Equation 5-42

$$J_{O_2,C} = a_{oc} J_{C,2}^{t+\Delta}$$

However, this maximum is reduced by the carbon utilized during denitrification, so that the maximum oxygen utilization become

Equation 5-43

 $J_{O_2,C} = a_{o,c} J_{C,2}^{t+\Delta t} - a_{oc} a_{cn} \kappa_{NO3,2} \Theta^{T-20} C_{NO3,2}^{t+\Delta t}$

where $\kappa_{NO3,2}$ is the product of the denitrification reaction rate (K_{NO3}) and the layer thickness (H₂), and $a_{oc}a_{cn}$ is 2.857.

Sulfides and Sulfates

The approach for modeling sulfide reactions varies between the steady-state model described by Di Toro (2001), the initial modeling approach incorporated in the CE-QUAL-ICM model (Di Toro and Fitzpatrick 1993, Cerco and Cole 1995) and that employed incorporated in code revisions during 1997. In the later, equations of the form of Equation 5-22 and Equation 5-23 are written for sulfate and sulfide in layers 1 and 2, for a total of four equations which are solved simultaneously. The source term for layer 2 is the carbon flux converted to oxygen equivalents and reduced by denitrification, as given by Equation 5-43. An additional refinement is that, based upon a continuous derivation, the depth of sulfate reduction (H_{SO4}) is computed which is then used to modify the rate of exchange between layers 1 and 2 (K_{L12}, $_{SO4}$ =K_{L12} H₂/H_{SO4}, Di Toro 2001). The loss term for the oxidation of sulfides in layer 1 is a source term for the overlying water column is computed from Equation 5-25.

The sulfide and sulfate equations are written in terms of oxygen equivalenets, so the stoichiometric relationship between sulfide oxidation and oxygen consumption is unity. The oxygen demand due to sulfide oxidation can then be computed from

Equation 5-44

$$J_{O_2,HS} = f_O \Biggl[\frac{\kappa_{D,H2S,1}^2}{s} f_{d1} + \frac{\kappa_{P,H2S,1}^2}{s} f_{p1} \Biggr] C_{H2S,1}^{\prime + \Delta t}$$

Methane

As with sulfides, the modeling approach for methane varies between the steady-state model described by Di Toro (2001), the initial modeling approach incorporated in the CE-QUAL-ICM model (Di Toro and Fitzpatrick 1993,

Cerco and Cole 1995) and that incorporated in code revisions during 1997. In the later, equations of the form of Equation 5-22 and Equation 5-23 are written for methane in layers 1 and 2. The source term for methane in layer two is the carbon diagenesis flux converted to oxygen equivalents and corrected by denitrification, as given by Equation 5-43, and further reduced by a relationship for the carbon diagenesis flux available for methane formation. Once the methane concentrations are known, the rate of flux to the overlying water column is computed from Equation 5-25.

The methane equations are written in terms of oxygen equivalents, so the stoichiometric relationship between methane oxidation and oxygen consumption in the aerobic layer is unity. The oxygen demand due to methane oxidation can then be computed from

Equation 5-45

$$J_{O_2,CH4} = f_O \frac{\kappa_{CH4,1}^2}{s} C_{CH4,1}^{\prime+\Delta t}$$

SOD

Once the concentrations of materials affecting oxygen are computed, and the stoichiometric relationships described above applied, the SOD is computed from

Equation 5-46

$$SOD = J_{O_2, NH_4} + J_{O_2, HS} + J_{O_2, CH4}$$

this estimate is compared to that from the previous iteration, and as discussed above, if it differs by more than a specified amount, a new value of s is computed and the solution iterated.

Phosphate and Silica

Once the SOD has been determined, and the sediment of the surface exchange rate (s) made, then the concentrations of phosphate and silica in the two layers are determined. For ammonia and phosphate, equations of the form of Equation 5-22 and Equation 5-23 are solved with constituent specific rate terms and coefficients for the phosphate or silica concentrations in layers 1 and 2. The source term for layer 2 for phosphate is the phosphate source from diagenesis reactions plus the flux of particulate inorganic phosphorus from the water column. For silica, the source term for layer 2 is the dissolution reaction and the flux of silica from the water column. Once the silica and phosphate concentrations are known, the rates of flux to the overlying water column are computed from Equation 5-25.

Water Quality Linkage

The output from the sediment diagenesis model includes SOD and fluxes of ammonia, nitrate, phosphate and silica to the overlying water column. The equations in the water quality model for linkage to a model of sediment diagenesis are analogous to those for the zeroth order reactions (Equation 5-18). That is, using the zeroth order approach, the water quality model equations for oxygen, ammonia, nitrate, phosphate and silica contain source/sink terms for the affect of sediments. However, with the coupling of the water quality and sediment diagenesis models those terms are now predicted, rather than described. This coupling of water column and sediment models provides a long-needed predictive capability, a way to link external loads with sediments and their consequent impact on water quality.

5.4. <u>Toxics modeling</u>

Eutrophication modeling, as described in the preceding section, typically deals with the natural cycle of organic production and decomposition, and often the over-stimulation of these natural processes causing problems such as excessive plant growth or low dissolved oxygen concentrations (Chapra 1997). While specific models of the eutrophication may vary in complexity, typically the suite of organisms (e.g. algae), chemicals (e.g. nutrients, dissolved oxygen, etc.), and kinetic processes included in those models are somewhat similar. For example, models of eutrophication deal with on the order of 10 specific "pollutants" (Chapra 1997).

In contrast, the suite of chemicals regarded as toxic is large and the chemical characteristics and environmental impact of those chemicals varies widely. Chemicals regarded as toxic include a number of organic, inorganic and organometallic chemicals. 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. As an example, the U.S. Environmental Protection Agency (EPA) lists over 100 "priority pollutants," including inorganic and organic toxicants and provides rankings of those chemicals based upon their potential exposure and effects on human health and aquatic life. The EPA ECOTOX (ECOTOXicology) database provides single chemical toxicity information for aquatic and terrestrial life for a wide variety of chemicals. The EPA's Toxics Release Inventory (TRI) contains information on over 650 toxic chemicals, their releases into the environment, and other waste management activities reported annually by certain covered industry groups as well as federal facilities. The EPA "Title III Consolidated List of Lists," a consolidated list of chemicals subject to reporting requirements, includes over 1700 chemicals. Many of these toxic pollutants occur naturally, but may result in toxic affects (chronic or acute) if in excess (e.g. nitrates and unionized ammonia). In modern technological societies, synthetic chemicals have been

manufactured, used, and disposed of in large quantities. In contrast to "conventional pollutants" such as those included in models of eutrophication, many of these synthetic chemicals do not occur naturally in the environment.

As a result of the number and diversity in the chemicals involved, and factors affecting their fate and transport, models of toxic pollutants typically differ in structure from those designed for conventional pollutants (e.g. eutrophication). One typical difference is that models of toxic pollutants are often much more general in structure. That is these models (such as the Water Analysis Simulation Program, Ambrose et al. 1993a,b) typically include a variety of transformation and degradation processes. Then through selection of the appropriate processes and specification of chemical specific rates, the models may be applied to the specific chemical(s) of interest.

Toxic chemical models also typically differ between those designed to simulate organic and inorganic contaminants. The factors affecting many metal and organic toxicants are sufficiently different that a single model is rarely applicable to both unless a number of simplifying assumptions are made. For example, for toxic organics the processes impacting their fate and transport differ from those impacting metals. In addition, the degree of interaction between organic compounds is such that typical modeling studies of organic chemicals consider only one to a few chemicals. However, the environmental system behavior and toxicity of metals is governed by "simultaneous and interacting advancement of all possible chemical reactions, each controlled by its individual rate law (Morel, 1983)." The distinction between models of organic and inorganic toxicants is the basis for the organization of this Section of Chapter 6.

Organic chemicals and metals can enter the aquatic environment by various pathways, including point source waste discharges and nonpoint source runoff. Atmospheric deposition is a significant source of some toxic chemicals, such as mercury (U.S. EPA 1997). A number of organic compounds, such as some metals and organics strongly sorb to sediments. As a result, many hydrophobic organic materials such as Polychlorinated Biphenyls (PCBs) and PAH compounds are highly persistent in the environment. Modeling of these chemicals and the sediments to which they sorb over long time periods (decades) is typically required to evaluate their impact. Some organic compounds may bioconcentrate through the food chain where increased concentrations cause adverse impacts. Some organic and inorganic chemicals can cause toxicity to aquatic organisms, having a direct adverse effect on aquatic life by making certain areas uninhabitable. Organic compounds may bioconcentrate through the food chain where increased concentrations cause adverse impacts. For example, the presence of sediments contaminated with polycyclic aromatic hydrocarbons (PAHs) may result in the development of cancerous tumors in fish. Humans and wildlife may be affected by ingesting contaminated water or fish. The bioaccumulation of toxic materials in fish has resulted in consumption

advisories in many areas. The prohibition or restriction of consumption of fish also has a negative economic impact on the effected areas (USEPA 1993).

A typical modeling goal for toxic chemicals is to evaluate the impacts of various management alternatives on the exposure of human and aquatic life to those chemicals and their resulting toxicity. To accomplish this and include the sources and impacts described above, complete models of toxic chemicals typically include: hydrodynamic fate and transport, sediment transport, chemical fate and transport, and bioaccumulation and toxicity. However, a number of these processes and relationships between them are poorly understood. In addition, modern models are typically designed to simulate chemical concentrations in the environment. But, environmental impact is often indicated by the presence of toxicity, where the specific causal factors for that toxicity are not fully known. Without specific relationships between chemical specific criterion and modeled concentrations, the application of toxic chemical models in the environmental management of toxic chemicals is problematic. Some of the methodologies commonly used in linking measured or predicted concentrations and toxic impact are discussed in the following section.

Risk and Hazard Assessments

Contamination by toxic materials is of concern primarily due to the potential risk it poses to humans and wildlife. Therefore, management of contamination by toxic chemicals includes risk management (USEPA 1993).

Humans may be exposed to contaminants through a variety of activities that result in the intake of contaminants through dermal, ingestion, and/or inhalation pathways. Risk may include non-carcinogenic (i.e. chronic or subchronic effects) and carcinogenic (i.e. probability of an individual developing cancer over a lifetime) effects over a range of exposure scenarios. For noncarcinogenic contaminants, typically a safe daily dose or reference dose is used to estimate risk. For carcinogenic chemicals, typically a cancer slope factor (e.g. mg/kg-day) is used along with estimates of uptake rates to determine risk. Reference doses and cancer slope factors have been estimated, and are available, for a wide variety of contaminants.

Guidance and methods for ecological risk assessments are not as well developed as methods of human health risk. Assessments of the impacts of contaminants often rely on toxicity testing and models to extrapolate data to different organisms or life stages. In some cases community impacts (i.e. benthic species diversity) or indirect population based impacts (such as toxicity tests on individual species) are used in an ecological risk assessment. The toxicity data may be site-specific or based upon experimental data. For example, experimental data has been used to estimate No Observable Adverse Effect Levels (NOAEL) or Lowest Observable Adverse Effect Levels (LOAEL) for some chemicals and organisms. A general approach to risk assessment includes a) the identification of existing risks at sites with contamination, b) estimating the potential impact of various remedial alternatives on contaminant concentrations in various media and their associated risk, and c) the comparison of existing and potential risks in order to aid in the selection of remedial alternatives. General steps in the process include (EPA 1993):

- An initial screening of areas of concern to identify sites that may pose a
 potential threat to human or ecological health
- Development of a remedial action plan, which characterizes the risk, identifies potential remedial actions, and provides estimates of resources needed to pursue the remaining elements of the risk management process.
- Development of a baseline risk and hazard evaluation, which estimates potential human and ecological risks resulting from direct or indirect exposure to the contaminants for existing conditions
- · Field sampling to provide for a detailed assessment of the site
- The ranking of information on hazards, risks and costs to prioritize specific sites.
- · Selection of remedial alternatives to be investigated
- Analysis of contaminated fate and transport related to the remedial alternatives, which provides estimates of pollutant releases from the various components of a remedial alternative during and following the implementation of that alternative. Typically in this step, data and models describing the chemical/physical and biological characteristics of the area are combined to evaluate the effects of remediation and changes over time,
- A comparative risk assessment to estimate increases or decreases (relative to the baseline) that would result in implementation of the remedial alternatives,
- Selection and implementation of the remedial alternative.
- Post remediation monitoring.

Contamination by toxic metals occurs in a variety of aquatic habitats. Aquatic resource management strategies, including the assessment of waste allocation, potential remedial action (restoration) effectiveness or to assess the potential consequences of contaminant loadings (Willingham and Medine, 1989), requires an estimation of the impacts of processes affecting metals

concentrations in the water, sediments and biota. These types of analyses are complicated by the fact that metal behavior is non-conservative in aquatic systems and that the transport, transformations, and attenuation depend upon the particular forms of metal present in the system.

Modeling 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 (Ambrose et al. 1993). In organic chemical models typically sorption and ionization are treated as equilibrium reactions. All other processes are typically 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. Available organic chemical models have recently been reviewed by Imhoff et al. (2003).

Sorption

Sorption is the process whereby a dissolved substance is transferred to and becomes associated with a solids material (Chapra 1997). Sorption is an important process controlling the environmental fate and the toxicity of chemicals. For example, sorption may cause the chemical to accumulate in bed sediment or bioconcentrate in fish. Since sorption reduces the fraction of the chemical in the dissolved form, sorption may retard such reactions as volatilization and base hydrolysis (Ambrose et al. 1993).

Sorption to solids is usually described using a linear partition coefficient,

Equation 5-47

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

where $C_{s'}$ is the concentration in the sorbed form (e.g. mg/kg), K_{ps} is the partition coefficient (L/kg), and C_w the concentration in the dissolved form (mg/L). Typical assumptions on which the above formulation is based include:

- The assumption that sorption reactions are fast relative to other environmental processes so that the sorption reaction can be considered to be in equilibrium.
- The assumption that the concentrations are low so that the partitioning relationship is linear. This is typically the case for environmentally relevant concentrations (less than 10⁻⁵ M or one-half water solubility; (Karickhoff, 1984)

 There is no hysteresis, or the rates of sorption and desorption are equal. Laboratory data for very hydrophobic chemicals suggest, however, that a hysteresis exists, with desorption being a much slower process than adsorption. This phenomenon is not well understood and no quantitative modeling framework is available to characterize it (Ambrose et al. 1993a,b).

At equilibrium, then, the distribution among the phases is controlled by the partition coefficient K_{ps} so that the fraction of chemical in the dissolved (f_D) and particulate (f_s) form may be estimated from

Equation 5-48

$$f_{D} = \frac{n}{n + \sum_{s} K_{ps} \bullet M_{s}}$$

and

Equation 5-49

$$f_{s} = \frac{K_{ps} \bullet M_{s}}{n + \sum_{s} K_{ps} \bullet M_{s}}$$

where M_{s} is the mass of the solid and n the porosity of the sediment or water layer.

Given the total concentration (C_T) and the phase fractions of the chemical, the dissolved and sorbed concentrations are uniquely determined:

Equation 5-50

 $C_w = C_T \bullet f_D$

Equation 5-51

$$C_s = C_T \bullet f_s$$

The processes impacting sorption can vary between chemicals, and may be associated with the surface characteristics of the solid, such as the surface charge. For many hydrophobic organic materials, the chemical often becomes associated with the organic matter in the particulate phase, such as such as benthic and suspended sediment, biological material, and sometimes dissolved or colloidal organic material. For non-polar organic chemicals, such as PCBs, the partition coefficient is commonly assumed a function of the organic content of the solids, as in (Chapra 1997)

Equation 5-52

$$K_{ps} = f_{oc} K_{oc}$$

where f_{oc} is the weight fraction of the total carbon in the particulate matter and K_{oc} is the organic carbon partition coefficient (L/kg). The f_{oc} is increasingly a commonly measured environmental parameter. The K_{oc} is commonly estimated from the octanol-water partition coefficient (K_{ow} , L_w/L_{oct}), such as from (Karickoff et al. 1984)

Equation 5-53

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

where typical values for a_0 and a_1 are 0.6 and 1.0, respectively (Ambrose et al. 1993). The K_{ow} may be obtained from field studies, published values, or published formulations (Chapra 1997).

Transformations and Daughter Products

Some organic chemicals may be treated individually. However, for some cases it may be necessary to simulate both the parent chemical and reaction (daughter) products in order to assess environmental impacts. Linked transformations are usually implemented by simulating two or three chemicals and by specifying appropriate yield coefficients for each process, such as give by for three chemicals (Ambrose et al. 1993):

Equation 5-54

$$S_{kcl} = \sum_{c} \sum_{k} K_{kc} C_{c} Y_{kcl}, \quad c = 2, 3$$

Equation 5-55

$$S_{kc2} = \sum_{c} \sum_{k} K_{kc} C_{c} Y_{kc2}, \quad c = 1, 3$$

Equation 5-56

$$S_{kc3} = \sum_{c} \sum_{k} K_{kc} C_{c} Y_{kc3}, \quad c = 1, 2$$

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

An example where the formation of daughter products was important was in the simulation of the 1991 metam-sodium spill into the Sacramento River in Northern California in 1991. Metam-sodium is used as a soil fumigant, and its use depends upon its decomposition to give the toxic and volatile product MITC. Therefore, simulation of both the parent and daughter product were necessary to assess the impact of the spill (Wang et al. 1997).

Biodegradation

Bacterial degradation, sometimes referred to as microbial transformation, biodegradation or biotransformation, refers to the microbially mediated transformation of organic chemicals (Chapra 1997). Although these transformations can detoxify and mineralize toxins and defuse potential toxins, they can also activate potential toxins (Ambrose et al. 1993 a,b).

Typical degrading organisms include heterotrophic bacteria, actinomycetes, autotrophic bacteria, fungi and protozoa (Chapra 1997). 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 EPA (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 (EPA, 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 (Ambrose et al. 1993a,b).

The growth kinetics of the bacterial population degrading a toxic chemical are not well understood. As a result, toxic chemical models assume a constant biological activity rather than modeling the bacteria directly (a pseudo-first order rate). Alternatively, measured first order biodegradation rate constants are used directly (Ambrose et al. 1993a,b). However, the water body's productivity tends to increase the effectiveness of biodegradation as a removal mechanism (Chapra 1997).

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 (Ambrose et al. 1993a,b). It is important both as a loss mechanism from the water column and as a source mechanism for the atmosphere.