolysis $KH2O_{3,i,1}$ $M^{-1}day^{-1}$
DOC	**221**	**821**	**1421**	
sediment	**226**	**826**	**1426**	
Alkaline	**231**	**831**	**1431**	Activation Energy E_{ak}, kcal/mole °K
Neutral	**236**	**836**	**1436**	
Acid	**241**	**841**	**1441**	

chemical, as summarized in Table 7.11. If ionization of the
chemical is allowed, then constants may be input for the
dissolved, DOC sorbed and sediment sorbed phases of each ionic
specie simulated. In addition, the pH must be supplied in order
to compute acid and base hydrolysis. The pH is input as a
parameter, which must be specified for each model segment and
may be constant or time variable. Separate pH time functions
may be specified for surface water and benthic segments.

     If the user wants TOXI5 to adjust the rates based on
temperature, then non-zero activation energies should be
specified which will invoke the temperature-based Arrhenius
function. Activation energies may be specified for each ionic
specie and each hydrolysis reaction (acid, neutral, base)
simulated. If no activation energies are given, then rates
constants will not be adjusted to ambient water temperatures.

     Base Hydrolysis Rate Constants, $M^{-1}day^{-1}$-- The user may
specify second order base hydrolysis rate constants for each
phase (dissolved, DOC-sorbed, and sediment-sorbed) and each
ionic specie using constant KH20. Constant numbers for the
neutral molecule are summarized in Table 7.11. $KH20_{1,1,1}$ refers
to the dissolved neutral chemical; $KH20_{1,2,1}$ refers to the DOC-
sorbed neutral chemical; $KH20_{1,3,1}$ refers to the sediment-sorbed
neutral chemical. Constant numbers for the ionic species are
given in Part B of this document.

     Neutral Hydrolysis Rate Constants, day^{-1}-- The user may
specify first order neutral hydrolysis rate constants for each
phase (dissolved, DOC-sorbed, and sediment-sorbed) and each
ionic specie using constant KH20. Constant numbers for the
neutral molecule are summarized in Table 7.11. $KH20_{2,1,1}$ refers
to the dissolved neutral chemical; $KH20_{2,2,1}$ refers to the DOC-
sorbed neutral chemical; $KH20_{2,3,1}$ refers to the sediment-sorbed
neutral chemical. Constant numbers for the ionic species are
given in Part B of this document.

     Acid-Catalyzed Hydrolysis Rate Constants, $M^{-1}day^{-1}$-- The
user may specify second order acid-catalyzed hydrolysis rate
constants for each phase (dissolved, DOC-sorbed, and sediment-
sorbed) and each ionic specie using constant KH20. Constant
numbers for the neutral molecule are summarized in Table 7.11.
$KH20_{3,1,1}$ refers to the dissolved neutral chemical; $KH20_{3,2,1}$ refers
to the DOC-sorbed neutral chemical; $KH20_{3,3,1}$ refers to the
sediment-sorbed neutral chemical. Constant numbers for the
ionic species are given in Part B of this document.

Arrhenius Activation Energy, kcal/mole-°K-- The user may specify activation energies for each chemical using constant EHOH. Constant numbers are summarized in Table 7.11. If EHOH is omitted or set to 0, hydrolysis rates will not be affected by temperature.

Reference Temperature,°C-- The user may specify the reference temperature at which hydrolysis rates were measured using constant TREFH. Constant numbers are summarized in Table 7.11. If a reference temperature is not supplied, then a default of 20 °C is assumed.

pH-- The user may specify time and segment variable pH values using parameter 11, PH, and time functions 10 and 11, PHNW and PHNS. The pH in a water segment will be the product of PH and PHNW; the pH in a benthic segment will be the product of PH and PHNS. For constant pH, the user should enter values via parameter PH. Time functions should be omitted. For time variable pH, the user should enter a series of pH versus time values via PHNW and PHNS. The parameter PH values will then represent the ratio of pH in each segment to the time function.

7.7 PHOTOLYSIS

Introduction

Photodegradation (photolysis) is the transformation or degradation of a compound that results directly from the adsorption of light energy. An example of several photochemical pathways is given in Figure 7.5. It is a function of the quantity and wavelength distribution of incident light, the light adsorption characteristics of the compound, and the efficiency at which absorbed light produces a chemical reaction. Photolysis is classified into two types that are defined by the mechanism of energy absorption. Direct photolysis is the result of direct absorption of photons by the toxic chemical molecule. Indirect or sensitized photolysis is the result of energy transfer to the toxic chemical from some other molecule that has absorbed the radiation.

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Overview of TOXI5 Photolysis Reactions

Photolysis is the transformation of a chemical due to absorption of light energy. The first order rate coefficient for photolysis can be calculated from the absorption rate and the quantum yield for each ionic specie and phase:

$$K_{pG} = \sum_i \sum_j k_{ai}\; \phi_{ij}\; f_{ij}$$

7.63

PHOTOLYSIS

Photochemical pathways of an excited molecule

A_o — ground state of reactant molecule

A^* — excited state

Q_o — ground state of quenching molecule

Q^* — excited molecule

PHOTOCHEMICAL PATHWAYS OF AN EXCITED MOLECULE.
EXCITED MOLECULES DO NOT ALWAYS CHEMICALLY REACT.
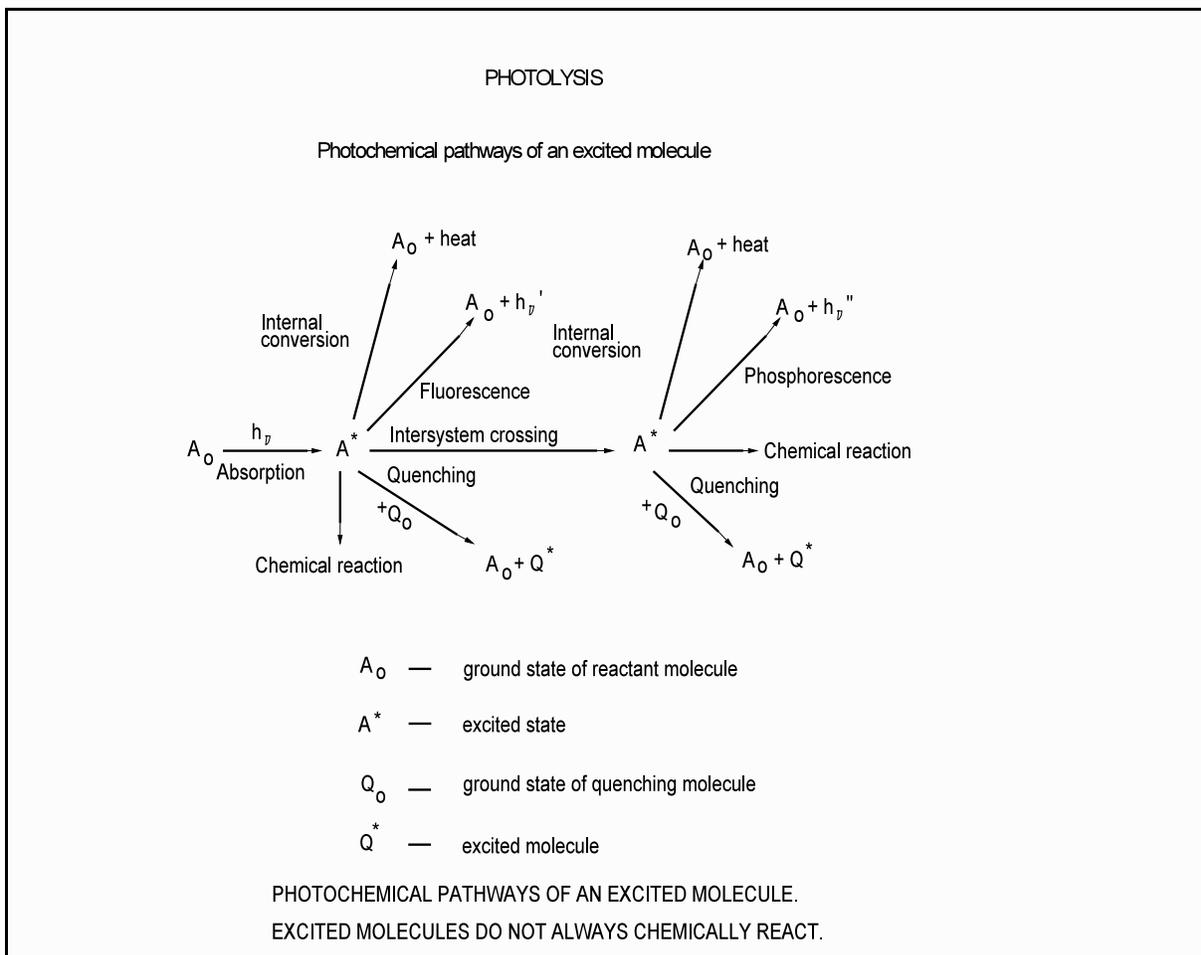
Figure 7.5 Photolysis reactions.

where:

K_{pG} = first order photolysis rate coefficient at ambient light intensity, day^{-1}

k_{ai} = specific sunlight absorption rate for specie i, E/mole-day or (E/L)/(mole/L)/day

f_{ij} = reaction quantum yield for specie i in phase j, mole/E

f_{ij} = fraction of chemical as specie i in phase j

The user may specify that the model calculate the first order photolysis rate constant or the user may provide a near water surface rate (for presumed cloudless conditions). If the user-supplied rate constant is representative of conditions at a location other than the water body being modeled, the model corrects the rate for the difference in latitude between the two and any difference in cloud cover. The options for computing the losses due to photolysis are briefly described below.

Photolysis Option 1.

Under this option, the photolysis rate is calculated from molar absorptivities, calculated light intensity, and quantum yield of the chemical. To calculate the rate constant, TOXI5 divides the wavelength spectrum between 280 and 800 nm into 46 intervals. For each interval the user must specify a molar absorptivity. The light intensity at each of the 46 wavelengths is internally calculated from the location of the water body (i.e., latitude), the time of year, and the atmospheric conditions (air mass type, relative humidity, atmospheric turbidity and ozone content, cloudiness). The location and time of year are used to define the light intensity at the outer edge of the atmosphere. The atmospheric conditions are used to define the light decay through the atmosphere. The light intensities and the molar absorptivities are used with a user defined optical path (d) to calculate the specific sunlight absorption rate. The first order rate constant is then calculated using equation 7.63. This calculation was taken directly from EXAMS II (Burns and Cline, 1985) and is based on formulations published by Green, Cross and Smith (1980).

The specific sunlight absorption rate is the integral or summation over all bandwidths of the average light multiplied by the molar absorptivity and the optical path:

$$k_{ai} = \sum_k I_{Gk}\, \epsilon_{ki}\, d\ (2303)\ (86400)/(6.022\ x\ 10^{23})$$ **7.64**

where:

I_{Gk} = average light intensity of wavelength k, photons/cm^2-sec

ϵ_{ki} = decadic molar absorptivity of wavelength k by specie i, L/mole-cm-ln 10

d = ratio of the optical path to the vertical path, cm/cm

2303 = (cm^3/L) (ln 10/ln e)

86400 = sec/day

6.022 x 10^{23} = Avagadro's number, photons/E

Light extinction is calculated with the integrated Beer-Lambert formulation for each wavelength k:

$$\frac{I_{Gk}}{I_{ok}} = \frac{1 - \exp(-d\ K_e\ D)}{d\ K_e\ D}$$ **7.64**

where:

I_{ok} = light intensity of wavelength k just below water surface, photons/cm^2-sec

K_e = spatially variable light extinction coefficient, m^{-1}

D = depth of water segment, m

I_{ok} is calculated for each wavelength based upon the time of year, latitude, ground elevation, cloud cover, air mass type, relative humidity, atmospheric turbidity, and ozone content. The atmospheric characteristics can vary monthly, or be specified as an annual average. The value of d, the ratio of the optical path to the vertical depth is difficult to compute, but a probable best value is 1.19 (Hutchinson, 1967). However, in the presence of a large concentration of scattering particles, it may approach 2.0. In order to ensure that an improper value is not loaded and used in computations, the input value is checked and set to 1.19 if the input is invalid.

The photolysis rate constants for each water column segment are determined from the calculated near-surface rate constant and the rate of light decay in the water column (K_e). The value of K_e is calculated for each wavelength based on a formulation taken from EXAMS II:

$$K_e = K_{ew} + \eta_1\ CHL + \eta_2\ DOC + \eta_3\ m \qquad\qquad\qquad 7.65$$

where

K_{ew} = pure water extinction coefficient, 1/m

CHL = phytoplankton chlorophyll concentration, mg/L

DOC = dissolved organic carbon concentration, mg/L

m = solids concentration, mg/L

1, 2, 3 = specific extinction coefficients, L/mg-m

Values of K_{ew}, 1, 2, 3 for each of the 46 wavelengths are supplied in the program as data statements in subroutine BEER and are shown in Tables 7.12 and 7.13. Segment average photolysis rate constants are computed for each wavelength and then summed to yield an overall rate.

Table 7.12 Wavelength Intervals and Specific Light Extinction Coefficients Used in the Photolysis Calculation. Values Taken From EXAMS II (Burns and Cline, 1985).

		Specific Light Extinction Coefficients			
Number	Wavelength	Pure Water l/m	Chlorophyll L/gm-m	DOC L/mg-m	Solids L/mg-m
1	280.0	0.288	145	7.90	0.34
2	282.5	0.268	138	7.65	0.34
3	285.0	0.249	132	7.41	0.34
4	287.5	0.231	126	7.11	0.34
5	290.0	0.215	120	6.95	0.34
6	292.5	0.194	115	6.73	0.34
7	295.0	0.174	109	6.52	0.34
8	297.5	0.157	106	6.30	0.34
9	300.0	0.141	101	6.12	0.34
10	302.5	0.133	95	5.94	0.34
11	305.0	0.126	90	5.76	0.34
12	307.5	0.119	85	5.57	0.34
13	310.0	0.105	80	5.39	0.34
14	312.5	0.0994	78	5.22	0.34
15	315.0	0.0952	75	5.06	0.34
16	317.5	0.0903	72	4.90	0.34
17	320.0	0.0844	70	4.74	0.34
18	323.1	0.0793	68	4.56	0.34
19	330.0	0.0678	64	4.17	0.34
20	340.0	0.0561	59	3.64	0.34
21	350.0	0.0463	55	3.15	0.34
22	360.0	0.0379	55	2.74	0.34
23	370.0	0.0300	51	2.34	0.34

Table 7.13 Wavelength Intervals and Specific Light Extinction Coefficients Used in the Photolysis Calculation. Values Taken From EXAMS II (Burns and Cline, 1985, completed).

		Specific Light Extinction Coefficients			
Number	Wavelength	Pure Water l/m	Chlorophyll L/gm-m	DOC L/mg-m	Solids L/mg-m
24	380.0	0.0220	46	2.00	0.34
25	390.0	0.0191	42	1.64	0.34
26	400.0	0.0171	41	1.39	0.34
27	410.0	0.0162	39	1.19	0.34
28	420.0	0.0153	38	1.02	0.34
29	430.0	0.0144	35	0.870	0.34
30	440.0	0.0145	32	0.753	0.34
31	450.0	0.0145	31	0.654	0.34
32	460.0	0.0156	28	0.573	0.34
33	470.0	0.0156	26	0.504	0.34
34	480.0	0.0176	24	0.444	0.34
35	490.0	0.0196	22	0.396	0.34
36	503.75	0.0295	19	0.357	0.34
37	525.0	0.0492	14	0.282	0.34
38	550.0	0.0638	10	0.228	0.34
39	575.0	0.0940	8	0.188	0.34
40	600.0	0.244	6	0.158	0.34
41	625.0	0.314	5	0.0	0.34
42	650.0	0.349	8	0.0	0.34
43	675.0	0.440	13	0.0	0.34
44	706.25	0.768	3	0.0	0.34
45	750.0	2.47	2	0.0	0.34
46	800.0	2.07	0	0.0	0.34

Photolysis Option 2.

Under this option, a reference surface sunlight absorption rate k_{aRi} (E/mole-day) is input by the user for each specie simulated. As with EXAMSII, the input rate is then adjusted as shown below

$$k_{ai} = \sum_i \sum_j k_{aRi}\ I_o'\ (I_G/I_o)\ (1-0.056C)\ X_L \qquad\qquad \textbf{7.66}$$

where

$\quad I_o'\quad =\quad$ user specified normalized light intensity time function, which is the ratio of ambient light intensity to the reference light intensity.

$\quad C\quad =\quad$ cloud cover (in tenths, 0-10)

$\quad X_L\quad =\quad$ latitude correction factor, calculated by:

$$X_L = \left[\frac{19169.65 + 87054.63\ \cos(0.039L)}{19169.65 + 87054.63\ \cos(0.039L_{Rf})}\right] \qquad\qquad \textbf{7.67}$$

where

$\quad L\quad =\quad$ latitude of the waterbody

$\quad L_{Rf}\quad =\quad$ reference latitude at which the surface photolysis rate was measured.

The average light intensity attenuation, I_G/I_o, is computed as above from the Beer-Lambert formulation (equation 7.65). Therefore, the light intensity has a value for each model segment ranging from zero to one.

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The extinction coefficient may be directly specified as a model parameter, which may be varied by model segment. If the extinction coefficient is not specified, it is determined from a user-specified wavelength of maximum light absorption for the particular chemical species (neutral, anionic or cationic) using equation 7.66 and the values listed in Tables 7.12 and 7.13. If the wavelength of maximum absorption is outside of the relevant spectral range (280-825 nm) then TOXI5 assumes a wavelength of 300 nm.

After adjusting the reference sunlight absorption rate to ambient conditions, the first order photolysis rate is computed from these and reaction quantum yields following equation 7.63.

Photolysis option 2 is often implemented using reference first order photolysis rate constants rather than reference sunlight absorption rates. If reference first order rate constants are input for k_{aRi}, then equation 7.67 calculates k_{ai} as first order rate constants (day^{-1}) adjusted to ambient light conditions. The overall first order photolysis rate constant is then calculated following equation 7.63 where quantum yields are set to 1.0.

Implementation

The TOXI5 photolysis data specifications are summarized in Table 7.14. In addition, an overall first-order rate constant may be supplied by the user for each chemical, as presented in Chapter 6. If the overall first order rate constant is specified, it will be used regardless of other input specifications. For the photolysis computations described in this chapter, input requirements are described below.

Photolysis Option 1

In option 1, TOXI5 computes the sunlight absorption and the surface photolytic decay rate.

Table 7.14 TOXI5 Photolysis Data.

Description	Notation	Range	Units
Observed rate constant for a chemical at reference light intensity I_R	K_{pR}	0 - 10	day^{-1}
Observed sunlight absorption rate for a chemical at reference light intensity I_R	k_{aR}	?	E/mole-day
Reference light intensity causing photolysis rate K_{pR} or absorption rate k_{aR}	I_R	$10^{-7}-2 \times 10^{-6}$	E/cm^2-sec
Ratio of surface light intensity to reference light intensity (I_o/I_R)	I_o'	0 - 10	-
Light extinction coefficient in water column	K_e	0.1 - 5	m^{-1}
Chlorophyll **a** concentration	CHL	$10^{-3} - 10^{-1}$	mg/L
Dissolved organic carbon	DOC	0 - 10	mg/L
Depth of water column segment	D	0.1 - 10	m
Reaction quantum yield fraction for specie i in phase j	$_{ij}$	0 - 0.5	moles/E
Molar absorptivity by wavelength k by specie i	$_{ki}$	0 - ?	L/mole-cm-ln 10
Waterbody elevation	ELEVG	0 - 5000	m
Waterbody latitude	L	0 - 90	degrees
Reference latitude	L_{Rf}	0 - 90	degrees
Cloud cover, fraction of sky	C_G	0 - 10	tenths
Air type (rural, urban, maritime, or tropospheric)	AIRTYG	1 - 4	-
Relative humidity	RHUMG	0 - 100	percent
Atmospheric turbidity, in equivalent aerosol layer thickness	ATURBG	0 - ?	km
Ozone content	OZONEG	0 - ?	cm NTP

Table 7.15 Photolysis 1 Constants.

VARIABLE	C_1	C_2	C_3
$ABS_{1,L}$	301-346	901 - 946	1501-1546
$QUANTG_{11}$	551	1151	1751
$QUANTG_{21}$	556	1156	1756
$QUANTG_{31}$	561	1161	1761

Photolysis Option-- The user should select the photolysis option using constant XPHOTO: 0 = no photolysis; 1 = photolysis rates will be computed from molar absorptivity; 2 = photolysis rates will be extrapolated from measured surface rates. Use constant numbers 286, 886, and 1486 for chemicals 1, 2, and 3, respectively.

Molar Absorptivity, L/mole-cm-ln10-- The user may specify molar absorptivity values for each ionic specie over 46 wavelengths using constant ABS. The wavelengths by number are listed in Tables 7.12 and 7.13. Absorptivity values for each ionic specie apply across all phases (aqueous, DOC-sorbed, sediment-sorbed). Constant numbers for the neutral ionic specie are summarized in Table 7.15.

Quantum Yield, moles/einstein-- The user may specify reaction quantum yield values for each phase (dissolved, DOC-sorbed, sediment-sorbed) and each ionic specie using constant QUANTG. Constant numbers for the neutral molecule are summarized in Table 7.15. $QUANTG_{11}$ refers to the dissolved neutral chemical; $QUANTG_{21}$ refers to the DOC-sorbed neutral chemical; $QUANTG_{31}$ refers to the sediment-sorbed neutral chemical.

Julian Date-- The user should specify the Julian date for the beginning of the simulation using constant 1 - TO.

Elevation, m-- The user should specify the average ground elevation using constant 3 - ELEVG.

Latitude, degrees and tenths-- The user should specify the latitude of the waterbody using constant 4 - LATG.

Light Option-- Using constant 6 - XLITE, the user has a choice of options controlling how TOXI5 computes and uses light intensity: 0 = do not compute light; 1 = compute annual average light intensity; 2 = compute average light intensity for the month indicated by TO; 3 = compute monthly light intensity as a step function.

Optical Path-- The user may specify the ratio of the optical path to the vertical depth using constant 7 - DFACG. A default value of 1.17 is assumed.

Cloud Cover, tenths-- The user should specify the mean monthly or annual average cloud cover using constant CLOUDG. Monthly values can be entered using constant numbers 11-22; the annual average can be entered using number 23.

Air Type-- The user should specify the mean air mass type using constant AIRTYG. Values of 1, 2, 3, or 4 will select rural, urban, maritime, or tropospheric, respectively. Monthly values can be entered using constant numbers 24-35; the annual average can be entered using number 36.

Relative Humidity, percent-- The user should specify the mean monthly daylight relative humidity using constant RHUMG. Monthly values can be entered using constant numbers 37-48; the annual average can be entered using number 49.

Atmospheric Turbidity, km-- The user should specify the mean atmospheric turbidity (in equivalent aerosol layer thickness, km) using constant ATURBG. Monthly values can be entered using constant numbers 50-61; the annual average can be entered using number 62.

Ozone Content, cm NTP-- The user should specify the mean ozone content (cm NTP) using constant OZONEG. Monthly values can be entered using constant numbers 63-74; the annual average can be entered using number 75.

Dissolved Organic Carbon, mg/L-- The user may specify segment variable dissolved organic carbon concentrations using parameter 6 - DOC. (Group G, Record 4, PARAM(I,6))

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Chlorophyll *a*, mg/L-- Time and segment variable phytoplankton chlorophyll *a* concentrations can be specified using parameter 10, CHPHL and time function 14, CHLN. If chlorophyll concentrations are to remain constant in time, the user should enter segment mean concentrations using parameter CHPHL. CHLN should be omitted.

The user may enter time-variable chlorophyll *a* concentrations via time function CHLN as a series of concentration versus time values. Parameter CHPHL will then represent the ratio of each segment concentration to the time function values. The product of CHPHL and the CHLN function gives the segment and time specific chlorophyll concentrations used by TOXI5. (Group G, Record 4, PARAM(I,10); Group I, Record 2, VALT(14,K)

Photolysis Option 2

In option 2, TOXI5 extrapolates either observed sunlight absorption rates or photolytic decay rates under "reference" conditions to ambient conditions. Required input data are described below.

Photolysis Option-- The user should select the photolysis option using constant XPHOTO: 0 = no photolysis; 1 = photolysis rates will be computed from molar absorptivity; 2 = photolysis rates will be extrapolated from measured surface rates. Use constant numbers 286, 886, and 1486 for chemicals 1, 2, and 3, respectively.

Measured Photolysis Rate, day^{-1}-- The user may specify the measured photolysis rate constant under reference conditions using constant KDPG. Values for the neutral molecule of chemicals 1, 2, and 3 can be entered using constants 291, 891, and 1491, respectively. Separate values can be entered for each ionic specie; constant numbers are listed in Part B of this document. If a reference first order rate constant is input, the quantum yield should be set to 1.0.

Measured Sunlight Absorption Rate, einstein/mole-day-- The user may specify measured sunlight absorption rates under reference conditions using constant KDPG. Values for the neutral molecule of chemicals 1, 2, and 3 can be entered using constants 291, 891, and 1491, respectively. Separate values can

be entered for each ionic specie; constant numbers are listed in Part B of this document. If a reference sunlight absorption rate is input, the corresponding quantum yield must be specified.

<u>Quantum Yield, moles/einstein</u>-- The user may specify reaction quantum yield values for each phase (dissolved, DOC-sorbed, sediment-sorbed) and each ionic specie using constant QUANTG. Constant numbers for the neutral molecule are summarized in Table 7.15. $QUANTG_{11}$ refers to the dissolved neutral chemical; $QUANTG_{21}$ refers to the DOC-sorbed neutral chemical; $QUANTG_{31}$ refers to the sediment-sorbed neutral chemical. Separate values can be entered for each ionic specie; constant numbers are listed in Part B of this document.

<u>Reference Latitude, degree and tenths</u>-- The user may specify the latitude at which the reference surface water photolytic rates were measured using constant RFLATG. Values for chemicals 1, 2, and 3 can be entered using constant numbers 288, 888, and 1488, respectively.

<u>Maximum Absorption Wavelength, nm</u>-- The user should specify the wavelength of maximum absorption using constant LAMAXG. Values for the neutral specie of chemicals 1, 2, and 3 can be entered using constants 296, 896, and 1496, respectively. Separate values can be entered for each ionic specie; constant numbers are listed in Part B of this document.

<u>Latitude, degrees and tenths</u>-- The user should specify the latitude of the waterbody using constant 4 - LATG.

<u>Cloud Cover, tenths</u>-- The user should specify the mean monthly or annual average cloud cover using constant CLOUDG. Monthly values can be entered using constant numbers 11-22; the annual average can be entered using number 23.

<u>Light Intensity</u>-- The user can specify time-variable normalized light intensity (dimensionless) using time function 15, PHTON. This function is used to adjust the measured rate constant under controlled reference light intensity to a predicted rate constant under ambient light intensity. The default value for this function is 1.0.

Light Extinction Coefficient, m^{-1}-- The user can specify
segment light extinction coefficients for the photochemically
active light using parameter 12, XKE2. When this number is
zero, the extinction coefficients are calculated from solids,
DOC and chlorophyll *a* concentrations for the wavelength of
maximum absorption. DOC and chlorophyll *a* are specified as
model parameters which may vary between segments and over time.
Their input is describe in the Photolysis Option 1 section
above. Light is set to zero under ice cover, which is assumed
when water temperatures reach 0 °C.

7.8 OXIDATION

Introduction

Chemical oxidation of organic toxicants in aquatic systems
can be a consequence of interactions between free radicals and
the pollutants. Free radicals can be formed as a result of
photochemical reactions. Free radicals that have received some
attention in the literature include alkylperoxy radicals, $RO_2 \cdot$;
OH radicals; and singlet oxygen.

Overview of TOXI5 Oxidation Reactions

In TOXI5, oxidation is modeled as a general second-order
process for the various species and phases of each chemical:

$$K_o = [RO_2] \sum_i \sum_j k_{oij} f_{ij} \qquad\qquad 7.68$$

where:

K_o =   net oxidation rate constant, day^{-1}

$[RO_2]$ =   molar concentration of oxidant, moles/L

k_{oij} =   second order oxidation rate constant for chemical
as specie i in phase j, L/mole-day

The reaction coefficients may be specified as constants, with activation energy constants left as 0. If the user wants TOXI5 to determine rates based on the temperature based Arrhenius function, then non-zero activation energies specified as constants will invoke the following calculation for each rate constant k:

$$k(T_K) = k(T_R) \exp[1000 \, E_{ao} (T_K - T_R)/(RT_K \, T_R)] \qquad\qquad \textbf{7.69}$$

where:

E_{ao} = Arrhenius activation energy for oxidation reaction, kcal/mole-°K

Activation energies may be specified for each ionic specie simulated. If no activation energies are given, then rate constants will not be adjusted to ambient water temperatures.

Because of the large number of alkylperoxy radicals that potentially exist in the environment, it would be impossible to obtain estimates of k_{ox} for each species. Mill et al. (1982) propose estimation of a rate coefficient using t-butyl hydroperoxide as a model oxidizing agent. They argue that other alkylperoxides exhibit similar reactivities to within an order of magnitude. The second-order rate coefficients are input to TOXI5 as constants.

In addition to estimating a rate coefficient, an estimate of free radical concentrations must be made to completely define the expression for free radical oxidation. Mill et al. (1982) report RO_2 concentrations on the order of 10^{-9} M and OH concentrations on the order of 10^{-17} M for a limited number of water bodies. Zepp and Cline (1977) report an average value on the order of 10^{-12} M for singlet oxygen in water bodies sampled. The source of free radicals in natural waters is photolysis of naturally occurring organic molecules. If a water body is turbid or very deep, free radicals are likely to be generated only near the air-water interface, and consequently, chemical oxidation will be relatively less important. In such cases, the concentrations cited above are appropriate in only the near-surface zones of water bodies. The molar oxidant

concentrations are input to TOXI5 using parameter OXRADG (ISEG).

<u>Implementation</u>

TOXI5 oxidation data specifications are summarized in Table 7.16. The water temperature and concentration of oxidants are input parameters, which may be specified for each model segment. The temperature may be time variable as well (input as a time series). If an activation energy is not supplied, no temperature corrections will be performed. Input data are described below.

Table 7.16 TOXI5 Oxidation Data.

Description	Notation	Range	Units
Oxidation rate constant for specie i, phase j	k_{oij}		L/mole-day
Activation energy for oxidation of specie i	E_{aoi}	15-25	kcal/mole °K
Water temperature	T	4-30	°C
Concentration of oxidants	$[RO_2]$	10^{-17}-10^{-8}	moles/L

<u>Oxidation Rate, L/mole-day</u>-- The user may specify second order oxidation rate constants for each phase (dissolved, DOC-sorbed, and sediment-sorbed) and each ionic specie using constant KOX20. Constant numbers for the neutral molecule are summarized in Table 7.17. $KOX20_{11}$ refers to the dissolved neutral chemical; $KOX20_{21}$ refers to the DOC-sorbed neutral chemical; $KOX20_{31}$ refers to the sediment-sorbed neutral chemical. Constant numbers for the ionic species are given in Part B of this document.

<u>Activation Energy, kcal/mole-°K</u>-- The user may specify activation energies for each chemical using constant EOX. Constant numbers are summarized in Table 7.17. If EOX is omitted or set to 0, oxidation rates will not be affected by temperature.

Reference Temperature,°C-- The user may specify the
reference temperature at which oxidation rates were measured
using constant TREFO. Constant numbers are summarized in Table
7.17. If a reference temperature is not supplied, then a
default of 20 °C is assumed.

Table 7.17 Oxidation Constants.

VARIABLE	C_1	C_2	C_3
TREFO	258	858	1458
$KOX20_{11}$	261	861	1461
$KOX20_{21}$	266	866	1466
$KOX20_{31}$	271	871	1471
EOX_1	276	876	1476

Oxidant Concentration, mole/L-- The user should specify
segment variable oxidant concentrations using parameter 13,
OXRAD. (Group G, Record 4, PARAM(I,13)

7.9   BIODEGRADATION

Introduction

Bacterial degradation, sometimes referred to as microbial
transformation, biodegradation or biolysis, is the breakdown of
a compound by the enzyme systems in bacteria. Examples are
given in Figure 7.6. Although these transformations can
detoxify and mineralize toxins and defuse potential toxins, they
can also activate potential toxins.

Biodegradation encompasses the broad and complex processes
of enzymatic attack by organisms on organic chemicals.
Bacteria, and to a lesser extent fungi, are the mediators of
biological degradation in surface water systems.
Dehalogenation, dealkylation, hydrolysis, oxidation, reduction,

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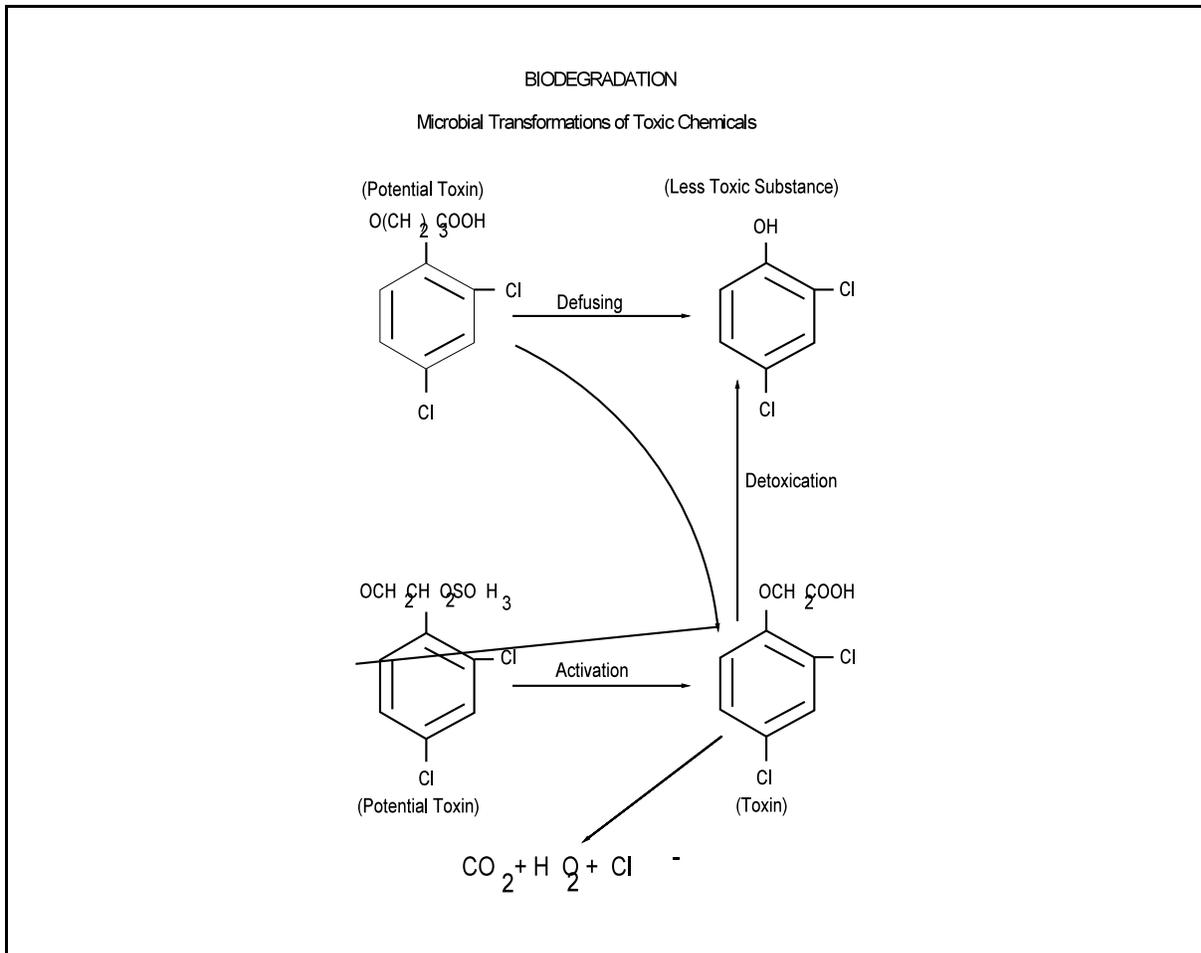
Figure 7.6 Microbial transformations of toxic chemicals (Alexander 1980).

ring cleavage, and condensation reactions are all known to occur

either metabolically or via organisms that are not capable of utilizing the chemical as a substrate for growth.

Two general types of biodegradation are recognized--growth metabolism and cometabolism. Growth metabolism occurs when the organic compound serves as a food source for the bacteria. Adaptation times from 2 to 20 days were suggested in Mills et al., 1985. Adaptation may not be required for some chemicals or in chronically exposed environments. Adaptation times may be lengthy in environments with a low initial density of degraders (Mills et al., 1985). For cases where biodegradation is limited by the degrader population size, adaptation is faster for high initial microbial populations and slower for low initial populations. Following adaptation, biodegradation proceeds at

fast first-order rates. Cometabolism occurs when the organic
compound is not a food source for the bacteria. Adaptation is
seldom necessary, and the transformation rates are slow compared
with growth metabolism.

The growth kinetics of the bacterial population degrading a
toxic chemical are not well understood. The presence of
competing substrates and of other bacteria, the toxicity of the
chemical to the degrading bacteria, and the possibilities of
adaptation to the chemical or co-metabolism make quantification
of changes in the population difficult. As a result, toxic
chemical models assume a constant biological activity rather
than modeling the bacteria directly. Often, measured first
order biodegradation rate constants from other aquatic systems
are used directly.

Overview of TOXI5 Biodegradation Reactions

In TOXI5, first order biodegradation rate constants or half
lives for the water column and the benthos may be specified. If
these rate constants have been measured under similar
conditions, this first order approach is likely to be as
accurate as more complicated approaches. If first order rates
are unavailable, or if they must be extrapolated to different
bacterial conditions, then the second-order approach may be
used. It is assumed that   bacterial populations are unaffected
by the presence of the compound at low concentrations.
Second-order kinetics for dissolved, DOC-sorbed, and sediment-
sorbed chemical are considered:

$$K_{Bw} = P_{bac}(t) \sum_i \sum_j k_{Bij} f_{ij} \qquad j = 1,2 \qquad\qquad \textbf{7.70}$$

$$K_{Bs} = P_{bac}(t) \sum_i \sum_j k_{Bij} f_{ij} \qquad j = 3 \qquad\qquad \textbf{7.71}$$

where:

K_{Bw} =   net biodegradation rate constant in water, day^{-1}

K_{Bs} =   net biodegradation rate constant on sediment, day^{-1}

k_{Bij} =   second order biodegradation rate constant for specie i, phase j, ml/cell-day

$P_{bac}(t)$ =   active bacterial population density in segment, cell/ml

f_{ij} =   fraction of chemical as specie i in phase j

In TOXI5, the biodegradation rate may be adjusted by temperature as shown below

$$k_{Bij}(T) = k_{Bij} \, Q_{Tij}^{(T-20)/10} \qquad\qquad \textbf{7.72}$$

where:

Q_{Tij} =   "Q-10" temperature correction factor for biodegradation of specie i, phase j

T =   ambient temperature in segment, °C

The temperature correction factors represent the increase in the biodegradation rate constants resulting from a 10°C temperature increase. Values in the range of 1.5 to 2 are common.

Environmental factors other than temperature and population size can limit bacterial rates. Potential reduction factors must be considered externally by the user. Nutrient limitation can be important in oligotrophic environments.

Low concentrations of dissolved oxygen can also cause reductions in biodegradation rates and this effect is not simulated in TOXI5. Below DO concentrations of about 1 mg/L, the rates start to decrease. When anoxic conditions prevail, most organic substances are biodegraded more slowly. Because biodegradation reactions are generally more difficult to predict than physical and chemical reactions, site-specific calibration becomes more important.

Biodegradation can be implemented using segment variable first order rate constants rather than bacterial populations. If first order rate constants are input for P_{bac}, then second order rate constants k_{Bij} should be set to 1.0 in equations 7.71 and 7.72.

Table 7.18 TOXI5 Bacterial Degradation Data.

Description	Notation	Common Range	Units
Observed first order degradation rate in water column	K_{Bw}	0-0.5	day^{-1}
Observed first order degradation rate in benthos	K_{Bs}	0-0.5	day^{-1}
Bacterial activity or concentration of bacterial agent	P_{bac}	10^2-10^7	cells/mL
Observed second-order rate coefficients for specie i	k_{Bij}	0-10^{-6}	mL/cell-day
Biodegradation temperature coefficients for specie i, phase j	Q_{Tij}	1.5-2.5	-
Water temperature	T	4-30	°C

<u>Implementation</u>

TOXI5 biodegradation data specifications are summarized in Table 7.18. The second order rate constants for water and for bed segments can be specified as constants. Temperature correction factors can be left at 0. If the user wants TOXI5 to correct the rate constants for ambient segment temperatures, then nonzero temperature correction factors should specified as

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constants. User input for implementing biodegradation is given below.

First Order Rates, day^{-1}-- The user may specify first order biodegradation rate constants for water column and benthic segments using constants KBW and KBS. If nonzero values are specified for these constants, they will be used directly, bypassing second order calculations. Constant numbers are given in Table 7.19.

Table 7.19 Biodegradation Constants.

VARIABLE	C_1	C_2	C_3
KBW	141	741	1341
KBS	142	742	1342
$KBIO2O_{11}$	146	746	1346
$KBIO2O_{21}$	151	751	1351
$KBIO2O_{31}$	156	756	1356
$Q10DIS_1$	161	761	1361
$Q10DOC_1$	166	766	1366
$Q10PAR_1$	171	771	1371

Second Order Rate Coefficients, mL/cell-day-- The user may specify second order biodegradation rate constants for each phase (dissolved, DOC-sorbed, and sediment-sorbed) and each ionic specie using constant KBIO2O. Constant numbers for the neutral molecule are summarized in Table 7.19. $KBIO2O_{11}$ refers to the dissolved neutral chemical; $KBIO2O_{21}$ refers to the DOC-sorbed neutral chemical; $KBIO2O_{31}$ refers to the sediment-sorbed neutral chemical. Constant numbers for the ionic species are given in Part B of this document.

Temperature Coefficients-- The user may specify temperature correction factors for the dissolved, DOC-sorbed, and sediment-sorbed phase of each chemical using constants Q10DIS, Q102DOC, and Q10PAR, respectively. These constants represent the

multiplication factor for biodegradation rates corresponding to a 10 °C temperature increase. Constant numbers are summarized in Table 7.19. If Q10 values are omitted or set to 0, biodegradation rates will not be affected by temperature.

   Bacterial Population Levels, cell/mL-- The user may specify segment and time variable bacterial concentrations using parameter 14, BAC, and time funcions 16 and 17, BACNW and BACNS. Typical population size ranges are given in Table 7.20.

If bacterial concentrations are to remain constant in time, the user should enter segment mean concentrations using parameter BAC. BACNW and BACNS should be omitted.

   The user may enter time-variable water column and benthic bacterial concentrations via time functions BACNW and BACNS, respectively, as a series of concentration versus time values. Parameter BAC will then represent the ratio of each segment concentration to the time function values. The product of BAC and the BACNW or BACNS function gives the segment and time specific bacterial concentrations used by TOXI5. (Group G, Record 4, PARAM(I,14); Group I, Record 2, VALT(16,K), VALT(17,K))

7.10   EXTRA REACTION

Introduction.

   An extra second-order reaction is included in TOXI5. The second order reaction allows the user to simulate the effect of processes not considered by TOXI5. The reaction depends upon a rate constant and an environmental parameter which may be taken to represent, for example, some reducing or oxidizing agent. The rate of reaction may also vary with temperature.

Overview of TOXI5 Extra Reaction

   TOXI5 allows the user to specify an additional second order reaction for the various species and phases of each chemical:

$$K_E = [E] \sum_i \sum_j k_{eij} f_{ij}$$ **7.73**

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Table 7.20 Size of Typical Bacterial Populations in Natural Waters.

Water Body Type	Bacterial Numbers (cells/ml)	Ref.
Oligotrophic Lake	50 - 300	a
Mesotrophic Lake	450 - 1,400	a
Eurtophic Lake	2000 - 12,000	a
Eutrophic Reservoir	1000 - 58,000	a
Dystrophic Lake	400 - 2,300	a
Lake Surficial Sediments	8×10^9 - 5×10^{10} cells/100 g dry wt	a
40 Surface Waters	500 - 1×10^6	b
Stream Sediments	10^7 - 10^8 cells/100 g	c
Rur River (winter)	3×10^4	d

References:

[a]Wetzel (1975). Enumeration techniques unclear

[b]Paris et al (1981). Bacterial enumeration using plate counts.

[c]Herbes & Schwall (1978). Bacterial enumeration using plate counts.

[d]Larson et al. (1981). Bacterial enumeration using plate counts.

where:

K_E = net extra reaction rate constant, day^{-1}

[E] = intensity of environmental property driving this reaction

k_{eij} = second order rate constant for chemical as specie in phase j, in $[E]^{-1}$ day^{-1}

f_{ij} = fraction of chemical as specie i in phase j

The reaction coefficients may be specified as constants, with activation energy constants left as 0. If the user wants TOXI5 to determine rates based on the temperature based Arrhenius function, then non-zero activation energies specified as constants will invoke the following calculation for each rate constant k:

$$k_e(T_K) = k_e(T_R) \exp[1000 \, E_{ae}(T_K - T_R)/(RT_K T_R)] \qquad 7.74$$

where:

E_{ae} = Arrhenius activation energy for extra reaction, kcal/mole-°K

Activation energies may be specified for each ionic specie simulated. If no activation energies are given, then rate constants will not be adjusted to ambient water temperatures.

An example of a kinetic process that may be modeled as this extra reaction is reduction. If reduction is modeled, [E] may be interpreted as the concentration of environmental reducing agents RH_2, so that

$$C + RH_2 \rightarrow P \qquad 7.75$$

and

[E] = concentration of RH_2, moles/L

k_e = second order rate constant, L/mole-day

P   =   reduced product

        The identity of the reducing agent and the second order
rate constant must be identified and quantified by laboratory
kinetics studies. If both the environmental oxidizing and
reducing agents are in excess, then two chemicals may be
simulated as a redox pair:

$$C_1 + RO_2 \rightleftharpoons C_2 + RH_2$$ **7.76**

where:

        C_1 =   reduced chemical

        C_2 =   oxidized chemical

        RO_2 =   oxidizing agent

        RH_2 =   reducing agent

        Laboratory kinetics studies can control the concentrations
of RO_2 and RH_2 to determine rate constants for both oxidation and
reduction. These may be specified as constants k_{ox} and k_E.
Yield coefficients Y_{012} and Y_{E21} must also be specified as
constants. The spatially variable concentrations $[RO_2]$ and $[RH_2]$
must be specified as parameters.

Implementation

        The input data requirements for the second order reactions
include the second order reaction rate constants which may be
specified for each specie and sorbed form (dissolved, DOC sorbed
and sorbed to particulate). If the rates are to be temperature
corrected, then the user may supply the reference temperature at
which the extra reaction rates were measured and the activation
energy for the reaction. The rates will then be adjusted using
a temperature-based Arrhenius function. If an activation energy
is not supplied, no temperature corrections will be performed.
The "extra" property of the aquatic environment that affects the
extra reaction is specified to the model as a parameter which

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may vary between segments. The units of the "extra" property
must be consistent with those used for the second-order rate
constant. The product of the extra property and second-order
rate constant must have units of day^{-1}. The temperature may be
time variable as well (input as a time series). Input data are
described below.

Extra Reaction Rate, L/mole-day-- The user may specify
second order extra rate constants for each phase (dissolved,

Table 7.21 Extra Reaction Constants.

VARIABLE	C_1	C_2	C_3
TREFE	573	1173	1773
$KE20_{11}$	576	1176	1776
$KE20_{21}$	581	1181	1781
$KE20_{31}$	586	1186	1786
EEX_1	591	1191	1791

DOC-sorbed, and sediment-sorbed) and each ionic specie using
constant KE20. Constant numbers for the neutral molecule are
summarized in Table 7.21. $KE20_{11}$ refers to the dissolved neutral
chemical; $KE20_{21}$ refers to the DOC-sorbed neutral chemical;
$KE20_{31}$ refers to the sediment-sorbed neutral chemical. Constant
numbers for the ionic species are given in Part B of this
document.

Activation Energy, kcal/mole-°K-- The user may specify
activation energies for each chemical using constant EEX.
Constant numbers are summarized in Table 7.21. If EEX is
omitted or set to 0, oxidation rates will not be affected by
temperature.

Reference Temperature,°C-- The user may specify the
reference temperature at which oxidation rates were measured
using constant TREFE. Constant numbers are summarized in Table
7.21. If a reference temperature is not supplied, then a
default of 20 °C is assumed.

<u>Extra Environmental Concentration, mole/L</u>-- The user should specify segment variable extra environmental concentrations using parameter 15, EXENV. (Group G, Record 4, PARAM(I,15)

REFERENCES

Alexander, M.   1980. Biodegradation of Toxic Chemicals in Water and Soil. In: Dynamics, Exposure, and Hazard Assessment of Toxic Chemicals, R. Haque, editor. Ann Arbor Science, Ann Arbor, MI.

Ambrose, R.B.   1987. Modeling Volatile Organics in the Delaware Estuary. American Society of Civil Engineers. Journal of Environmental Engineering, V. 113, No. 4, pp 703-721.

Ambrose, R.B. et al.   1988. WASP4, A Hydrodynamic and Water Quality Model--Model Theory, User's Manual, and Programmer's Guide. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-87-039.

APHA (American Public Health Association).   1985. Standard Methods for the Examination of Water and Wastewater, 15th Edition. APHA. Washington, DC.

Bannister, T.T. 1974a. Production Equations in Terms of Chlorophyll Concentration, Quantum Yield, and Upper Limit to Production. Limnol. Oceanogr. 19:1-12.

Bannister, T.T. 1974b. A General Theory of Steady State Phytoplankton Growth in a Nutrient Saturated Mixed Layer. Limnol. Oceanogr. 19:13-30.

Barber, M.C., L.A. Suarez, and R.R. Lassiter.   1991. Modelling Bioaccumulation of Organic Pollutants in Fish with an Application to PCBs in Lake Ontario Salmonids. Canadian J. Fisheries and Aquatic Sciences. Vol. 48, pp. 318-337.

Bella, D.A. and W.J. Grenney.   1970. Finite-Difference Convection Errors. Journal of the Sanitary Engineering Division, ASCE, Vol. 96, No. SA6, pp. 1361-1375.

Berner, R.A.   1974. Kinetic Models for the Early Digenesis of Nitrogen Sulfur, Phosphorus, and Silicon in Anoxic Marine Sediments. In: The Sea, Vol. 5, ed. E.D. Goldberg. J. Wiley and Sons. New York.

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Bowie, G.L., W.B. Mills, D.B. Porcella, C.L. Campbell, J.R. Pagenkopf, G.L. Rupp, K.M. Johnson, P.W.H. Chan, S.A. Gherini and C.E. Chamberlin. 1985. Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling. Second Edition. U.S. Environmental Protection Agency Athens, GA. EPA-600/3-85-040.

Brown, L.C. and T.O. Barnwell. 1987. The Enhanced Stream Water Quality Models QUAL2E and QUAL2E-UNCAS: Documentation and User Manual. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-87-007.

Brown, L.C. 2002. Addendum to The Enhanced Stream Water Quality Models QUAL2E and QUAL2E-UNCAS: Documentation and User Manual. Tufts University, Medford, Massachusetts.

Burns, L.A., D.M. Cline, and R.R. Lassiter. 1982. Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation, U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-82-023.

Burns, L.A. and D.M. Cline. 1985. Exposure Analysis Modeling System, Reference Manual for EXAMS II. U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-85-038.

Cerco, C.F. and M. Meyers, 2000. Tributary refinements to Chesapeake Bay model. *Journal of Environmental Engineering, ASCE,* Volume 124, Number 2, Pages 164-174.

Cerco, C.F. and S.P. Seitzinger, 1997. Measured and modeled effects of benthic algae on eutrophication in Indian River Rehoboth Bay, Delaware. *Estuaries*, Volume 20, Number 1, Pages 231-248.

Collins, C. and J.H. Wlosinski, 1989. A macrophyte submodel for aquatic ecosystems. *Aquatic Botany,* Volume 33, Pages 191-206.

Connolly, J.P. and R. Winfield. 1984. A User's Guide for WASTOX, a Framework for Modeling the Fate of Toxic Chemicals in

Aquatic Environments. Part 1: Exposure Concentration. U.S. Environmental Protection Agency, Gulf Breeze, FL. EPA-600/3-84-077.

Connolly, J.P. and R.V. Thomann. 1985. WASTOX, A Framework for Modeling the Fate of Toxic Chemicals in Aquatic Environments. Part 2: Food Chain. U.S. Environmental Protection Agency, Gulf Breeze, FL and Duluth, MN. Covar, A.P. 1976. Selecting the Proper Reaeration Coefficient for Use in Water Quality Models. Presented at the U.S. EPA Conference on Env. Simulation and Modelling.

Cosby, B.J. and G.M. Hornberger, 1984. Identification of photosynthesis-light model for aquatic systems. I. Theory and simulations. *Ecological Modelling,* Volume 22, Pages 1-24.

Cosby, B.J., G.M. Hornberger, and M.G. Kelly, 1984. Identification of photosynthesis-light model for aquatic systems. II. Application to a macrophyte dominated stream. *Ecological Modelling,* Volume 22, Pages 25-51.

Cosgrove, J.F. and C.C. Obropta, 1995. Modeling the Impact of Macrophytes on Instream Dissolved Oxygen Dynamics in the Pennsauken Watershed. In: Integrated Water Resources Planning for the 21st Century, Proceedings of the 22nd Annual Conference, Cambridge, MA, USA, May 7-11, 1995, pp. 504-507, American Society of Civil Engineers, New York.

Covar, A.P. 1976. Selecting the Proper Reaeration Coefficient for Use in Water Quality Models. Presented at the U.S. EPA Conference on Environmental Simulation Modeling, April 19-22, 1976. Cincinnati, Ohio.

Di Toro, D.M., D.J. O'Connor, and R.V. Thomann. 1971. A Dynamic Model of the Phytoplankton Population in the Sacramento San Joaquin Delta. Adv. Chem. Ser. 106, Am. Chem. Soc., Washington, DC., pp. 131-180.

Di Toro, D.M. and J.P. Connolly. 1980. Mathematical Models of Water Quality in Large Lakes, Part 2: Lake Erie. EPA-600/3-80-065. pp. 90-101.

Di Toro, D.M. and W.F. Matystik. 1980. Mathematical Models of Water Quality in Large Lakes, Part 1: Lake Huron and Saginaw Bay. EPA-600/3-80-056. pp. 28-30.

Di Toro, D.M., J.J. Fitzpatrick, and R.V. Thomann. 1981, rev. 1983. Water Quality Analysis Simulation Program (WASP) and Model Verification Program (MVP) - Documentation. Hydroscience, Inc., Westwood, NY, for U.S. EPA, Duluth, MN, Contract No. 68-01-3872.

Di Toro, D.M. 1985. A Particle Interaction Model of Reversible Organic Chemical Sorption, Chemosphere 14(10):1503-1538.

Eppley, R.W. and P.R. Sloane. 1966. Growth Rates of Marine Phytoplankton: Correlation with Light Absorption by Cell Chlorophyll **a**. Physiol. Plant. 19:47-59.

Foree, E.C. and P.L. McCarty. 1970. Anaerobic Decomposition of Algae. Environ. Sci. & Technol. 4(10), pp. 842-849.

Graf, W.H. 1971. Hydraulics of Sediment Transport. McGraw-Hill, New York.

Green, A.E.S., K.R. Cross, and L.A. Smith. 1980. Improved Analytical Characterization of Ultraviolet Skylight, Photochem. and Photobio. 31:59-65.

Hendry, G.S. 1977. Relationships Between Bacterial Levels and Other Characteristics of Recreational Lakes in the District of Muskoka. Interim Microbiology Report, Laboratory Services Branch, Ontario Ministry of the Environment.

Henrici, Arthur T., 1938. Seasonal Fluctuation of Lake Bacteria in Relation to Plankton Production. J. Bacteriol., 35:129-139.

Herbes, S.E. and L.R. Schwall. 1978. Microbial Transformation of Polycyclic Aromatic Hydrocarbons in Pristine and Petroleum-Contaminated Sediments. Appl. and Environ. Microbiology, Volume 35, No. 2. pp. 306-316.

Hutchinson, G.E. 1967. A Treatise on Limnology. Vol. II. Introduction to Lake Biology and Limnoplankton. Wiley. New York. pp. 306-354.

Janse, J.H., 1998. A model of ditch vegetation in relation to eutrophication. *Water Science & Technology*, Volume 37, Number 3, Pages 139-149.

Jewell, W.J. And P.L. McCarty. 1971. Aerobic Decomposition of Algae. Environ. Sci. Technol. 1971. 5(10). p. 1023.

JRB, Inc. 1984. Development of Heavy Metal Waste Load Allocations for the Deep River, North Carolina. JRB Associates, McLean, VA, for U.S. EPA Office of Water Enforcement and Permits, Washington, DC.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Res. 13:241-248.

Karickhoff, S.W. 1984. Organic Pollutant Sorption in Aquatic Systems. J. Hydraul. Eng. Div. ASCE. Vol. 110, p. 707.

Karickhoff, S.W. and K.R. Morris. 1985. Sorption Dynamics of Hydrophobic Pollutants in Sediment Suspensions. Environ. Toxicology and Chem. 4:469-479.

Kemp, W.M., W.R. Boynton, and A.J. Hermann, 1995. Simulation models of an estuarine macrophyte ecosystem. In B.C. Patten (editor), *Complex Ecology*, Pages 262-277, Prentice Hall, Englewood Cliffs, NJ, USA.

Kok, B. 1960. Efficiency of Photosynthesis. In: W. Ruhland (Edisor), Hanbuch der Pfanzenphysiologie. Vol 5, Part 1. Springer, Berlin. pp. 563-633.

Larson, R.J. G.G. Clinckemaillie, and L. VanBelle. 1981. Effect of Temperature and Dissolved Oxygen on Biodegradation of Nitrilotriacetate. Water Research, Volume 15. pp. 615-620.

Lau, Y.L., 1990. Modelling the consumption of dissolved contaminants by biofilm periphyton in open-channel flow. *Water Research*, Volume 24, Number 10, Pages 1269-1274. October 1990.

Leopold, L.B. and T. Maddox. 1953. The Hydraulic Geometry of Stream Channels and Some Physiographic Implications, Professional Paper 252, U.S. Geological Survey, Washington, DC.

Leopold, L.B., M.B. Wolman and J.P. Miller. 1964. Fluvial Processes in Geomorphology, W. H. Freeman and Co., San Francisco, CA.

Lowe, W.E. 1976. Canada Centre for Inland Waters 867 Lakeshore Road, Burlington, Canada L7R 4A6. Personal communication.

Mackay, D. and P.J. Leinonen. 1975. Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmospheres. Environ. Sci. Technology. 7:611-614.

Mackay, D. and W.Y. Shiu. 1984. Physical-Chemical Phenomena and Molecular Properties, in Gas Transfer at Water Surfaces. Brutsaert, W. and G.H. Jirka, Eds. D. Reidel, Boston.

Madden, C.J. and W.M. Kemp, 1996. Ecosystem Model of an Estuarine Submersed Plant Community: Calibration and Simulation of Eutrophication Responses. *Estuaries* Volume 19, Number 2B, Pages 457-474.

McIntire, C.D., 1973. Periphyton dynamics in laboratory streams: A simulation model and its implications. *Ecological Monographs*, Volume 43, Number 3, Pages 399-420, Summer 1973.

Menon, A.S., W.A. Gloschenko, and N.M. Burns. 1972. Bacteria-Phytoplankton Relationships in Lake Erie. Proc. 15th Conf. Great Lakes Res. 1972:94:101. Inter. Assoc. Great Lakes Res.

Mill, T., W.R. Mabey, P.C. Bomberger, T.W. Chou, D.G. Herdry, and J.H. Smith. 1982. Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water. U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-82-0220.

Mills, W.B., D.B. Porcella, M.J. Ungs, S.A. Gherini, K.V. Summers, Lingfung Mok, G.L. Rupp, G.L. Bowie, and D.A. Haith. 1985. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants, Parts 1 and 2. U.S. Environmental Protection Agency, Athens, GA. EPA-600/6-85-002a and b.

Muhammetoðlu, A. and S. Soyupak, 2000. A three-dimensional water quality-macrophyte interaction model for shallow lakes. *Ecological Modelling,* Volume 133, Pages 161-180.

Nriagu, J.O. 1972. Stability of Vivianite and Ion-Pair Formation in the System $Fe_3(PO_4)_2-H_3PO_4H_2O$. Geochim. Cosmochim Acta. 36. p. 459.

O'Connor. D.J. and R.V. Thomann. 1972. Water Quality Models: Chemical, Physical and Biological Constituents. In: Estuarine Modeling: An Assessment. EPA Water Pollution Control Research Series 16070 DZV, Section 702/71. pp. 102-169.

O'Connor, D.J., J.A. Mueller, and K.J. Farley. 1983. Distribution of Kepone in the James River Estuary. Journal of the Environmental Engineering Division, ASCE. 109(EE2):396-413.

O'Connor, D.J. 1983. Wind Effects on Gas-Liquid Transfer Coefficients. Journal of Environmental Engineering, Volume 109, Number 9, pp. 731-752.

Paris, D.F., W.C. Steen, G.L. Baughman and J.T. Barnett, Jr. 1981. Second-Order Model to Predict Microbial Degradation of Organic Compounds in Natural Waters. Applied and Environmental Microbiology. 4(3):603-609.

Rao, S.S. 1976. Observations on Bacteriological Conditions in the Upper Great Lakes. 1968-1974. Scientific Series. No. 64. Inland Waters Directorate CCIW Branch, Burlington, Ontario.

Rao, P.S.C. and J.M. Davidson. 1980. Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollution Models. Environmental Impact of Nonpoint Source Pollution. Ann Arbor Science, Ann Arbor, MI. pp. 23-67.

Rauch, W. and P.A. Vanrolleghem, 1998. Modelling benthic activity in shallow eutrophic rivers. *Water Science & Technology*, Volume 37, Number 3, Pages 1129-137.

Riley, G.A., H. Stommel and D.F. Bumpus. 1949. Quantitative Ecology of the Plankton of the Western North Atlantic. Bull. Bingham Oceanog. Coll. 12(3):1-169.

Robinson, N., ed. 1966. Solar Radiation. Elsevier Publishing, Amsterdam, London, and New York. 347 pp.

Rutherford, J.C., M.R. Scarbrook, and N. Beoekhuizen, 2000. Grazer control of stream algae: Modeling temperature and flood effects. *Journal of Environmental Engineering, ASCE,* Volume 126, Number 4, Pages 331-339, April 2000.

Smith, E.L. 1936. Photosynthesis in relation to light and carbon dioxide. National Academy of Sciences Proceedings. Volume 22, pp. 504-511.

Smith, R.A. 1980. The Theoretical Basis for Estimating Phytoplankton Production and Specific Growth Rate from Chlorophyll, Light and Temperature Data. Ecological Modeling. 10. pp. 243-264.

Steele, J.H. 1962. Environmental Control of Photosynthesis in the Sea. Limnol. Oceanogr. 7:137-150.

Streeter, H.W. and E.B. Phelps. 1925. A Study of the Pollution and Natural Purification of the Ohio River, III, Factors Concerned in the Phenomena of Oxidation and Reaeration. U.S. Public Health Service, Public Health Bulletin No. 146, 75 pp. Reprinted by U.S. DHEW, PHA, 1958.

Thomann, R.V. 1975. Mathematical Modeling of Phytoplankton in Lake Ontario, 1. Model Development and Verification. U.S. Environmental Protection Agency, Corvallis, OR. EPA-600/3-75-005.

Thomann, R.V., R.P. Winfield, D.M. Di Toro, and D.J. O'Connor. 1976. Mathematical Modeling of Phytoplankton in Lake Ontario, 2. Simulations Using LAKE 1 Model. U.S. Environmental Protection Agency, Grosse Ile, MI, EPA-600/3-76-065.

Thomann, R.V., R.P. Winfield, and J.J. Segna. 1979. Verification Analysis of Lake Ontario and Rochester Embayment Three Dimensional Eutrophication Models. U.S. Environmental Protection Agency, Grosse Ile, MI, EPA-600/3-79-094.

Thomann, R.V. and J.J. Fitzpatrick. 1982. Calibration and Verification of a Mathematical Model of the Eutrophication of the Potomac Estuary. Prepared for Department of Environmental Services, Government of the District of Columbia, Washington, D.C.

TDNR, 1985. QUAL-TX User's Manual, Version 3.1. Texas Department of Water Resources, Austin, Texas. July 24, 1985.

Tsivoglou, E.E. and J.R. Wallace. 1972. Characterization of Stream Reaeration Capacity. U.S. Environmental Protection Agency, Washington, DC EPA-R3-72-012.

Uehlinger, U., H. Bührer, and P. Reichert, 1996. Periphyton dynamics in a floodprone prealpine river: Evaluation of significant processes by modelling. *Freshwater Biology*, Volume 36, Pages 249-263.

Warburg, O. and E. Negelein. 1923. Uber den einfluss der Wellenlange auf den Energieumsatz bei der Kohlensaureassimilation. A. Phys. Chem. 106:191-218.

Weast, R.C., and M.J. Astle, ed. 1980. CRC Handbook of Chemistry and Physics. CRC Press, Boca Raton, FL.

Welch, E.B., R.R. Horner, and C.B. Patmont, 1989. Prediction of nuisance periphytic biomass: a management approach. *Water Research*, Volume 23, Number 4, Pages 401-405. April 1989.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co. Philadelphia. 743 pp.

Whitman, R.G. 1923. A Preliminary Experimental Confirmation of the Two-Film Theory of Gas Absorption. Chem. Metallurg. Eng. 29:146-148.

Wiland, B.L. and K. LeBlanc, 2000. LA-QUAL for Windows, User's Manual, Model Version 3.02, Manual Rev. B. Louisiana Department of Environmental Quality, Baton Rouge, Louisiana.

Wischmeier, W.H. and D.D. Smith. 1978. Predicting Rainfall Erosion Losses - A Guide to Conservation Planning. Agriculture Handbook No. 537. U.S. Dept. of Agriculture, Washington, DC.

Wolfe, N.L. 1980. Determining the Role of Hydrolysis in the Fate of Organics in Natural Waters. pp. 163-178 in R. Haque

(Ed.) Dynamics, Exposure, and Hazard Assessment of Toxic
Substances. Ann Arbor Science Publishers, Ann Arbor.

Wright, R.M. and A.J. McDonnell, 1986a. Macrophyte growth in
shallow streams: field investigations. *Journal of Environmental
Engineering, ASCE,* Volume 112, Number 5, Pages 953-966.

Wright, R.M. and A.J. McDonnell, 1986b. Macrophyte growth in
shallow streams: biomass model. *Journal of Environmental
Engineering, ASCE,* Volume 112, Number 5, Pages 967-982.

Zepp, R.G. and D.M. Cline. 1977. Rates of Direct Photolysis in
Aquatic Environment. Environ. Sci. Technol. 11:359-366.