# 1. Simple Toxicants

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 indigenous 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 WASP6, 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. WASP6 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 WASP6 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, WASP6 can be used as a first-order water pollutant model to conduct simulations of dye tracers, salinity intrusion, or coliform die-off.

**Table 1-1 Overview of Simple WASP6 Toxicants**

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

Simple toxicants and associated solids are simulated using the TOXI program. TOXI simulates the transport and transformation of one to three chemicals and one to three types of particulate material (solids classes, Table 1-1). 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 2.

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.

WASP6 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 **Error! Reference source not found.**.

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.

Some limitations should be kept in mind when applying TOXI. 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.

**Table 1-2 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. $M_j = m_j \cdot 10^{-6}$ | $kg_s/L$ |
| $M'_{sj}$ | 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" | - |

In TOXI, it is convenient to define concentration related symbols as in Table 1-2. Please note that in the general development of the equations below, subscripts "i" and "j" are sometimes omitted for convenience.

## 1.1.   Simple Transformation Kinetics

TOXI 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 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 2. For example, the user may specify a first-order rate for biodegradation and have TOXI compute a loss rate for volatilization.

### 1.1.1. Option 1: Total Lumped First Order Decay

The simplest rate expression allowed by TOXI 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.

**Equation 1-1**

$$\frac{\partial C_{ij}}{\partial t}\Big|_{reaction} = K_{ij}\, C_{ij}$$

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.

### 1.1.2. 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

**Equation 1-2**

$$\frac{\partial C_{ij}}{\partial t}\Big|_{reaction} = \sum_{k=1}^{N} K_{ki}\, C_{ij}$$

where:

$K_{ki}$ = 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:

**Equation 1-3**

$$K_{ki} = 0.693\,/\,T_{Hki}$$

where:

$T_{Hki}$ = half-life of reaction k for chemical i, days.

## 1.2. 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:

**Equation 1-4**

$$C_{s'} = K_{ps} \bullet C_{w'}$$

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

**Equation 1-5**

$$f_D = \frac{n}{n + \sum_s K_{ps} \bullet M_s}$$

and

**Equation 1-6**

$$f_s = \frac{K_{ps} \bullet M_s}{n + \sum_s K_{ps} \bullet M_s}$$

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:

**Equation 1-7**

$$C_{wij} = C_{ij} \bullet f_{Dij}$$

**Equation 1-8**

$$C_{sij} = C_{ij} \bullet f_{sij}$$

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. TOXI 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.

## 1.3. Transformations and Daughter Products

The three chemicals that may be simulated by TOXI 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:

**Equation 1-9**

$$S_{kc1} = \sum_c \sum_k K_{kc} C_c Y_{kc1}, \quad c = 2, 3$$

**Equation 1-10**

$$S_{kc2} = \sum_c \sum_k K_{kc} C_c Y_{kc2}, \quad c = 1, 3$$

**Equation 1-11**

$$S_{kc3} = \sum_c \sum_k K_{kc} C_c Y_{kc3}, \quad c = 1, 2$$

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," $mg_i/mg_c$

0 illustrates some of the linked reactions that can be simulated by specifying appropriate yield coefficients.

==Potential reaction products in WASP==

## 1.4. Model Implementation

To simulate simple toxicants with WASP6, use the preprocessor to create a TOXI 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 WASP6, 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.

### 1.4.1. Model Input Parameters

This section summarizes the input parameters that must be specified in order to solve the simple toxicant equations in TOXI. The user is referred to Chapter 3 for a summary of input parameters for the sediment balance equations. Input parameters are prepared for WASP6 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.

### 1.4.2. 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.

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.

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.

## 1.4.3. 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.

Water Column Flows, $m^3$/sec-- Time variable water column flows can be specified, as detailed in Chapter **Error! Reference source not found.**.

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.

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.

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.

Water Column Dispersion, $m^3$/sec-- Time variable water column dispersion can be specified, as detailed in Chapter 2.

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.

<u>Cross-Sectional Areas, m$^2$</u>-- 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.

<u>Characteristic Mixing Lengths, m</u>-- 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.

## 1.4.4. 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 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.

<u>Waste Loads, kg/day</u>-- 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.

<u>Solids Transport Field</u>-- The transport field associated with total solids or each solids type must be specified under initial conditions.

<u>Solid Density, g/cm$^3$</u>-- 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.

<u>Initial Concentrations, mg/L</u>-- 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.

<u>Dissolved Fraction</u>-- 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.

## 1.4.5. 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.

<u>First-Order Degradation</u>-- There are two options to input first-order toxicant degradation:

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.

Option 2: Individual First Order Transformation

| 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 | |

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.

Partition Coefficients-- TOXI allows the input of either a single constant partition coefficient, or a set of spatially-variable partition coefficients:

Option 1: Constant Partition Coefficient.

| | $C_1$ | $C_2$ | $C_3$ |
|---|---|---|---|
| Solids 1 | 111 | 711 | 1311 |
| Solids 2 | 116 | 716 | 1316 |
| Solids 3 | 121 | 721 | 1321 |

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 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.

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.

| 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 | | |

<u>Reaction Yields</u>-- 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.

## 2. Organic Chemicals

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. WASP6 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.

WASP6 allows the simulation of a variety of processes that may affect toxic chemicals. However, WASP6 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 WASP6 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 WASP6 Organic Chemicals

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

Organic chemicals and associated solids are simulated using the TOXI program. TOXI 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).

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 (0). 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 WASP6 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 properties are included in TOXI 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.

| 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) |

## 2.1.    Organic Chemical Model Reactions and Transformations

In an aquatic environment, an organic chemical may be transferred between phases and may be degraded by any of a 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.

WASP6 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 TOXI 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 TOXI. 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. TOXI does not include such feedback phenomena.

## 2.2.    Model Implementation

To simulate organic chemicals with WASP6, use the preprocessor or text editor to create a TOXI 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 WASP6, 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.

### 2.2.1.    Model Input Parameters

Input parameters are prepared for WASP6 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.

## 2.2.2. 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.

Water Temperature, °C-- 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 TOXI.

TEMP and TMPFN are identified in TOXI as parameters 3 and 2, respectively. TEMPN(1-4) are identified in TOXI 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 TOXI, 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.

| 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. | $L_w/kg_B$ |
| $f_{Dij}$ | Fraction of chemical i in segment j in dissolved phase | - |
| $f_{Bij}$ | Fraction of chemical i in segment j in DOC-sorbed phase | - |
| $f_{sij}$ | Fraction of chemical i in segment j in solid phase "s" | - |

## 2.3. Ionization

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.
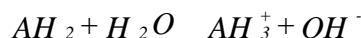
Ionization can be important because of the different toxicological and chemical properties of the neutral and ionized species. For example, in some cases only the neutral form of the chemical may react or be transported through biotic membranes resulting in toxicity. As a result, it is often necessary 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 TOXI different sorption and reaction constants (e.g. for hydrolysis, biodegradation, photolysis, etc.) may be specified for each ionic form of the chemical.

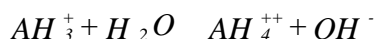### 2.3.1.    Overview of Ionization Reactions

In TOXI, 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. TOXI makes no direct assumptions as to the formation of the ionic species or their reactivity. The user controls the formation by specification of model input.

A chemical being modeled by TOXI 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:

**Equation 2-1**

$$AH_2 + H_2O \_ AH_3^+ + OH^-$$

**Equation 2-2**

$$AH_3^+ + H_2O \_ AH_4^{++} + OH^-$$

**Equation 2-3**

$$AH_2 + H_2O \_ AH^- + H_3O^+$$

**Equation 2-4**

$$AH^- + H_2O \_ A^{--} + H_3O^+$$

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:

**Equation 2-5**

$$K_{b_1} = \frac{[AH_3^+][OH^-]}{[AH_2]}$$

**Equation 2-6**

$$K_{b_2} = \frac{[AH_4^{++}][OH^-]}{[AH_3^+]}$$

**Equation 2-7**

$$K_{a1} = \frac{[AH^-][H^+]}{[AH_2]}$$

**Equation 2-8**

$$K_{a2} = \frac{[A^{--}][H^+]}{[AH^-]}$$

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

**Equation 2-9**

$$C = AH_2 + AH_3^+ + AH_4^{++} + AH^- + A^{--}$$

which may be combined with the law of mass action to form

**Equation 2-10**

$$C = AH_2 \left[ \frac{K_{b1}}{[OH^-]} + \frac{K_{b1}K_{b2}}{[OH^-]^2} + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} \right]$$

By definition, $[H^+] = 10^{-pH}$ and $[OH^-] = 10^{14-pH}$; the bracketed term in equation 7.10, denoted D, can be written

**Equation 2-11**

$$D = \left[ \frac{K_b 1}{10^{pH-14}} + \frac{K_b 1 K_b 2}{(10^{pH-14})^2} + \frac{K_a 1}{10^{-pH}} + \frac{K_a 1 K_a 2}{(10^{-pH})^2} \right]$$

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:

**Equation 2-12**

$$f^0 = \frac{1}{D}$$

**Equation 2-13**

$$f^+ = \frac{K_b 1 / 10^{pH-14}}{D}$$

**Equation 2-14**

$$f^{++} = \frac{K_b 1 K_b 2 / (10^{pH-14})^2}{D}$$

**Equation 2-15**

$$f^- = \frac{K_a 1 / 10^{-pH}}{D}$$

**Equation 2-16**

$$f'' = \frac{K_a 1 \, K_a 2/(10^{-pH})^2}{D}$$

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:

**Equation 2-17**

$$\frac{d \ln K_i}{d T_K} = \frac{E_{ai}}{R T_K^2}$$

or in its integrated form:

$$\log K_i(T_K) = \log K_i(T_{Ri}) + \frac{E_{ai}}{2.303 \, R} \bullet \left[ \frac{T_K - T_{Ri}}{T_K T_{Ri}} \right] = - pK_{ai} + \frac{E_{ai}}{2.303 \, R} \bullet \left[ \frac{T_K - T_{Ri}}{T_k T_{Ri}} \right]$$

where

| | | |
|---|---|---|
| $K_i$ | = | 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. |

| 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 |

## 2.4. Implementation

The data required for the implementation of ionization in TOXI 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 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.

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.

| 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 |

The transformation input parameters for ionization are summarized below. Constant numbers are given in Table 7.5.

Ionization Switches-- The user may choose to simulate ionic species by specifying values of 1.0 for constant SFLG.

Ionization Constants-- 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 constant PKA. If the activation energy is 0, then this is equivalent to the $pK_a$ or $pK_b$.

Reaction Enthalpy, kcal/mole-- 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.

pH-- The user may specify segment and time variable bacterial concentrations using parameter 11, PH, and time functions 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 TOXI. (Group G, Record 4, PARAM(I,11); Group I, Record 2, VALT(10,K), VALT(11,K))

## 2.5.	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:

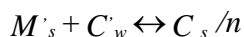**Equation 2-18**

$$C_s' = K_{ps} \bullet C_w'$$

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.
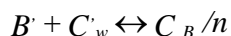
## 2.5.1.	Overview of Sorption Reactions

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:

**Equation 2-19**

$$M_s' + C_w' \leftrightarrow C_s / n$$

**Equation 2-20**

$$B' + C_w' \leftrightarrow C_B / n$$

where n is the porosity (volume of water divided by total volume),

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):

**Equation 2-21**

$$K_{ps0} = \frac{C_s / n}{M_s' C_w'} = \frac{C_s'}{C_w'}$$

**Equation 2-22**

$$K_{pB} = \frac{C_B/n}{B\cdot C'_w} = \frac{C'_B}{C'_w}$$

These equations give the linear form of the Freundlich isotherm, applicable when sorption sites on sediment and DOC are plentiful:

**Equation 2-23**

$$C'_s = K_{ps}\, C'_w$$

**Equation 2-24**

$$C'_B = K_{pB}\, C'_w$$

The total chemical concentration is the sum of the five phase concentrations

**Equation 2-25**

$$C = C'_w\, n + \sum_s C'_s\, M_s + C'_B\, B$$

Substituting in equations 7.24 and 7.25, factoring, and rearranging terms gives the dissolved fraction $f_D$:

**Equation 2-26**

$$f_D = \frac{C'_w\, n}{C} = \frac{n}{n + K_{pB}\bullet B + \sum_s K_{ps}\bullet M_s}$$

Similarly, the sediment-sorbed and DOC-sorbed fractions are

**Equation 2-27**

$$f_s = \frac{C'_s\, M_s}{C} = \frac{K_{ps}\bullet M_s}{n + K_{pB}\bullet B + \sum_s K_{ps}\bullet M_s}$$

**Equation 2-28**

$$f_B = \frac{C'_B\, B}{C} = \frac{K_{pB}\bullet B}{n + K_{pB}\bullet B + \sum_s K_{ps}\bullet M_s}$$

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:

**Equation 2-29**

$$C_w = C \bullet f_D$$

**Equation 2-30**

$$C_s = C \bullet f_s$$

**Equation 2-31**

$$C_B = C \bullet f_B$$

These five concentrations have units of mg/L, and can be expressed as concentrations within each phase:

**Equation 2-32**

$$C'_w = C_w / n$$

**Equation 2-33**

$$C'_s = C_s / M_s$$

**Equation 2-34**

$$C'_B = C_B / B$$

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:

**Equation 2-35**

$$k_d^{-1} = 0.03 \, k_{ps}$$

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.

## 2.5.2. 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 the sediment. TOXI provides several optional methods for the description or computation of the partition coefficients. These options are identified by the data input, as described below.

## 2.5.3. 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).

## 2.5.4. 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 TOXI are

**Equation 2-36**

$$K_{ps0} = f_{ocs} K_{oc}$$

**Equation 2-37**

$$K_{pB} = 1.0 \, K_{oc}$$

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 $K_{ow}$ ($L_w/L_{oct}$):

**Equation 2-38**

$$\log K_{oc} = a_o + a_1 \log K_{ow}$$

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.

## 2.5.5. 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:

**Equation 2-39**

$$K_{ps} = \frac{K_{ps0}}{1 + M_s K_{ps0} / v_x}$$

where:

| | | |
|---|---|---|
| $K_{ps0}$ | = | limiting partition coefficient with no particle interaction ($f_{ocs}$ $K_{oc}$ for neutral organic chemicals) |
| $M_s$ | = | solids concentration, kg/L |
| $v_x$ | = | ratio of adsorption to particle-induced desorption rate |

Di Toro found that $\upsilon_x$ was of order 1 over a broad range of chemical and solids types. This formulation has been included in TOXI. If $\upsilon_x$ is specified to be 1.0, then TOXI will predict a maximum particulate fraction in the water column of 0.5 for all hydrophobic chemicals ($K_{psO}M_s > 10$).

Implementation

| 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 | $\upsilon_x$ | $1$-$10^{12}$ | - |

| VARIABLE | $C_1$ | $C_2$ | $C_3$ | DEFINITION |
|---|---|---|---|---|
| LKOW | **84** | 684 | 1284 | $\text{Log}_{10}$ octanol-water partition coefficient |
| LKOC | 101 | 701 | 1301 | $\text{Log}_{10}$ 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 |

TOXI 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 $\upsilon_x$ 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.

## 2.5.6.    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 specified it will be used regardless. The user is referred to Chapter 6 for details on directly specifying partition coefficients.

Solids Partition Coefficient, L/kg-- 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.

DOC Partition Coefficient-- The user may specify partition coefficients for sorption of ionic species to DOC using constant PIDOC.

### 2.5.7.    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.

### 2.5.8.    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).  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.

### 2.5.9.    Option 4:  Solids Dependant Partitioning.

The user may include the effect of solids concentration on adsorption by using a value of $\upsilon_x$ of order 1 (see Di Toro, 1985 for more detail).  If the user does not provide an input value for $\upsilon_x$, 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.

## *2.6.  Volatilization*

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).

### 2.6.1.  Overview of Volatilization

The dissolved concentration attempts to equilibrate with the gas phase concentration, as illustrated in 0 and given by

**Equation 2-40**

$$\frac{\partial C}{\partial t}\bigg|_{volat} = \frac{K_v}{D}\left( f_d C - \frac{C_a}{\frac{H}{R T_K}} \right)$$

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, $8.206 \times 10^{-5}$ 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. |

Equilibrium occurs when the dissolved concentration equals the partial pressure divided by Henry's Law Constant.

In TOXI, 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:

**Equation 2-41**

$$K_v = (R_L + R_G)^{-1} = \left[ K_L^{-1} + \left( K_G \frac{H}{R T_K} \right)^{-1} \right]^{-1}$$

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.

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:

**Equation 2-42**

$$K_{v,T} = K_{20} \Theta^{T-20}$$

where

| $\Theta_v$ | = | 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 TOXI. 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.

### 2.6.2.    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.

### 2.6.3.    Volatilization Option 2.

This option allows the user to input an oxygen reaeration constant that 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

**Equation 2-43**

$$K_L = K_a \bullet K_{vo}$$

where

$K_a$      =      reaeration velocity, m/day
$K_{vo}$      =      ratio of volatilization rate to reaeration rate.

If $K_{vo}$ is not provided, TOXI will compute the ratio based on the molecular weights of $O_2$ and that of the chemical as shown below

**Equation 2-44**

$$K_L = K_a \sqrt{32/M_w}$$

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).

### 2.6.4.    Volatilization Option 3.

If this option is specified, the liquid film transfer coefficient will be computed as in Option 2. However, the gas film transfer coefficient will be computed using Mackay's method (see Option 5).

### 2.6.5.    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:

**Equation 2-45**

$$K_a = 5.349 \frac{u^{0.67}}{D^{0.85}}$$

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:

**Equation 2-46**

$$K_L = \left(\frac{D_w u}{D}\right)^{0.5} 8.64 \bullet 10^4$$

where $D_w$ is the diffusivity of the chemical in water (m$^2$/s), computed from

**Equation 2-47**

$$D_w = \frac{22 \bullet 10^{-9}}{M_w^{2/3}}$$

In all other cases, the Churchill formula is used to calculate reaeration rate:

**Equation 2-48**

$$K_a = 5.049 \frac{u^{0.969}}{D^{0.673}}$$

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:

**Equation 2-49**

$$K_L = u^* \left(\frac{\rho_a}{\rho_w}\right)^{0.5} \frac{\kappa^{0.33}}{\lambda_2} S_{cw}^{-0.67}$$

**Equation 2-50**

$$K_G = u^* \frac{\kappa^{0.33}}{\lambda_2} Sc_a^{-0.67}$$

where $u^*$ is the shear velocity (m/s) computed from

**Equation 2-51**

$$u^* = C_d^{0.5} W_{10}$$

where

| | | |
|---|---|---|
| $C_d$ | = | drag coefficient (0.0011) |
| $W_{10}$ | = | wind velocity 10 m above water surface, m/sec |
| $\rho_a$ | = | density of air, internally calculated from air temperature, |

$$\varrho_w \quad = \quad \text{density of water, internally calculated from water temperature,}$$
kg/m³

$$\begin{array}{lll} \varrho_w & = & \text{density of water, internally calculated from water temperature,} \\ & & \text{kg/m}^3 \\ \varkappa & = & \text{von Karmen's constant (0.74)} \\ \lambda_2 & = & \text{dimensionless viscous sublayer thickness (4)} \end{array}$$

$S_{ca}$ and $S_{cw}$ are air and water Schmidt Numbers, computed from

**Equation 2-52**

$$S_{ca} = \frac{\mu_a}{\rho_a D_a}$$

**Equation 2-53**

$$S_{cw} = \frac{\mu_w}{\rho_w D_w}$$

where

$$\begin{array}{lll} D_a & = & \text{diffusivity of chemical in air, m}^2/\text{sec} \\ D_w & = & \text{diffusivity of chemical in water, m}^2/\text{sec} \\ \mu_a & = & \text{viscosity of air, internally calculated from air temperature,} \\ & & \text{kg/m-sec} \\ \mu_w & = & \text{viscosity of water, internally calculated from water} \\ & & \text{temperature, kg/m-sec} \end{array}$$

The diffusivity of the chemical in water is computed using Equation 7.48 while the diffusivity of the chemical in air ($D_a$, m²/sec) is computed from

**Equation 2-54**

$$D_a = \frac{1.9 \bullet 10^{-4}}{M_w^{2/3}}$$

Thus $K_G$ is proportional to wind and inversely proportional to molecular weight to the 4/9 power.

## 2.6.6. 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:

**Equation 2-55**

$$K_L = 10^{-6} + 0.00341 \, u^* \, Sc_w^{-0.5} \qquad u^* > .3 \, m/s$$

**Equation 2-56**

$$K_L = 10^{-6} + 0.0144 \, u^{*2.2} \, Sc_w^{-0.5} \qquad u^* < .3 \, m/s$$

**Equation 2-57**

$$K_G = 10^{-3} + 0.0462 \, u^* \, Sc_a^{-0.67}$$

Implementation

| 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 | µg/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 |

Although there are many calculations involved in determining volatilization, most are performed internally using a small set of data. TOXI 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.

| 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, ug/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:<br>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 |

Volatilization Option-- The user should chose the volatilization option using constant XV. Specifying a value of 0 will prevent volatilization from occurring. 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 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 TOXI. 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 TOXI. 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 TOXI. 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.

## *2.7. Hydrolysis*

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 0. The reaction can be catalyzed by hydrogen ions or proceed by consuming hydroxide ions. 0 illustrates the effects of base hydrolysis on carbaryl, neutral hydrolysis on chloromethane, and acid and base hydrolysis on 2,4-D.

### 2.7.1. Overview of Hydrolysis Reactions

Hydrolysis may be simulated by TOXI 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.

### 2.7.2. 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).

### 2.7.3. 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:

**Equation 2-58**

$$K_{HN} = \sum_i \sum_j k_{nij} f_{ij}$$

**Equation 2-59**

$$K_{HH} = \sum_i \sum_j k_{aij} [H^+] f_{ij}$$

**Equation 2-60**

$$K_{HOH} = \sum_i \sum_j k_{bij} [OH^-] f_{ij}$$

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, $day^{-1}$ |

$$f_{ij} \quad = \quad \text{fraction of chemical as ionic specie i in phase j}$$

The rates are also affected by temperature. TOXI adjusts the rates using the temperature-based Arrhenius function

**Equation 2-61**

$$k(T_k) = k(T_R) \exp[1000\, E_{aH}(T_K - T_R)/(RT_k T_R)]$$

where:

$$
\begin{array}{lll}
T_K & = & \text{water temperature, °K} \\
T_R & = & \text{reference temperature for which reaction rate is reported, °K} \\
E_{aH} & = & \text{Arrhenius activation energy for hydrolysis reaction, kcal/mole °K} \\
R & = & 1.99 \text{ cal/mole °K} \\
1000 & = & \text{cal/kcal}
\end{array}
$$

Implementation

| Description | Notation | Range | Units |
|---|---|---|---|
| Negative log of hydrogen ion activity [H⁺] | pH | 5-9 | - |
| Acid hydrolysis rate constant for specie i, phase j | $k_{HAij}$ | $0\text{-}10^7$ | |
| Neutral hydrolysis rate constant for specie i, phase j | $k_{HNij}$ | $0\text{-}10^2$ | day$^{-1}$ |
| Base hydrolysis rate constant for specie i, phase j | $k_{HBij}$ | $0\text{-}10^7$ | |
| Water temperature | T | 4-30 | °C |
| Activation energy for hydrolysis reaction for specie i | $E_{aHi}$ | 15-25 | |

TOXI 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 TOXI reactions. If no hydrolysis data are input, then the effect of hydrolysis will not be included in simulations.

Option 1.

Under this option, the user inputs one or more of the following: an acid, neutral, and base hydrolysis rate constant.

First-Order Hydrolysis Rate Constants, day$^{-1}$-- 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.

| 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 | |

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 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 TOXI to adjust the rates based on temperature, then non-zero activation energies should be specified which would 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.

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.

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.

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.

## 2.8. Photolysis

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 0. 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.

## 2.8.1. Overview of 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:

**Equation 2-62**

$$K_{pG} = \sum_i \sum_j k_{ai} \phi_{ij} f_{ij}$$

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

$\Phi_{ij}$ = 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, TOXI 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:

**Equation 2-63**

$$k_{ai} = \sum_k I_{Gk}\, \varepsilon_{ki}\, d\, (2303)(86400) / (6.022 \times 10^{23})$$

where:

| | | |
|---|---|---|
| $I_{Gk}$ | = | average light intensity of wavelength k, photons/cm$^2$-sec |
| $\varepsilon_{ki}$ | = | 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:

**Equation 2-64**

$$\frac{I_{Gk}}{I_{ok}} = \frac{1 - \exp(-d\, K_e\, D)}{d\, K_e\, D}$$

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 |

Specific Light Extinction Coefficients

| Number | Wavelength | Pure Water 1/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 |

| Number | Wavelength | Specific Light Extinction Coefficients | | | |
|---|---|---|---|---|---|
| | | Pure Water 1/m | Chlorophyll L/gm-m | DOC L/mg-m | Solids L/mg-m |
| 1 | 280.0 | 0.288 | 145 | 7.90 | 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 |

| Number | Wavelength | Specific Light Extinction Coefficients | | | |
|---|---|---|---|---|---|
| | | Pure Water 1/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 |

$I_{ok}$ 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:

**Equation 2-65**

$$K_e = K_{ew} + \eta_1 CHL + \eta_2 DOC + \eta_3 m$$

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 |
|  | $\eta1, \eta2, \eta3$ | = | specific extinction coefficients, L/mg-m |

Values of $K_{ew}$, $\eta1$, $\eta2$, $\eta3$ 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.

## 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

**Equation 2-66**

$$k_{ai} = \sum_i \sum_j k_{aRi} \, I_o' \, ( I_G / I_o )( 1 - 0.056 \, C \,) X_L$$

where

| $I_o'$ | = | user specified normalized light intensity time function, which is the ratio of ambient light intensity to the reference light intensity. |
| $C$ | = | cloud cover (in tenths, 0-10) |
| $X_L$ | = | latitude correction factor, calculated by: |

**Equation 2-67**

$$X_L = \left[ \frac{19169.65 + 87054.63 \cos(0.039 \, L)}{19169.65 + 87054.63 \cos(0.039 \, L_{Rf})} \right]$$

where

| L | = | latitude of the waterbody |
| $L_{Rf}$ | = | 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.

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 TOXI 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.

| 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 $k_{aR}$ | $I_R$ | $10^{-7}$-$2\times10^{-6}$ | 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 | $\Phi_{ij}$ | 0 - 0.5 | moles/E |
| Molar absorptivity by wavelength k by specie i | $\varepsilon_{ki}$ | 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 |

## 2.8.2.    Implementation

The TOXI 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, TOXI computes the sunlight absorption and the surface photolytic decay rate.

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

| 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 |

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 TOXI 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))

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 TOXI. (Group G, Record 4, PARAM(I,10); Group I, Record 2, VALT(14,K)

Photolysis Option 2

In option 2, TOXI 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.  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. If a reference sunlight absorption rate is input, the corresponding quantum yield must be specified.

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.  Separate values can be entered for each ionic specie.

Reference Latitude, degree and tenths-- 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.

Maximum Absorption Wavelength, nm-- 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.

Latitude, degrees and tenths-- The user should specify the latitude of the waterbody using constant 4 - LATG.

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.

Light Intensity-- 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.

## 2.9.  Oxidation

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, $RO_2.$; OH radicals; and singlet oxygen.

## 2.9.1.    Overview of Oxidation Reactions

In TOXI, oxidation is modeled as a general second-order process for the various species and phases of each chemical:

**Equation 2-68**

$$K_o = [RO_2] \sum_i \sum_j k_{oij} f_{ij}$$

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 TOXI 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:

**Equation 2-69**

$$k(T_K) = k(T_R) \exp[1000 E_{ao} (T_K - T_R)/(RT_K T_R)]$$

where:

$E_{ao}$    =    Arrhenius activation energy for oxidation reaction, kcal/mole-°K

Activation energies may be specified for each ionic species 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 TOXI 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 TOXI using parameter OXRADG (ISEG).

Implementation

| 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 |

TOXI 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.

| 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 |

Oxidation Rate, L/mole-day-- 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.

Activation Energy, kcal/mole-°K-- 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.

Oxidant Concentration, mole/L-- The user should specify segment variable oxidant concentrations using parameter 13, OXRAD. (Group G, Record 4, PARAM(I,13)

## 2.10. Biodegradation

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 0. 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, 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.

## 2.10.1.    Overview of Biodegradation Reactions

In TOXI, 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:

**Equation 2-70**

$$K_{Bw} = P_{bac}(t) \sum_i \sum_j k_{Bij} f_{ij} \qquad j = 1,2$$

**Equation 2-71**

$$K_{Bs} = P_{bac}(t) \sum_i \sum_j k_{Bij} f_{ij} \qquad j = 3$$

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 TOXI, the biodegradation rate may be adjusted by temperature as shown below

**Equation 2-72**

$$k_{Bij}(T) = k_{Bij} Q_{Tij}^{(T-20)/10}$$

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 TOXI.  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.

Implementation

TOXI 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 TOXI to correct the rate constants for ambient segment temperatures, then nonzero temperature correction factors should specified as constants. User input for implementing biodegradation is given below.

| 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 |

| VARIABLE | $C_1$ | $C_2$ | $C_3$ |
|---|---|---|---|
| KBW | 141 | 741 | 1341 |
| KBS | 142 | 742 | 1342 |
| KBIO2O$_{11}$ | 146 | 746 | 1346 |
| KBIO20$_{21}$ | 151 | 751 | 1351 |
| KBIO20$_{31}$ | 156 | 756 | 1356 |
| Q10DIS$_1$ | 161 | 761 | 1361 |
| Q10DOC$_1$ | 166 | 766 | 1366 |
| Q10PAR$_1$ | 171 | 771 | 1371 |

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.

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 KBIO20. Constant numbers for the neutral molecule are summarized in Table 7.19. KBIO20$_{11}$ refers to the dissolved neutral chemical; KBIO20$_{21}$ refers to the DOC-sorbed neutral chemical; KBIO20$_{31}$ refers to the sediment-sorbed neutral chemical.

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.

<u>Bacterial Population Levels, cell/mL</u>-- The user may specify segment and time variable bacterial concentrations using parameter 14, BAC, and time functions 16 and 17, BACNW and BACNS. Typical population size ranges are given in Table 7.19.

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.

| 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 | $8x10^9$ - $5x10^{10}$ cells/100 g dry wt | a |
| 40 Surface Waters | 500 - $1x10^6$ | b |
| Stream Sediments | $10^7$ - $10^8$ cells/100 g | c |
| Rur River (winter) | $3x10^4$ | d |

References:

[a]Wetzel (1975). Enumeration techniques unclear

[b]Paris <u>et al</u> (1981). Bacterial enumeration using plate counts.

[c]Herbes & Schwall (1978). Bacterial enumeration using plate counts.

[d]Larson <u>et al</u>. (1981). Bacterial enumeration using plate counts.

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 TOXI. (Group G, Record 4, PARAM(I,14); Group I, Record 2, VALT(16,K), VALT(17,K))

## 2.11. Extra Reaction

An extra second-order reaction is included in TOXI. The second order reaction allows the user to simulate the effect of processes not considered by TOXI. The reaction depends upon a rate constant and a environmental parameter which may be taken to represent, for example, some reducing or oxidizing agent. The rate of reaction may also vary with temperature.

### 2.11.1. Overview of TOXI Extra Reaction

TOXI allows the user to specify an additional second order reaction for the various species and phases of each chemical:

**Equation 2-73**

$$K_E = [E] \sum_i \sum_j k_{eij} f_{ij}$$

where:

$K_E$ = net extra reaction rate constant, $day^{-1}$

$[E]$ = intensity of environmental property driving this reaction

$$k_{eij} \qquad = \qquad \text{second order rate constant for chemical as specie in phase j,}$$
$$\text{in } [E]^{-1} \text{ day}^{-1}$$
$$f_{ij} \qquad = \qquad \text{fraction of chemical as specie i in phase j}$$

The reaction coefficients may be specified as constants, with activation energy constants left as 0. If the user wants TOXI 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:

**Equation 2-74**

$$k_e(T_K) = k_e(T_R) \exp[1000\, E_{ae}(T_K - T_R)/(RT_K T_R)]$$

where:

$$E_{ae} \qquad = \qquad \text{Arrhenius activation energy for extra reaction, kcal/mole-°K}$$

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

**Equation 2-75**

$$C + RH_2 \rightarrow P$$

and

$$[E] \qquad = \qquad \text{Concentration of } RH_2, \text{ moles/L}$$
$$k_e \qquad = \qquad \text{second order rate constant, L/mole-day}$$
$$P \qquad = \qquad \text{reduced product}$$

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:

**Equation 2-76**

$$C_1 + RO_2 \_ C_2 + RH_2$$
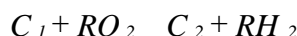
where:

$$C_1 \qquad = \qquad \text{reduced chemical}$$
$$C_2 \qquad = \qquad \text{oxidized chemical}$$
$$RO_2 \qquad = \qquad \text{oxidizing agent}$$
$$RH_2 \qquad = \qquad \text{reducing agent}$$

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 that 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 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 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.

| 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 |

Extra Reaction Rate, L/mole-day-- The user may specify second order extra rate constants for each phase (dissolved, 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.

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.

Extra Environmental Concentration, mole/L-- The user should specify segment variable extra environmental concentrations using parameter 15, EXENV. (Group G, Record 4, PARAM(I,15)