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Technical Guidance Manual for Performing Waste Load Allocations

Book III Estuaries

Part 1 Estuaries and Waste Load Allocation Models



**TECHNICAL GUIDANCE MANUAL
FOR PERFORMING WASTE LOAD ALLOCATIONS**

BOOK III: ESTUARIES

PART 1: Estuaries and Waste Load Allocation Models

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Glossary

Acute Toxicity¹ - Any toxic effect that is produced within a short period of time, usually 24-96 hours. Although the effect most frequently considered is mortality, the end result of acute toxicity is not necessarily death. Any harmful biological effect may be the result.

Aerobic¹ - Refers to life or processes occurring only in the presence of free oxygen; refers to a condition characterized by an excess of free oxygen in the aquatic environment.

Algae (Alga)¹ - Simple plants, many microscopic, containing chlorophyll. Algae form the base of the food chain in aquatic environments. Some species may create a nuisance when environmental conditions are suitable for prolific growth.

Allochthonous¹ - Pertaining to those substances, materials or organisms in a waterway which originate outside and are brought into the waterway.

Anaerobic² - Refers to life or processes occurring in the absence of free oxygen; refers to conditions characterized by the absence of free oxygen.

Autochthonous¹ - Pertaining to those substances, materials, or organisms originating within a particular waterway and remaining in that waterway.

Autotrophic¹ - Self nourishing; denoting those organisms that do not require an external source of organic material but can utilize light energy and manufacture their own food from inorganic materials; e.g., green plants, pigmented flagellates.

Bacteria¹ - Microscopic, single-celled or noncellular plants, usually saprophytic or parasitic.

Benthal Deposit² - Accumulation on the bed of a watercourse of deposits containing organic matter arising from natural erosion or discharges of wastewaters.

Benthic Region¹ - The bottom of a waterway; the substratum that supports the benthos.

Benthal Demand² - The demand on dissolved oxygen of water overlying benthal deposits that results from the upward diffusion of decomposition products of the deposits.

Benthos¹ - Organisms growing on or associated principally with the bottom of waterways. These include: (1) sessile animals such as sponges, barnacles, mussels, oysters, worms, and attached algae; (2) creeping

forms such as snails, worms, and insects; (3) burrowing forms, which include clams, worms, and some insects; and (4) fish whose habits are more closely associated with the benthic region than other zones; e.g., flounders.

Biochemical Oxygen Demand² - A measure of the quantity of oxygen utilized in the biochemical oxidation of organic matter in a specified time and at a specific temperature. It is not related to the oxygen requirements in chemical combustion, being determined entirely by the availability of the material as a biological food and by the amount of oxygen utilized by the microorganisms during oxidation. Abbreviated BOD.

Biological Magnification¹ - The ability of certain organisms to remove from the environment and store in their tissues substances present at nontoxic levels in the surrounding water. The concentration of these substances becomes greater each higher step in the food chain.

Bloom¹ - A readily visible concentrated growth or aggregation of minute organisms, usually algae, in bodies of water.

Brackish Waters¹ - Those areas where there is a mixture of fresh and salt water; or, the salt content is greater than fresh water but less than sea water; or, the salt content is greater than in sea water.

Channel Roughness² - That roughness of a channel, including the extra roughness due to local expansion or contraction and obstacles, as well as the roughness of the stream bed proper; that is, friction offered to the flow by the surface of the bed of the channel in contact with the water. It is expressed as roughness coefficient in the velocity formulas.

Chlorophyll¹ - Green photosynthetic pigment present in many plant and some bacterial cells. There are seven known types of chlorophyll; their presence and abundance vary from one group of photosynthetic organisms to another.

Chronic Toxicity¹ - Toxicity, marked by a long duration, that produces an adverse effect on organisms. The end result of chronic toxicity can be death although the usual effects are sublethal; e.g., inhibits reproduction, reduces growth, etc. These effects are reflected by changes in the productivity and population structure of the community.

Coastal Waters¹ - Those waters surrounding the continent which exert a measurable influence on uses of the land and on its ecology. The Great Lakes and the waters to the edge of the continental shelf.

Component Tide² - Each of the simple tides into which the tide of nature is resolved. There are five principal components; principal lunar, principal solar, N₂, K, and O. There are between 20 and 30 components which are used in accurate predictions of tides.

Coriolis Effect² - The deflection force of the earth's rotation. Moving bodies are deflected to the right in the northern hemisphere and to the left in the southern hemisphere.

Datum² - An agreed standard point or plane of state elevation, noted by permanent bench marks on some solid immovable structure, from which elevations are measured or to which they are referred.

Density Current² - A flow of water through a larger body of water, retaining its unmixed identity because of a difference in density.

Deoxygenation² - The depletion of the dissolved oxygen in a liquid either under natural conditions associated with the biochemical oxidation of organic matter present or by addition of chemical reducing agents.

Diagenetic Reaction - Chemical and physical changes that alter the characteristics of bottom sediments. Examples of chemical reactions include oxidation of organic materials while compaction is an example of a physical change.

Dispersion² - (1) Scattering and mixing. (2) The mixing of polluted fluids with a large volume of water in a stream or other body of water.

Dissolved Oxygen² - The oxygen dissolved in water, wastewater, or other liquid, usually expressed in milligrams per liter, or percent of saturation. Abbreviated DO.

Diurnal² - (1) Occurring during a 24-hr period; diurnal variation. (2) Occurring during the day time (as opposed to night time). (3) In tidal hydraulics, having a period or cycle of approximately one tidal day.

Drought² - In general, an extended period of dry weather, or a period of deficient rainfall that may extend over an indefinite number of days, without any quantitative standard by which to determine the degree of deficiency needed to constitute a drought. Qualitatively, it may be defined by its effects as a dry period sufficient in length and severity to cause at least

partial crop failure or impair the ability to meet a normal water demand.

Ebb Tide¹ - That period of tide between a high water and the succeeding low water; falling tide.

Enrichment¹ - An increase in the quantity of nutrients available to aquatic organisms for their growth.

Epilimnion¹ - The water mass extending from the surface to the thermocline in a stratified body of water; the epilimnion is less dense than the lower waters and is wind-circulated and essentially homothermous.

Estuary¹ - That portion of a coastal stream influenced by the tide of the body of water into which it flows; a bay, at the mouth of a river, where the tide meets the river current; an area where fresh and marine water mix.

Euphotic Zone¹ - The lighted region of a body of water that extends vertically from the water surface to the depth at which photosynthesis fails to occur because of insufficient light penetration.

Eutrophication¹ - The natural process of the maturing (aging) of a lake; the process of enrichment with nutrients, especially nitrogen and phosphorus, leading to increased production of organic matter.

Firth¹ - A narrow arm of the sea; also the opening of a river into the sea.

Fjord (Fiord)¹ - A narrow arm of the sea between highlands.

Food Chain¹ - Dependence of a series of organisms, one upon the other, for food. The chain begins with plants and ends with the largest carnivores.

Flood Tide² - A term indiscriminately used for rising tide or landward current. Technically, flood refers to current. The use of the terms "ebb" and "flood" to include the vertical movement (tide) leads to uncertainty. The terms should be applied only to the horizontal movement (current).

Froude's Number² - A numerical quantity used as an index to characterize the type of flow in a hydraulic structure that has the force of gravity (as the only force producing motion) acting in conjunction with the resisting force of inertia. It is equal to the square of characteristic velocity (the mean, surface, or maximum velocity) of the system, divided by the product of a characteristic linear dimension, such as diameter or expressed in consistent units so that the combinations will be dimensionless. The number is used in

open-channel flow studies or in cases in which the free surface plays an essential role in influencing motion.

Heavy Metals² - Metals that can be precipitated by hydrogen sulfide in acid solution, for example, lead, silver, gold, mercury, bismuth, copper.

Heterotrophic¹ - Pertaining to organisms that are dependent on organic material for food.

Hydraulic Radius² - The right cross-sectional area of a stream of water divided by the length of that part of its periphery in contact with its containing conduit; the ratio of area to wetted perimeter. Also called hydraulic mean depth.

Hydrodynamics² - The study of the motion of, and the forces acting on, fluids.

Hydrographic Survey² - An instrumental survey made to measure and record physical characteristics of streams and other bodies of water within an area, including such things as location, areal extent and depth, positions and locations of high-water marks, and locations and depths of wells.

Inlet¹ - A short, narrow waterway connecting a bay, lagoon, or similar body of water with a large parent body of water; an arm of the sea, or other body of water, that is long compared to its width, and that may extend a considerable distance inland.

Inorganic Matter² - Mineral-type compounds that are generally non-volatile, not combustible, and not biodegradable. Most inorganic-type compounds, or reactions, are ionic in nature, and therefore, rapid reactions are characteristic.

Lagoon¹ - A shallow sound, pond, or channel near or communicating with a larger body of water.

Limiting Factor¹ - A factor whose absence, or excessive concentration, exerts some restraining influence upon a population through incompatibility with species requirements or tolerance.

Manning Formula² - A formula for open-channel flow, published by Manning in 1890, which gives the value of *c* in the Chezy formula.

Manning Roughness Coefficient² - The roughness coefficient in the Manning formula for determination of the discharge coefficient in the Chezy formula.

Marsh¹ - Periodically wet or continually flooded area with the surface not deeply submerged. Covered dominantly with emerged aquatic plants; e.g., sedges, cattails, rushes.

Mean Sea Level² - The mean plane about which the tide oscillates; the average height of the sea for all stages of the tide.

Michaelis-Menton Equation² - A mathematical expression to describe an enzyme-catalyzed biological reaction in which the products of a reaction are described as a function of the reactants.

Mineralization² - The process by which elements combined in organic form in living or dead organisms are eventually reconverted into inorganic forms to be made available for a fresh cycle of plant growth. The mineralization of organic compounds occurs through combustion and through metabolism by living animals. Microorganisms are ubiquitous, possess extremely high growth rates and have the ability to degrade all naturally occurring organic compounds.

Modeling² - The simulation of some physical or abstract phenomenon or system with another system believed to obey the same physical laws or abstract rules of logic, in order to predict the behavior of the former (main system) by experimenting with latter (analogous system).

Monitoring² - Routine observation, sampling and testing of designated locations or parameters to determine efficiency of treatment or compliance with standards or requirements.

Mouth² - The exit or point of discharge of a stream into another stream or a lake, or the sea.

Nautical Mile² - A unit of distance used in ocean navigation. The United States nautical mile is defined as equal to one-sixteenth of a degree of a great circle on a sphere with a surface equal to the surface of the earth. Its value, computed for the Clarke spheroid of 1866, is 1,853.248 m (6,080.20ft). The International nautical mile is 1,852 m (6,070.10 ft).

Nanoplankton² - Very minute plankton not retained in a plankton net equipped with no. 25 silk bolting cloth (mesh, 0.03 to 0.04 mm.).

Neap Tides¹ - Exceptionally low tides which occur twice each month when the earth, sun and moon are at right angles to each other; these usually occur during the moon's first and third quarters.

Neuston² - Organisms associated with, or dependent upon, the surface film (air-water) interface of bodies of water.

Nitrogenous Oxygen Demand (NOD)² - A quantitative measure of the amount of oxygen required for the biological oxidation of nitrogenous material, such as

ammonia nitrogen and organic nitrogen, in wastewater; usually measured after the carbonaceous oxygen demand has been satisfied.

Nutrients¹ - Elements, or compounds, essential as raw materials for organism growth and development; e.g., carbon, oxygen, nitrogen, phosphorus, etc.

Organic¹ - Refers to volatile, combustible, and sometimes biodegradable chemical compounds containing carbon atoms (carbonaceous) bonded together and with other elements. The principal groups of organic substances found in wastewater are proteins, carbohydrates, and fats and oils.

Oxygen Deficit¹ - The difference between observed oxygen concentration and the amount that would theoretically be present at 100% saturation for existing conditions of temperature and pressure.

Pathogen¹ - An organism or virus that causes a disease.

Periphyton (Aufwuchs)¹ - Attached microscopic organisms growing on the bottom, or other submerged substrates, in a waterway.

Photosynthesis¹ - The metabolic process by which simple sugars are manufactured from carbon dioxide and water by plant cells using light as an energy source.

Phytoplankton¹ - Plankton consisting of plant life. Unattached microscopic plants subject to movement by wave or current action.

Plankton¹ - Suspended microorganisms that have relatively low powers of locomotion, or that drift in the water subject to the action of waves and currents.

Quality² - A term to describe the composite chemical, physical, and biological characteristics of a water with respect to its suitability for a particular use.

Reaeration² - The absorption of oxygen into water under conditions of oxygen deficiency.

Respiration¹ - The complex series of chemical and physical reactions in all living organisms by which the energy and nutrients in foods is made available for use. Oxygen is used and carbon dioxide released during this process.

Roughness Coefficient² - A factor, in the Chezy, Darcy-Weisbach, Hazen-Williams, Kutter, Manning, and other formulas for computing the average velocity of flow of water in a conduit or channel, which repre-

sents the effect of roughness of the confining material on the energy losses in the flowing water.

Seiche¹ - Periodic oscillations in the water level of a lake or other landlocked body of water due to unequal atmospheric pressure, wind, or other cause, which sets the surface in motion. These oscillations take place when a temporary local depression or elevation of the water level occurs.

Semidiurnal² - Having a period or cycle of approximately one half of a tidal day. The predominating type of tide throughout the world is semidiurnal, with two high waters and two low waters each tidal day.

Slack Water² - In tidal waters, the state of a tidal current when its velocity is at a minimum, especially the moment when a reversing current changes direction and its velocity is zero. Also, the entire period of low velocity near the time of the turning of the current when it is too weak to be of any practical importance in navigation. The relation of the time of slack water to the tidal phases varies in different localities. In some cases slack water occurs near the times of high and low water, while in other localities the slack water may occur midway between high and low water.

Spring Tide¹ - Exceptionally high tide which occurs twice per lunar month when there is a new or full moon, and the earth, sun, and moon are in a straight line.

Stratification (Density Stratification)¹ - Arrangement of water masses into separate, distinct, horizontal layers as a result of differences in density; may be caused by differences in temperature, dissolved or suspended solids.

Tidal Flat¹ - The sea bottom, usually wide, flat, muddy and nonproductive, which is exposed at low tide. A marshy or muddy area that is covered and uncovered by the rise and fall of the tide.

Tidal Prism² - (1) The volume of water contained in a tidal basin between the elevations of high and low water. (2) The total amount of water that flows into a tidal basin or estuary and out again with movement of the tide, excluding any fresh-water flows.

Tidal Range² - The difference in elevation between high and low tide at any point or locality.

Tidal Zone (Eulittoral Zone, Intertidal Zone)¹ - The area of shore between the limits of water level fluctuation; the area between the levels of high and low tides.

Tide¹ - The alternate rising and falling of water levels, twice in each lunar day, due to gravitational attraction

of the moon and sun in conjunction with the earth's rotational force.

Tide Gage² - (1) A staff gage that indicates the height of the tide. (2) An instrument that automatically registers the rise and fall of the tide. In some instruments, the registration is accomplished by printing the heights at regular intervals; in others by a continuous graph in which the height of the tide is represented by ordinates of the curve and the corresponding time by the abscissae.

Toxicant¹ - A substance that through its chemical or physical action kills, injures, or impairs an organism; any environmental factor which, when altered, produces a harmful biological effect.

Water Pollution¹ - Alteration of the aquatic environment in such a way as to interfere with a designated beneficial use.

Water Quality Criteria¹ - A scientific requirement on which a decision or judgement may be based concerning the suitability of water quality to support a designated use.

Water Quality Standard¹ - A plan that is established by governmental authority as a program for water pollution prevention and abatement.

Zooplankton² - Plankton consisting of animal life. Unattached microscopic animals having minimal capability for locomotion.

¹Rogers, B.G., Ingram, W.T., Pearl, E.H., Welter, L.W. (Editors). 1981, Glossary, Water and Wastewater Control Engineering, Third Edition, American Public Health Association, American Society of Civil Engineers, American Water Works Association, Water Pollution Control Federation.

²Matthews, J.E., 1972, Glossary of Aquatic Ecological Terms, Manpower Development Branch, Air and Water Programs Division, EPA, Oklahoma.

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Executive Summary

The Technical Guidance Manual for Performing Waste Load Allocations, Book III: Estuaries is the third in a series of manuals providing technical information and policy guidance for the preparation of waste load allocations (WLAs) that are as technically sound as current state of the art permits. The objective of such load allocations is to ensure that water quality conditions that protect designated beneficial uses are achieved. This book provides technical guidance for performing waste load allocations in estuaries.

PART I: ESTUARIES AND WASTE LOAD ALLOCATION MODELS

Introduction

Estuaries are coastal bodies of water where fresh water meets the sea. Most rivers and their associated pollutant loads eventually flow into estuaries. The complex loading, circulation, and sedimentation processes make water quality assessment and waste load allocation in estuaries difficult. Transport and circulation processes in estuaries are driven primarily by river flow and tidal action. As a consequence of its complex transport processes, estuaries cannot be treated as simple advective systems such as many rivers.

Wastewater discharges into estuaries can affect water quality in several ways, both directly and indirectly. In setting limits on wastewater quantity and quality, the following potential problems should be assessed: salinity, sediment, pathogenic bacteria, dissolved oxygen depletion, nutrient enrichment and overproduction, aquatic toxicity, toxic pollutants and bioaccumulation and human exposure.

A WLA provides a quantitative relationship between the waste load and the instream concentrations or effects of concern as represented by water quality standards. During the development of a WLA, the user combines data and model first to describe present conditions and then to extrapolate to possible future conditions. The WLA process sequentially addresses the topics of hydrodynamics, mass transport, water quality kinetics, and for some problems, bioaccumulation and toxicity.

For each of the topics addressed in a modeling study, several steps are applied in an iterative process: problem identification, model identification, initial model calibration, sensitivity analysis, model testing, refinement, and validation.

After the WLAs have been put into effect, continued monitoring, post-audit modeling and refinement should lead to more informed future WLAs.

Overview of Processes Affecting Estuarine Water Quality

The estuarine waste load allocation process requires a fundamental understanding of the factors affecting water quality and the representation of those processes in whatever type of model is applied (conceptual or mathematical) in order to determine the appropriate allocation of load. Insight into processes affecting water quality may be obtained through examination of the schemes available for their classification. Estuaries have typically been classified based on their geomorphology and patterns of stratification and mixing. However, each estuary is to some degree unique and it is often necessary to consider the fundamental processes impacting water quality.

To determine the fate and effects of water quality constituents it is necessary first to determine processes impacting their transport. That transport is affected by tides, fresh water inflow, friction at the fluid boundaries and its resulting turbulence, wind and atmospheric pressure, and to a lesser degree (for some estuaries) the effects of the earth's rotation (Coriolis force). The resulting transportation patterns may be described (determined from field studies) in waste load allocation studies, or, as is becoming more frequently the case, estimated using hydrodynamic models. Hydrodynamic models are based on descriptions of the processes affecting circulation and mixing using equations based on laws of conservation of mass and momentum. The fundamental equations generally include: (A) the conservation of water mass (continuity), (B) conservation of momentum, and (C) conservation of constituent mass.

An important aspect of estuarine WLA modeling often is the capability to simulate sediment transport and sediment/water interactions. Sediments not only affect water transparency, but can carry chemicals such as nutrients and toxic substances into receiving waters. Unlike rivers, which have reasonably constant water quality conditions, the large changes in salinity and pH in an estuary directly affect the transport behavior of many suspended solids. Many colloidal particles agglomerate and settle in areas of significant salinity gradients. Processes impacting sediment transport include settling, resuspension, scour and erosion, coagulation and flocculation.

The water quality parameters of interest vary with the objectives of the waste load allocation study, from "conventional pollutants" (e.g. organic waste, dissolved oxygen and nutrients) to toxic organics and trace metals.

The focus of WLA models of conventional pollutants is often DO and biochemical oxygen demand (BOD) as a general measure of the health of the system, or the focus can be primary productivity when eutrophication is the major concern. Conventional WLA models usually include temperature, major nutrients, chemical characteristics, detritus, bacteria, and primary producers. WLA models may include higher trophic levels (i.e. zooplankton and fish) because of higher trophic level effects on other more important variables, such as phytoplankton, BOD and DO. Synthetic organic chemicals include a wide variety of toxic materials whose waste loads are allocated based upon threshold concentrations as well as tolerable durations and frequencies of exposure. These pollutants may ionize and different forms may have differing toxicological affects. The transport of the materials also may be affected by sorption and they can degrade through such processes as volatilization, biodegradation, hydrolysis, and photolysis.

Trace metals may be of concern in many estuaries due to their toxicological effects. The toxicity of trace metals and their transport is affected by their form. Upon entry to a surface water body, metal speciation may change due to complexation, precipitation, sorption, and redox reactions. Metals concentrations are diluted further by additional stream flow and mixing. Physical loss can be caused by settling and sedimentation, whereas a physical gain may be caused by resuspension.

Model Identification and Selection

The first steps in the modeling process are model identification and selection. The goals are to identify the simplest conceptual model that includes all the important estuarine phenomena affecting the water quality problems, and to select the most useful analytical formula or computer model for calculating waste load allocations. During model identification, available information is gathered and organized to construct a coherent picture of the water quality problem. There are four basic steps in model identification: establish study objectives and constraints, determine water quality pollutant interactions, determine spatial extent and resolution, and determine temporal extent and resolution. Following model identification, another important step is advised: perform rapid, simple screening calculations to gain a better understanding of expected pollutant levels and the spatial extent of water quality problems.

The first step in identifying an appropriate WLA model for a particular site is to review the applicable water quality standards and the beneficial uses of the estuary to be protected. Local, state, and federal regulations may contribute to a set of objectives and constraints. The final result of this step should be a clear understanding of the pollutants and water quality indicators, the areas, and the time scales of interest.

After the pollutants and water quality indicators are identified, the significant water quality reactions must be determined. These reactions must directly or indirectly link the pollutants to be controlled with the primary water quality indicators. All other interacting water quality constituents thought to be significant should be included at this point. This can best be done in a diagram or flow chart representing the mass transport and transformations of water quality constituents in a defined segment of water. The final result of this step should be the assimilation of all the available knowledge of a system in a way that major water quality processes and ecological relationships can be evaluated for inclusion in the numerical model description.

The next step is to specify the spatial extent, dimensionality, and scale (or computational resolution) of the WLA model. This may be accomplished by determining the effective dimensionality of the estuary as a whole, defining the boundaries of the study area, then specifying the required dimensionality and spatial resolution within the study area. The effective dimensionality of an estuary includes only those dimensions over which hydrodynamic and water quality gradients significantly affect the WLA analysis. Classification and analysis techniques are available. Specific boundaries of the study area must be established, in general, beyond the influence of the discharge(s) being evaluated. Data describing the spatial gradients of important water quality constituents within the study area should be examined. Dye studies can give important information on the speed and extent of lateral and vertical mixing. It is clear that choice of spatial scale and layout of the model network requires considerable judgment.

The final step in model identification is to specify the duration and temporal resolution of the WLA model. The duration of WLA simulations can range from days to years, depending upon the size and transport characteristics of the study area, the reaction kinetics and forcing functions of the water quality constituents, and the strategy for relating simulation results to the regulatory requirements. One basic guideline applies in all cases - the simulations should be long enough to eliminate the effect of initial conditions on important water quality constituents at critical locations.

The temporal resolution of WLA simulations falls into one of three categories - dynamic, quasi-dynamic, and steady state. Dynamic simulations predict hour to hour variations caused by tidal transport. Quasidynamic simulations predict variations on the order of days to months. The effects of tidal transport are time-averaged. Other forcing functions such as freshwater inflow, pollutant loading, temperature, and sunlight may vary from daily to monthly. Steady state simulations predict monthly to seasonal averages. All inputs are time-averaged. Two schools of thought have persisted regarding the utility of dynamic versus quasidynamic and steady state simulations. For some problems the choice is reasonably clear.

In general, if the regulatory need or kinetic response is on the order of hours, then dynamic simulations are required; if regulatory needs are long term averages and the kinetic response is on the order of seasons to years, then quasidynamic or steady simulations are indicated.

The goal of model selection is to obtain a simulation model that effectively implements the conceptual model identified for the WLA. Models selected for discussion here are general purpose, in the public domain, and available from or supported by public agencies. The selection of an estuarine WLA model need not be limited to the models discussed in this document. Other models that are available to a project or organization should also be considered. The models summarized in this report represent the typical range of capabilities currently available. Estuarine WLA models can be classified as Level I to Level IV according to the temporal and spatial complexity of the hydrodynamic component of the model. Level I includes desktop screening methodologies that calculate seasonal or annual mean pollutant concentrations based on steady state conditions and simplified flushing time estimates. These models are designed to examine an estuary rapidly to isolate trouble spots for more detailed analyses.

Level II includes computerized steady state or tidally averaged quasidynamic simulation models, which generally use a box or compartment-type network to solve finite difference approximations to the basic partial differential equations. Level II models can predict slowly changing seasonal water quality with an effective time resolution of 2 weeks to 1 month. Level III includes computerized one-dimensional (1-d) and quasi two-dimensional (2-d), dynamic simulation models. These real time models simulate variations in tidal heights and velocities throughout each tidal cycle. Their effective time resolution is usually limited to average variability over one week because tidal input parameters generally consist of only average or slowly

varying values. The effective time resolution could be reduced to under 1 day given good representation of diurnal water quality kinetics and precise tidal input parameters. The required data and modeling effort are usually not mobilized in standard WLAs. Level IV consists of computerized 2-d and 3-d dynamic simulation models. Dispersive mixing and seaward boundary exchanges are treated more realistically than in the Level III 1-d models. These models are almost never used for routine WLAs.

The effective time resolution of the Level IV models can be less than 1 day with a good representation of diurnal water quality and intratidal variations.

The advantages of Level I and II models lie in their comparatively low cost and ease of application. The disadvantages lie in their steady state or tidally averaged temporal scale. When hydrodynamics and pollutant inputs are rapidly varying, steady state models are difficult to properly calibrate.

The dynamic models (Levels III and IV) have advantages over steady state and tidally averaged models in representing mixing in partially mixed estuaries because advection is so much better represented. The success with which these models can predict transient violations depends upon both the accuracy and resolution of the loading and environmental data, and the model's treatment of short time scale kinetics such as desorption or diurnal fluctuations in temperature, pH, or sunlight. While dynamic models are capable of predicting diurnal and transient fluctuations in water quality parameters, the input data requirements are much greater.

PART II: APPLICATION OF ESTUARINE WASTE LOAD ALLOCATION MODELS

Monitoring Protocols for Calibration and Validation of Estuarine Waste Load Allocation Models

The monitoring data collected in support of a modeling study is used to: (1) determine the type of model application required (e.g. dimensionality, state variables); (2) perturb the model (e.g. loadings, flows); (3) provide a basis for assigning rate coefficients and model input parameters (model calibration); and (4) determine if the model adequately describes the system (model evaluation).

The specific types of data and quantity required will vary with the objectives of the WLA modeling study and the characteristics of the estuary. Data are always required to determine model morphometry, such as depths and volumes (e.g. available from sounding data

or navigation charts). Data are also required for transport. Transport within the modeled system may either be specified (measured, e.g. current meters) or computed from hydrodynamic models. Flows into the system must be measured, or in the case of the open boundary, water surface elevations must be determined.

The water quality data required, beyond that needed to quantify transport, will vary depending on how the variables will be used and their anticipated impact on the system. Data requirements will differ if the WLA modeling study is intended for dissolved oxygen, eutrophication or toxics. Concentrations for all pertinent water quality variables should be provided at the model boundaries, providing the perturbation for model predictions, as well as at points within the water-body to provide a basis for estimating model parameters and evaluating model predictions. Data should be available to determine variations in water quality parameters over space and time.

Planning monitoring studies should be a collaborative effort of participants involved in budgeting, field collection, analysis and processing of data, quality assurance, data management and modeling activities.

Collaboration insures that fundamental design questions are properly stated so that the available resources are used in the most efficient manner possible and that all critical data for modeling are collected. The use of monitoring and modeling in an iterative fashion, wherever possible, is often the most efficient means of insuring that critical data are identified and collected. A rigorous, well documented, quality assurance, quality control (QA/QC) plan should be an integral part of any waste load allocation program.

Model Calibration, Validation, and Use

While models can be run with minimal data, their predictions are subject to large uncertainty. Models are best operated to interpolate between existing conditions or to extrapolate from existing to future conditions, such as in the projection of conditions under anticipated waste loads. The confidence that can be placed on those projections is dependent upon the integrity of the model, and how well the model is calibrated to that particular estuary, and how well the model compares when evaluated against an independent data set (to that used for calibration).

Model calibration is necessary because of the semi-empirical nature of present day (1989) water quality models. Although the waste load allocation models used in estuary studies are formulated from the mass balance and, in many cases, from conservation of momentum principles, most of the kinetic descriptions

in the models that describe the change in water quality are empirically derived. These empirical derivations contain a number of coefficients and parameters that are usually determined by calibration using data collected in the estuary of interest.

Calibration alone is not adequate to determine the predictive capability of a model for a particular estuary. To map out the range of conditions over which the model can be used to determine cause and effect relationships, one or more additional independent sets of data are required to determine whether the model is predictively valid. This testing exercise, which also is referred to as confirmation testing, defines the limits of usefulness of the calibrated model. Without validation testing, the calibrated model remains a description of the conditions defined by the calibration data set. The uncertainty of any projection or extrapolation of a calibrated model would be unknown unless this is estimated during the validation procedure.

In addition, the final validation is limited to the range of conditions defined by the calibration and validation data sets. The uncertainty of any projection or extrapolation outside this range also remains unknown. The validation of a calibrated model, therefore, should not be taken to infer that the model is predictively valid over the full range of conditions that can occur in an estuary. For example, a model validated over the range of typical tides and low freshwater inflow may not describe conditions that occur when large inflows and atypical tides occur.

This is especially true when processes such as sediment transport and benthic exchange occur during atypical events but not during the normal, river flow and tidal events typically used to calibrate and validate the model.

Following model calibration and validation, several types of analyses of model performance are of importance. First, a sensitivity analysis provides a method to determine which parameters and coefficients have the greatest impact on model predictions. Second, there are a number of statistical tests that are useful for defining when adequate agreement has been obtained between model simulations and measured conditions in order to estimate the confidence that may be assigned to model predictions. Finally, a components analysis indicates the relative contribution of processes to variations in predicted concentrations. For example, the cause of violations of a dissolved oxygen standard can be determined from the relative contribution of various loads and the effect of sediment oxygen demand, BOD decay, nitrification, photosynthesis, and reaeration.

Once the model is calibrated and validated, it is then used to investigate causes of existing problems or to simulate future conditions to determine effects of changes in waste loads as part of the waste load allocation procedure. Once critical water quality conditions are defined for the estuary, harbor or coastal area of concern, determining the waste assimilative capacity is relatively straightforward. Models are available to relate critical water quality responses to the loads for most problems. However, the definition of critical conditions for estuaries is not straightforward. For streams receiving organic loads, this is a straightforward matter of determining the low flow and high temperature conditions. In estuaries, fresh water, tides, wind, complex sediment transport, and other factors can be important to determining the critical conditions. As of yet, there are no clear methods of establishing critical conditions, especially in terms of the probability of occurrence. The analyst must use considerable judgement in selecting critical conditions for the particular system. Once loads and either critical conditions or estimated future conditions are specified, the calibrated model can be used to predict the water quality response. The investigation may involve study of extreme hydrological, meteorological, or hydrographic events that affect mixing; waste loadings from point and non-point sources; and changes in benthic demands.

Simplified Illustrative Examples

This section presents illustrative examples of estuarine modeling using both simple screening procedures and the water quality model WASP4. The screening procedures are based upon simple analytical equations and the more detailed guidance provided in "Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants - Part 2." WASP4 examples demonstrate model based estuarine WLA application.

WASP4 is a general multi-dimensional compartment model supported and available through the U.S. EPA Center for Exposure Assessment Modeling.

The examples provided consider eight water quality concerns in three basic types of estuaries. A one dimensional estuary is analyzed by screening methods for conservative and nonconservative toxicants and chlorine residual. Bacteria and DO depletion are simulated. Nutrient enrichment, phytoplankton production, and DO depletion in a vertically stratified estuary are simulated. Finally, ammonia toxicity and a toxicant in a wide, laterally variant estuary are simulated.

The screening procedures can be applied using calculator or spreadsheet. While they may not be suitable as the sole justification for a WLA, they can be valuable for initial problem assessment. Three screening methods are presented for estimating estuarine water quality impacts: analytical equations for an idealized estuary, the fraction of freshwater method, and the modified tidal prism method. These example procedures are only applicable to steady state, one-dimensional estuary problems.

Deterministic water quality modeling of estuarine systems can be divided into two separate tasks: description of hydrodynamics, and description of water quality. The WASP4 model was designed to simulate water quality processes, but requires hydrodynamic information as input. Hydrodynamic data may be directly specified in an input dataset, or may be read from the output of a separate hydrodynamic model. The examples here illustrate tidal-averaged modeling with user-specified hydrodynamics. Both the eutrophication and toxicant programs are described and used.

For the six examples using WASP4, background information is provided, the required input data are summarized, selected model results are shown, and certain WLA issues are briefly described.

Preface

The document is the third of a series of manuals providing information and guidance for the preparation of waste load allocations. The first documents provided general guidance for performing waste load allocation (Book I), as well as guidance specifically directed toward streams and rivers (Book II). This document provides technical information and guidance for the preparation of waste load allocations in estuaries. The document is divided into four parts:

Part 1 of this document provides technical information and policy guidance for the preparation of estuarine waste load allocations. It summarizes the important

water quality problems, estuarine characteristics and processes affecting those problems, and the simulation models available for addressing these problems. This part, "Part 2: Application of Estuarine Waste Load Allocation Models," provides a guide to monitoring and model calibration and testing, and a case study tutorial on simulation of waste load allocation problems in simplified estuarine systems. The third part summarizes initial dilution and mixing zone processes, available models, and their application in waste load allocation. Finally, the fourth part summarizes several historical case studies, with critical reviews by noted experts.

Organization: "Technical Guidance Manual for Performing Waste Load Allocations. Book III: Estuaries"

Part	Title
1	Estuaries and Waste Load Allocation Models
2	Application of Estuarine Waste Load Allocation Models
3	Use of Mixing Zone Models in Estuarine Waste Load Allocation Modeling
4	Critical Review of Estuarine Waste Load Allocation Modeling

1. Introduction

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1.1. Background

This document is the third in a series of manuals providing technical information and policy guidance for the preparation of waste load allocations (WLAs) that are as technically sound as current state of the art permits. The objective of such load allocations is to ensure that water quality conditions that protect designated beneficial uses are achieved. An additional benefit of a technically sound WLA is that excessive degrees of treatment, that do not produce corresponding improvements in water quality, can be avoided. This can result in more effective use of available funds.

This guidance document contains seven elements: 1) an overview of water quality problems and estuarine characteristics, 2) descriptions of estuarine simulation models, 3) descriptions of the monitoring and data collection necessary for model application, 4) guidance on the model calibration and validation, 5) simplified example case studies, 6) review and discus-

sion of past WLA studies, and 7) guidance on use of mixing zone models.

Table 1-1 lists the various "books" and "chapters" that make up the set of technical guidance manuals. 303(d)/TMDL program guidance is currently under development. This guidance will address programs and procedural issues related to total maximum daily loads, wasteload allocations, and load allocations (TMDLs/WLAs/LAs).

Users of this manual also should be aware that other information may affect the wasteload allocation process. For instance, criteria and standards for DO, ammonia, and other parameters are in a continuous process of change. Therefore, any standards used in examples contained in this chapter should not be applied to real-life situations without first consulting the latest applicable criteria and standards.

Table 1-1. Organization of Guidance Manuals for Performance of Wasteload Allocations

BOOK I	303 (d)/TMDL PROGRAM GUIDANCE
	Under development
BOOK II	STREAMS AND RIVERS
	Chapter 1 - BOD/Dissolved Oxygen Impacts and Ammonia Toxicity
	Chapter 2 - Nutrient/Eutrophication Impacts
	Chapter 3 - Toxic Substance Impacts
BOOK III	ESTUARIES
BOOK IV	LAKES, RESERVOIRS AND IMPOUNDMENTS
	Chapter 1 - BOD/Dissolved Oxygen Impacts and Ammonia Toxicity
	Chapter 2 - Nutrient/Eutrophication Impacts
	Chapter 3 - Toxic Substance Impacts

1.2. Introduction to Estuaries

Estuaries are coastal bodies of water where fresh water meets the sea. They are traditionally defined as semi-enclosed bodies of water having a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage (Pritchard, 1967). These classical estuaries are the lower reaches of rivers where saline and fresh water mix due to tidal action. The term has been extended to include coastal waters such as bays and sounds that receive riverine discharge. The backwater river reaches draining into the Great Lakes have also been included as estuaries.

Estuaries are biologically productive bodies of water. They are the spawning and nursery grounds for many important coastal fish and invertebrates. Thus they support commercial and recreational fishing and shellfishing. Many are valuable for recreational boating and bathing, and prized for their aesthetics. At the same time, many estuaries house important harbors, ports, and navigation channels. Many have been used to dilute and flush municipal and industrial wastewater. These various uses of an estuary may cause conflicting demands and burdens on its water quality.

1.2.1. Factors Affecting Estuarine Water Quality

Estuaries are the crossroads of river, sea, atmosphere, and sediment. Most rivers and their associated pollutant loads eventually flow into estuaries. Many major cities and ports are located on estuaries, affecting their quality through domestic and industrial wastewater and dredging. Estuarine circulation can trap nutrients and other pollutants from these waste discharges, the upstream river drainage basin, subsurface waters of the coastal ocean, and atmospheric deposition. Underlying sediments can store and transform these pollutants, either releasing them to the water or burying them. Sedimentation processes are filling or altering all estuaries in response to sea level changes, sediment influx, and intra-estuarine circulation patterns (Shubel, 1971). The complex loading, circulation, and sedimentation processes make water quality assessment and waste load allocation in estuaries difficult.

As estuaries mix fresh water with sea water, their chemistry varies dramatically in space as well as with time. Average values of the major constituents of seawater, and average concentrations and ranges for macronutrients are reported in Table 1-2. As a general rule, in sea water nitrogen limits phytoplankton productivity, whereas in fresh water, phosphorus is the primary limiting nutrient. In estuaries, either nutrient may limit growth.

The importance of atmospheric nitrogen deposition to estuaries has recently received attention with estimates that up to 39% of nitrogen reaching Chesapeake Bay originated in atmospheric deposition (Fisher, et al, 1988). Nitrogen may deposit to watersheds or directly to estuaries in rainfall and dryfall, which includes the deposition of particles greater than 3 microns, aerosol impaction, and gas absorption. A significant amount of nitrogen input to a watershed is removed through denitrification. Estimates range from 20 - 75% (Waddell, 1989). Annual nitrogen inputs of inorganic nitrogen in bulk precipitation across the United States range from 0.1 g/m²/year in some western locations to as high as 0.8 g/m²/year in the east. Organic nitrogen inputs range from 0.1 to 0.4 g/m²/year (Waddell, 1989). Dry deposition may account for about the same input, doubling the total nitrogen inputs.

1.2.2. Estuarine Transport

Transport and circulation processes in estuaries are driven primarily by river flow and tidal action. In shallow estuaries, wind stress can dominate transport. Longitudinal salinity gradients lead to a net upstream drift of heavier sea water. Strong river flow or weak tidal mixing can lead to vertical stratification, where relatively fresh water flows over saline bottom water. Entrainment of bottom water may dilute pollutants in the surface, but upstream transport of salt and pollutants can occur along the bottom. Coriolis acceleration, deflecting currents to the right in the northern hemisphere, may be significant in large estuaries.

As a consequence of these complex transport processes, estuaries cannot be treated as simple advective systems such as many rivers. In rivers, flushing of pollutants is driven primarily by advection. In estuaries, however, both advection and dispersion must be con-

Table 1-2. Major Constituents and Macronutrients in Seawater [Smith (1974)]

Constituent	Average Conc. (mg/L)	Conc. Range (mg/L)
chloride	19350.0	
sodium	10760.0	
magnesium	1300.0	
sulfate	2700.0	
calcium	400.0	
potassium	400.0	
bicarbonate	145.0	
bromine	67.3	
silicon	2.0	0.0 - 4.9
nitrogen	0.28	0.0 - 0.56
phosphorus	0.03	0.0 - 0.09

sidered. Equations and models used for riverine waste load allocation must be carefully considered before application to estuaries.

1.3. Potential Problems to Address

Wastewater discharges into estuaries can affect water quality in several ways, both directly and indirectly. In setting limits on wastewater quantity and quality, all potential problems should be assessed. Wastewater limits should be set to assure attainment of water quality standards.

1.3.1. Salinity

Salinity is important in determining available habitat for estuarine organisms. Large wastewater discharges into relatively small estuaries or embayments can alter the local salinity regime through dilution. Large saline discharges could introduce excess salinity into freshwater embayments of the Great Lakes. Even when the salinity is not affected by the discharge, it is measured and modeled in order to quantify advection and dispersion. These processes help determine how wastewater is assimilated into the estuary.

1.3.2. Sediment

Sediment enters estuaries from many sources, and can alter the habitat of benthic organisms. Sediment is also an important carrier of such pollutants as hydrophobic organic chemicals, metals, and nutrients. Sediment transport can move pollutants upstream, or between the water column and the underlying bed. Even when wastewater does not introduce excess sediment into an estuary, it is often measured and modeled in order to quantify the transport of sediment-bound pollutants.

1.3.3. Bacteria and Viruses

Bacteria and viruses may enter estuaries in runoff from farms and feedlots and in effluent from marinas as well as from municipal or industrial wastewater discharges. These pathogens may be transported to bathing beaches and recreational areas, causing direct human exposure and possibly disease. Pathogens also may be transported to shellfish habitat; there they may accumulate in oysters, clams, and mussels and, subsequently, cause disease when eaten by humans.

1.3.4. Dissolved Oxygen Depletion

Adequate, sustained DO concentrations are a requirement for most aquatic organisms. Seasonal or diurnal depletion of DO, then, disrupts or displaces estuarine communities. Ambient DO levels are affected by many natural processes, such as oxidation of organic material, nitrification, diagenesis of benthic sediments, photosynthesis and respiration by phytoplankton and submerged aquatic vegetation, and reaeration. The

natural balance can be disrupted by excessive wastewater loads of organic material, ammonia, and nutrients. Other sources of nutrients, such as runoff from agricultural, residential, and urban lands and atmospheric deposition, also can disrupt the DO balance. Excessive heat input from power plants can aggravate existing problems. Because of its intrinsic importance, and because it is affected by so many natural and man-influenced processes, DO is perhaps the best conventional indicator of water quality problems.

1.3.5. Nutrient Enrichment and Overproduction

Adequate concentrations of nitrogen and phosphorus are important in maintaining the natural productivity of estuaries. Excessive nutrient loading, however, can stimulate overproduction of some species of phytoplankton, disrupting the natural communities. Periodic phytoplankton "blooms" can cause widely fluctuating DO concentrations, and DO depletion in benthic and downstream areas. Nutrient loads can be introduced in wastewater and runoff and through atmospheric deposition.

1.3.6. Aquatic Toxicity

Ammonia, many organic chemicals, and metals, at often very low concentrations, can disable or kill aquatic organisms. Acute toxicity is caused by high exposure to pollutants for short periods of time (less than 4 days). Chronic toxicity is caused by lower exposures for long periods of time (greater than four days). The toxicity of a chemical can be affected by such environmental factors as pH, temperature, and sediment concentrations. Overall toxicity results from the combined exposure to all chemicals in the effluent and the ambient waters.

1.3.7. Bioaccumulation and Exposure to Humans

Lower concentrations of organic chemicals and metals that do not cause aquatic toxicity can be taken up and concentrated in the tissues of estuarine organisms. As fish predators consume contaminated prey, bioaccumulation of these chemicals can occur. This food chain contamination can persist long after the original chemical source is eliminated. Humans that regularly consume tainted fish and shellfish can receive harmful doses of the chemical.

Human exposure to harmful levels of organic chemicals and metals can also occur through drinking water withdrawals from fresh water tidal rivers.

1.4. Overview of the Waste Load Allocation

Book I, 303 (d)/TMDL Guidance discusses the overall TMDL process, procedures, and considerations. The

reader is referred to this book for procedural guidance. This book gives specialized modeling guidance.

A WLA provides a quantitative relationship between the waste load and the instream concentrations or effects of concern as represented by water quality standards. The reliability of this relationship depends upon the accuracy and completeness of the data, certain characteristics of the model, and the skill and judgment of the modeler. During the development of a WLA, the user combines data and model first to describe present conditions and then to extrapolate to possible future conditions. The process is iterative: observed data are used to refine model input (or even model equations) and modeling results are used to guide monitoring efforts.

The WLA process sequentially addresses the topics of hydrodynamics, mass transport, water quality kinetics, and for some problems, bioaccumulation and toxicity.

1.4.1. Hydrodynamics

The topic of hydrodynamics addresses where the water goes. Both primary and secondary water circulation patterns can significantly affect water quality. In some estuaries, monitoring programs can adequately quantify the primary circulation patterns associated with tidal excursions and tributary inflow. Hydrodynamic models may be needed, however, to investigate secondary currents associated with the net residual tidal action, wind, density differences, or Coriolis acceleration. Hydrodynamic models also may be used to interpolate data between monitoring stations or to extrapolate data to future conditions. The final result of the hydrodynamics study is a record of water flow and volume (or velocity and elevation) throughout the water body over an appropriate period of time.

1.4.2. Mass Transport

Mass transport addresses the fate of dissolved, non-reactive substances. These tracers are subject to advection with the water currents and to turbulent diffusion. If only the primary circulation is resolved in the hydrodynamics step, then secondary circulation, such as density currents and lateral shear, are parameterized into dispersion coefficients. The values of these coefficients are determined by calibrating the model to salinity or dye tracer data. This calibration process also can be used to refine the advective flows estimated in the hydrodynamics step. Recalibration of advective flows based on tracer data can be particularly important in cases where net tributary inflow to the estuary is uncertain. The final result of the mass transport step is a record of advective and dispersive fluxes (or the appropriate model coefficients) for dis-

solved, nonreactive substances throughout the water body over the period of study.

1.4.3. Water Quality Kinetics

Water quality kinetics describe what happens to a set of physical, chemical, and biological constituents as they are transported throughout the water body. The set of constituents modeled depends upon the water quality problem of concern. General models are available describing the primary constituents and reactions for the water quality problems outlined in this manual. For most WLA studies, the user must provide appropriate site-specific values for the reaction coefficients and the environmental conditions (such as temperature, sunlight, and pH). In some complex studies, the user may have to modify model equations describing the reactions or add more simulated constituents. Although literature values are available to guide initial model parameterization, local monitoring data are required to refine these values and construct a site-specific model. The user arrives at appropriate parameter values through an iterative model calibration and testing process. The final result of the water quality kinetics step is a record of constituent concentrations throughout the water body for the period of study and for hypothetical future periods under various waste load management strategies.

1.4.4. Bioaccumulation and Toxicity

Often, water quality constituent concentrations (or toxicity units) are directly compared with appropriate standards to infer potential risk to humans or the aquatic community. Waste loads may be adjusted so that concentrations do not exceed (or fall below) these standards under design conditions. Alternatively, waste loads may be adjusted so that concentrations exceed standards for less than a specified frequency and duration over a realistic range of future conditions.

Recent advances in environmental toxicology allow the direct calculation or simulation of bioaccumulation and toxicity for some classes of chemicals. To simulate bioaccumulation by individual fish (or a local species of fish), the user must specify an exposure scenario plus a few physiological parameters. Although literature values for the parameters are available, monitoring data should be used for site-specific calibration. Direct toxicity due to the narcotic effects of neutral hydrophobic organic chemicals can be predicted. To simulate food chain bioaccumulation, the user must define the main components of the local food web (who eats whom), and calibrate the physiological parameters for each. This task requires considerable judgment and a good data base.

1.5. Steps in the Modeling Process

For each of the topics addressed in a modeling study, several steps are applied in an iterative process. The first step is problem identification. The modeler reviews existing data related to all potential problems, which were discussed in Section 1.2. The second step is model identification. Starting with knowledge of the site and the water quality problems of concern, the modeler reviews existing data and identifies an appropriate simulation model or data base. Additional monitoring is planned to gain further knowledge about existing conditions and important processes.

The third step is initial calibration of the model to existing data. Where site-specific data are lacking, literature values and user judgment are employed. Sensitivity analysis is used to estimate the uncertainty in model predictions due to each uncertain input. This information can be used to guide ongoing monitoring efforts.

As more data sets become available, the calibrated model is tested and refined. Recalibration should address all previous data sets. Throughout this step, the user should be guided by the principle of parsimony - calibration and validation of the model should be accomplished with the fewest possible parameters. A single longitudinal dispersion coefficient that adequately represents an entire estuary is preferable to a series of coefficients that allow a slightly better fit to data. Model parameter values should be consistent across the range of tested data. If values must vary, they should follow some rational function. This functional relationship becomes an external part of the model that should be documented and tested.

After some effort at recalibration and testing, the modeler decides either that the model is sufficiently reliable to produce a sound waste load allocation, or that available time and resources do not permit continued refinement. At this point, the degree of model validation must be assessed. Traditional practice dictates that an independent data set be used for a final validation test of the model. Sometimes such a data set is unavailable, or has already been used in the recalibration process. In any case, a final uncertainty analysis should document the model's expected reliability over the range of conditions tested. Validation is contingent upon the waste load options to be considered. A model may be considered valid to study some options, but invalid to study others.

After the WLAs have been put into effect, some degree of monitoring should be pursued to track the effectiveness of the actual waste load reductions in meeting water quality goals. When sufficient data are available, a post-audit should test model predictions under the new conditions. Refinements in the model at this point may guide refinements in the waste load allocation and contribute to more informed judgment in future studies involving similar pollutants and estuaries.

1.6. Organization and Scope

The basic estuarine guidance document is comprised of four parts. Part 1, "Estuaries and Waste Load Allocation Models," summarizes the important water quality problems, estuarine characteristics and processes affecting these problems, and the simulation models that are available for addressing these problems. Part 2, "Application of Estuarine Waste Load Allocation Models," provides a guide to monitoring and model calibration and testing, and a case study tutorial on simulation of waste load allocation problems in simplified estuarine systems.

Part 3, "Use of Mixing Zone Models in Estuarine Waste Load Allocations," summarizes initial dilution and mixing zone processes, available models, and their application in waste load allocation. Part 4, "Critical Review of Estuarine Waste Load Allocation Modeling," summarizes several historical case studies, with critical reviews by noted experts.

1.7. References

- Fisher, D., Ceraso, J., Mathew, T., and Oppenheimer, M. 1988. *Polluted Coastal Waters: The Role of Acid Rain*. Environmental Defense Fund, New York.
- Pritchard, D.W. 1967. *What is an Estuary: Physical Viewpoint*. Estuaries. ed: Lauff, G.H., American Association for the Advancement of Science, Publication No. 83, Washington, D.C.
- Shubel, J.R. 1971. *The Origin and Development of Estuaries. The Estuarine Environment-Estuaries and Estuarine Sedimentation*. American Geological Institute.
- Smith, F.G.W., ed. 1974. *CRC Handbook of Marine Science, Vol. I*. CRC Press, Cleveland, OH.
- Waddell, T.E. 1989. *Draft Report: State of the Science Assessment: Watershed and Estuarine Nitrogen Transport and Effects*. U.S. Environmental Protection Agency, Athens, GA.

2. Overview of Processes Affecting Estuarine Water Quality

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2.1. Organization Of This Section

This section is organized into six major parts. Section 2.2 contains an overview of estuarine morphology and classification. A more detailed description of physical processes impacting estuarine circulation and mixing is provided in Section 2.3. Subsequent parts of Section 2 deal with major processes affecting water quality, including sediment transport and sediment water quality interactions (Section 2.4), organic wastes, dissolved oxygen (DO) and nutrients (Section 2.5), synthetic organic chemicals (Section 2.6), and metals (Section 2.7). Sections 2.2 to 2.7 provide an overview of processes followed by supplemental text describing in greater detail how each of these basic processes are described in estuarine waste load allocation (WLA) models.

2.2. Estuarine Morphology and Classification

The geomorphology of estuaries strongly affects the transport of pollutants and ultimately their water quality characteristics. Estuarine depth controls propagation of the tidal wave. Shallow channels and sills increase vertical mixing; deep channels are more likely to be stratified and to have greater upstream salinity intrusion. Shallow sills near the mouth of an estuary may limit circulation and flushing of bottom waters. The length of the estuary and conditions at the upstream boundary determine the type of tidal wave, the phase between current velocities, and the tidal heights. The width affects velocities (narrow constrictions increase vertical mixing and narrow inlets restrict tidal action).

Wind-induced circulation is transient and interacts with channel geometry to produce various circulation patterns. Estuaries have typically been classified based on their geomorphology and patterns of stratification and mixing.

Based on their hydrodynamics, estuaries have been classified as sharply stratified, partially stratified and well mixed (Bowden 1967, Pritchard 1967). Sharply stratified estuaries exhibit little mixing between the salt wedge and fresh water flow. Examples include fjords and salt-wedge estuaries, such as the Mississippi River estuary. In sharply stratified estuaries tidal action is not sufficient to mix the separate layers. Completely mixed estuaries do not exhibit significant vertical density variations and tidal flow is normally greater than fresh water inflow. Examples of this include the Delaware and Raritan River estuaries which are normally well mixed. Partially stratified estuaries are intermediate between sharply stratified and completely mixed estuaries. Partially stratified estuaries exhibit significant vertical density gradients but the gradients are less sharp than in sharply stratified estuaries. Examples include the James River Estuary (Mills et al. 1985).

Hannsen and Rattray (1966) proposed a classification scheme based on vertical variations in salinity and the strength of the internal density-driven circulation. A stratification parameter is computed from the vertical salinity gradient which is then compared to a circulation parameter computed from net surface and fresh water flow velocities. These parameters are calculated at various points along the estuarine channel and may be used to estimate degree of stratification of the system. Further description of the method is provided by Mills et al. (1985).

Based on their geomorphology, typical classifications (Fischer et al. 1978) are: (1) drowned river valleys or coastal plain estuaries (e.g., Chesapeake Bay, Delaware Estuary), (2) bar-built estuaries (e.g., Galveston Bay, Pamlico Sound), (3) fjords (e.g., Puget Sound), and (4) other diverse formations (e.g., San Francisco Bay).

Coastal plain estuaries are generally broad and relatively shallow (rarely over 30 m in depth) with gently sloping bottoms and depths increasing uniformly towards the mouth and with extensive areas of deposited sediment. Such estuaries usually have been cut by erosion and are drowned river valleys, often displaying a dendritic pattern fed by several streams. Coastal plain estuaries are usually moderately stratified and can be highly influenced by wind. The majority of estuaries in the contiguous United States are of the drowned river or coastal plain type.

Bar-built estuaries are bodies enclosed by the deposition of a sand bar off the coast through which one or more channels provide exchange with the open sea. These are usually unstable estuaries, subject to gradual seasonal and catastrophic variations in configuration. Many estuaries along the Gulf Coast and Lower Atlantic regions are of this type. They are generally shallow (e.g. a few meters deep or less), often vertically well mixed, and highly influenced by wind.

Fjords are generally long and narrow with steep sides and relatively deep waters. They typically are strongly stratified and have shallow sills at the estuarine mouth that often limit mixing of deep waters. They usually are formed by glaciation and are typically found in Alaska. The fresh water streams that feed a fjord generally pass through rocky terrain. Little sediment is carried to the estuary and the bottom is likely to be a rocky surface.

Estuaries not covered by the above classifications usually are produced by tectonic activity, faulting, landslides or volcanic eruptions. An example is San Francisco Bay which was formed by movement of the San Andreas Fault system (Mills et al. 1985).

2.3. Factors Affecting Circulation And Mixing

Estuaries and coastal seas have circulation patterns that are highly variable in time and space. Awareness of characteristic time and space scales of flows generated by the tides, winds, density gradients resulting from the interaction of fresh and ocean water, and the effects of the earth's rotation (the Coriolis force) will help to define the mixing regime of the water body. Estuaries generally are large water bodies that have more vigorous circulations than occur in rivers and most lakes. Like rivers and lakes, however, internal factors such as friction and vertical mixing play similar physical roles in the marine environment to those in fresh water systems in the redistribution of pollutants. The existence of stratification (vertical density gradients) in estuaries, as well as the more complex external forcings (such as tidal fluctuations), modify the effects of vertical mixing and friction to the extent that parameterizations used to evaluate mixing in fresh water must be used with caution if at all. This section

briefly discusses the physical forces affecting estuaries. More extensive discussions can be found in standard texts on estuaries such as that by Fischer et al. (1978).

2.3.1. Tides

The ocean tides are produced principally by interaction of the gravitational fields of the earth, moon, sun and, to a lesser degree, other solar system bodies. The principal effects are caused by the moon and occur on a roughly 12.4-hour period. Solar effects occur at 1-day periods. Because all the bodies in the solar system are in motion relative to one another, the effects of their gravitational fields vary in time. One result is the familiar spring-neap cycle of tides. Astronomical tidal motion is highly predictable. Such information is published annually in the National Ocean Service Tide Tables and Tidal Current Tables. Tide tables provide predictions of times and heights of high and low water. Tidal current tables provide predicted times, magnitudes and directions of maximum ebb and flood and high and low water slacks for principal coastal stations referenced to the standard locations.

Tides are expressed in terms of amplitude (the variation of water level about some datum level) and tidal current (the ebb and flood velocity fields). Tidal amplitudes in North America vary from tenths of meters in the Gulf of Mexico to more than 10 meters in parts of Alaska and the Canadian Maritime Provinces. Tidal current magnitudes are also highly variable, with the highest values being recorded in topographically constrained straits. Tidal amplitude and tidal current are usually out of phase so the time of high water is not the same as the time of high water slack. Such differences in phase and interaction between main and side channels can lead to tidal trapping of parcels of water in side channels or embayments.

The effect of the tides is to cause: (1) time-variable mixing through frictional interaction with the bottom and (2) spatially asymmetric flow patterns on ebb and flood through interaction with the bottom topography. The interactions of the tides with other driving forces and with topography also may result in residual circulation patterns of small magnitude but great persistence, which could play a significant role in the transport of pollutants.

2.3.2. Earth's Rotation Effects - Coriolis Force

The effect of the earth's rotation on the motion of fluids is to deflect the flow to the right (left) in the northern (southern) hemisphere. In estuaries wide enough to be affected by this force, the effect is to move less dense water to the right (left) side, looking seaward, of the estuary. A further effect is that the interface between

waters of different densities tends to be sloped as the pressure gradient forces and the Coriolis force balance each other to achieve geostrophic balance. The effect can be enhanced in estuaries by the action of the tides and can result in regions of persistent inflow of sea water on the left and outflow of fresher water on the right. The Coriolis effect is considered important for low Rossby numbers ($N_R < 0.1$, where N_R is the Rossby number, the ratio of the inertial force to the Coriolis force).

The time scale for rotational effects is the local inertial period, which increases north to south. Inertial periods for the contiguous states range from about 15 hours in Washington state to 30 hours in southern Florida. The appropriate length scale in estuaries is the internal Rossby radius, which is the ratio of the internal wave speed to the local inertial frequency. This length scale accounts for both local density structure (degree of stratification) and water depth.

2.3.3. Fresh Water Inflow

Fresh water inflow volume to an estuary can vary from short-term response to local storms or the passage of hurricanes to seasonal wet and dry cycles. In some estuaries, the volume of fresh water is sufficient to maintain a density difference over large distances before being completely mixed into sea water. Such density differences result in flow patterns that tend to maintain the density differences. Areas with high gradients, the pycnocline and fronts, tend to resist the localized processes of mixing and may result in "pools" of fresher water confined along one section of the coast. Examples include the Chesapeake Bay Plume and a band of fresher water confined within about 15 km of the shore along the South Atlantic Bight (Georgia and the Carolinas). Pollutants introduced into these waters may be confined there for relatively long periods.

Increased fresh water inflow can change the character of an estuary from well-mixed to partially mixed or possibly stratified. Decreased inflow could have the opposite effect with concomitant increased upstream intrusion of sea water. Such changes in the vicinity of an outfall can change the degree of mixing of the effluent. Fresh water inflow varies primarily on seasonal scales but large amounts of fresh water can be introduced to estuarine systems by severe storms, especially tropical cyclones along the East and Gulf Coasts during late summer and fall. The response of estuarine circulation to changes in fresh water flow will vary according to the type of estuary. The time scale of the response is roughly the flushing time of the water body, which can vary from a few days for an estuary with large fresh water flows and strong tides (the Columbia River estuary) or for numerous shallow estuaries along the

Gulf Coast (the Brazos River and Colorado River Estuaries) to several months for an estuary that is shallow and has weak tides such as Pamlico Sound.

2.3.4. Friction and Vertical Mixing

Friction is the term in the equations of fluid motion that accounts for the dissipation of energy by small scale turbulent motions. Similarly, turbulence generated by vertical shear in the fluid tends to mix dissolved constituents and acts to reduce sharp vertical gradients. Friction forces retard or change the direction of fluid flow. The friction term is used here to parameterize the turbulent transfer of momentum and mass within a fluid or between the fluid and the boundaries, such as between the atmosphere and the water (wind stress) or between the water and the bottom. Frictional effects are seen in the formation of turbulent boundary layers in fluids and in the turbulent mixing of properties in those layers. Frictional effects have rather short time scales for small scale turbulence but several hours may be required for the frictional spin-down of a fluid flow after its driving force is removed. Bottom boundary layers may have vertical scales up to 10 meters, whereas horizontal boundary layers can be several kilometers wide. In general, the effects of horizontal boundary layers are ignored and efforts concentrate on the vertical layers caused by wind stress and bottom interactions. Because the scale of the vertical layers is small, shallow water is more easily affected by friction than deep ocean waters. Generally, the stronger the flows, either due to tides or wind effects, the more turbulent the water column with a tendency for rapid vertical mixing.

2.3.5. Meteorological Effects

Meteorological effects considered here are the result of both local and remote wind forcing and other atmospheric pressure forcing separate from the wind. Rainfall as an input of fresh water is considered separately. Wind effects include generation of persistent circulation patterns caused by seasonal weather changes in a particular area, modification of circulation patterns by localized weather, and generation of waves and storm surges. Water responds to an applied wind stress within a few hours and to the cessation of the wind in about the same time frame. The winds vary on a variety of time scales, such as diel variations (sea breeze), the time scale of frontal passages and the seasonal changes in prevailing winds. Variability of wind speed and direction over periods shorter than the frontal passage scale will be evidenced primarily in the production of turbulent mixing within a few meters of the surface.

Atmospheric pressure affects sea level through the "inverse barometer" effect where low atmospheric pressures cause the sea level to be higher than normal

(about 1 cm per millibar) and high atmospheric pressure lowers the sea level. This effect and those associated with strong winds (wind setup and setdown) modify the astronomical tides and are called meteorological tides.

In estuaries with relatively small input of fresh water and small tide range, such as Mobile Bay, Alabama, wind is the dominant force in driving the overall circulation and in generating turbulent mixing. The wind driven circulation has time scales of a few days at the period of local frontal passages. On open coastlines the winds are also the dominant forcing mechanism through the generation of long-period waves (length scales of order 100 to 1000 km, time scales 2 to 10 days). Sea level fluctuations due to strong storms (i.e. winter or extratropical cyclones) are called storm surges which can have devastating effects on low lying coastal regions. In this way, both local and remote winds can play a large role in the dynamics of an open coast.

See Supplement I for greater detail on how processes affecting circulation and mixing are described in estuarine models. This Supplement is found on page 2.10 at the end of this chapter.

2.4. Sediment Transport and Sediment/Water Quality Interactions

2.4.1. Concepts

Sediment typically is associated with agricultural and urban runoff. Sediment not only affects water transparency, but can carry chemicals such as nutrients and toxic substances into receiving waters. Therefore, an important aspect of water quality modeling is the capability to simulate sediment transport and sediment/water interactions.

Unlike rivers, which have reasonably constant water quality conditions, the large changes in salinity and pH in an estuary directly affect the transport behavior of many suspended solids. Many colloidal particles agglomerate and settle in areas of significant salinity gradients.

Sediments are also in a constant state of flux due to the time varying currents in estuaries, and movement of sediments along the bottom often does not occur in a net downstream direction as in stream reaches. Consequently estuaries tend to trap sediments (Mills et al. 1985).

Estuarine sediment transport has two main components – bed load and suspended load – both of which may be important.

Even when no sediment is transported by the flow, deposited sediments can have a strong influence on water quality in the overlying water. Through adsorption, biofilm assimilation and other chemical/biochemical transformations, sediments can become sinks or sources of materials such as oxygen, toxic chemicals, or nutrients.

For water quality assessment purposes, the finer fractions of materials (silts, clays, organic detritus and live plankton materials) are often of most importance. Particles are characterized by size, shape, density, surface area, and surface physical and chemical properties including electric charge. A review of particle regime composition, behavior and interaction with water density was given by Lal (1977).

2.4.2. Processes

2.4.2.1. Fall Velocities, Settling, Deposition

For water quality modeling, the fall velocity of particles and their resistance to resuspension under shear stress, once they are deposited, are most significant. Fall velocities are functions of size, shape (drag coefficient) and density (of both the water and particle) and can be reasonably well predicted for larger mineral particles (Dietrich 1982; Gibbs et al. 1971). For micrometer-size particles and particularly for organic particles, the large diversity in sizes, shapes, and density (Lal 1977; Ives 1973) often require indirect determinations of fall velocities from settling traps or mass balances. Settling velocities are used to calculate the movement of sorbed chemical downward through the water column. The settling characteristics of particles may vary as they respond to water quality conditions in an estuary (See 2.4.2.4.).

2.4.2.2. Resuspension, Scouring, Erosion

The resuspension or entrainment of sediments is a function of the sediment properties, and flow-induced shear stress at the sediment-water interface. For non-cohesive sediments, this relationship is "explosive" in nature. Very low or no resuspension occurs until a threshold shear stress is reached. Then resuspension rates increase in proportion to some power of the excess shear stress.

For cohesive sediments, which are of primary interest in water quality studies, entrainment is affected by salinity, sediment type, microfauna, organic content, and the time-history of the bottom sediments (Sheng 1983). Bed compaction may result in there being a finite

amount of sediment that can be entrained at a given shear stress (Lick et al. 1987), where the amount depends upon the time-history of the bottom sediment, rather than entrainment depending solely on particle density and shear velocity. The lack of well established descriptions of entrainment for cohesive particles requires site-specific calibration to refine initial estimates.

2.4.2.3. Cohesion

Cohesion of particles in the deposited bed increases the resistance to resuspension and is a function of consolidation history (Stefan, Ambrose and Dortch 1988). Investigations of this behavior have been reviewed by Mehta (1986). In addition to bed shear, stresses due to wind driven flows and perturbations by boat movement or organisms (bioturbation) can greatly increase rates of resuspension of cohesive sediments. Resuspension effects of wind have been conceptualized by Rodney and Stefan (1987).

2.4.2.4. Coagulation and Flocculation

Extremely fine particles often destabilize (coagulate) in regions of significant salinity gradients and agglomerate to form larger particles (flocculate). The resulting floc may then settle at a much different rate, due to the greater agglomerated mass, than the individual particles. Coagulation occurs when electrolytes, such as sodium chloride, neutralize the repulsive forces between clay particles allowing them to adhere upon collision (flocculate). Flocculation rates are dependent upon the size distribution and relative composition of the clays and electrolytes and upon local boundary shear stresses (Mills et al. 1985; Stefan, Ambrose and Dortch 1988).

2.4.2.5. Sorption

Suspended sediment, besides being a very important water quality parameter in its own right, also can have a very strong relationship with chemical species dissolved in the water through adsorption/desorption, for example, of nutrients or synthetic organics (often toxic materials). This is an area of very active research (e.g. Golterman et al. 1983; Stumm and Morgan 1981; Karickhoff 1984) and will be addressed in a later section in more detail.

2.4.2.6. Bottom Boundary Layer

The interaction between particles and water chemistry becomes particularly complex near the bed because of: (a) strong vertical velocity gradients associated with shear forces; (b) activities of organisms such as biofilms, invertebrates, crustaceans and fish; and (c) pore water movement, which leaches into and out of the outlying waters.

Microcosm models or measurements of these systems are necessary to provide the input or withdrawal rates of dissolved substances. Examples include sedimentary oxygen demand (Chen et al. 1984, Gantzer et al. 1988), phosphorus release and polychlorinated biphenyl (PCB) resuspension.

See Supplement II for greater detail on sediment transport and sediment/water quality interactions. This Supplement is found on page 2-18 at the end of this chapter.

2.5. Organic Wastes, Dissolved Oxygen And Nutrients

2.5.1. Concepts

This section is a brief overview of the common processes used to model organic wastes, DO and nutrients (referred to as conventional pollutants) and their interactions. For more detailed information, the reader should refer to other resources (Bowie et al. 1985; Orlob 1983; Chapra and Reckhow 1983; Thoman and Mueller 1987). The focus of WLA models of conventional pollutants is often DO and biochemical oxygen demand (BOD) as a general measure of the health of the system, or the focus can be primary productivity when eutrophication is the major concern. Conventional WLA models usually include temperature, major nutrients, chemical characteristics, detritus, bacteria, and primary producers. WLA models may include higher trophic levels (i.e. zooplankton and fish) because of their effects on other more important variables, such as phytoplankton, BOD and DO.

Zooplankton and fish also provide a means of controlling lower trophic levels, which can affect nutrients and DO (bio-manipulation). Additional information on modeling these processes is provided in Section 3.

2.5.2. Fate Processes

Upon entry to the estuary, settling of particulate organic matter and particulate nutrients generally occurs. High flow events may scour previously deposited material. Organic matter is oxidized, drawing upon the DO supply, which is replenished by reaeration.

Organic nitrogen is mineralized to ammonia, which reaches equilibrium with its ammonium form. Nitrification further draws upon the DO supply converting ammonia to nitrite and then nitrate. Nitrate may be converted back to ammonia or to nitrogen gas through

denitrification in low DO regions of the estuary. Ammonia and nitrate may be taken up by phytoplankton and aquatic plants and incorporated into the food chain, eventually returning to the water as organic nitrogen.

Organic phosphorus is mineralized to orthophosphate, which reaches sorptive equilibrium with suspended or benthic sediment. Particulate sorbed phosphate settles; dissolved phosphate is rapidly taken up by phytoplankton and aquatic plants and incorporated into the food chain, eventually returning to the water as organic phosphorus.

Organic material deposited to benthic sediment is oxidized in the upper aerobic layer, and reduced in the lower anaerobic layers. Upward fluxes of ammonia and reduced organic species are produced, the latter contributing to sediment oxygen demand.

The transfer, or flux of phosphorus, across the sediment water interface is enhanced by anaerobic conditions as particulate phosphorus may be resolubilized and reenter the water. In some aquatic environments, net sedimentation buries a substantial fraction of the nutrients and organic matter deposited to the bed.

Although many of these interacting fate pathways are well known and included in most recent conventional water quality models, accurate simulations remain difficult. Extensive site-specific data collection is required to characterize both the sources and the process rates over the range of expected conditions. Many of the rates are biologically mediated, with descriptive constants and parameters that vary both with environmental conditions and predominant species. The major pathways and cycles will be briefly discussed in the following sections and the supplement from the model developer's perspective. Additional information is provided in Section 3.

2.5.2.1. Phytoplankton Kinetics

Phytoplankton kinetics assume a central role in eutrophication affecting both the nitrogen and phosphorus cycles, the DO balance, and food chain response.

The reaction term for phytoplankton is expressed as the difference between the growth rate and the death and settling rates in each volume element. The growth rate of phytoplankton is a complicated function of the species present and their differing reactions to solar radiation, temperature, and the balance between nutrient availability and phytoplankton requirements. Phytoplankton "death" rates are conventionally expressed as the sum of the endogenous respiration rate, the death rate, and the grazing rate. Available information does not allow simulation of individual species in

a natural environment. Hence, models either simulate the phytoplankton community as a whole, or as classes such as greens, diatoms, blue-greens, and dinoflagellates.

Phytoplankton kinetics affect the oxygen, nitrogen, phosphorus, and carbon cycles primarily through uptake and secondarily through death. Proper specification of average stoichiometry is necessary to accurately model these interactions. The ratios of phytoplankton carbon to phytoplankton nitrogen, phosphorus, and chlorophyll-a vary among species and in time. Few applied modeling frameworks account for the dynamics of stoichiometry. The user is forced to specify average values or those characteristic of stressed systems.

2.5.2.2. The Phosphorus Cycle

Organic phosphorus in the water is present in various particulate and dissolved forms that mineralize and settle at different rates. Some models lump all organic phosphorus into a single state variable; others divide organic phosphorus into two, three, or four state variables that differ in settling and mineralization rates. Mineralization or bacterial decomposition is generally modeled as a first order temperature-corrected reaction, although second order and saturating rates based upon phytoplankton biomass have been employed.

Dissolved inorganic phosphorus sorbs to suspended particulate matter in the water column. Subsequent settling of the solids and sorbed phosphorus can provide a significant loss mechanism of phosphorus from the water column to the benthos. Process based functions that accurately calculate the phosphorus partition coefficient would improve prediction of this important variable significantly. Phosphorus may resolubilize under anaerobic conditions and the flux of phosphorus to the water column may be enhanced under anaerobic conditions at the sediment-water interface as well as by high pH conditions.

Dissolved inorganic phosphorus is taken up by phytoplankton at the stoichiometrically modified growth rate.

Although there is evidence for "luxury storage" of inorganic phosphorus in phytoplankton, most models assume the internal pool of phosphorus is biomass. Grazing causes transfer of phytoplankton phosphorus up the food chain. Upon respiration and death, biomass phosphorus is recycled to the various forms of organic and inorganic phosphorus at user-specified ratios.

2.5.2.3. The Nitrogen Cycle

Nitrogen may be characterized as organic and inorganic forms, where inorganic forms may include ammonia-nitrogen, nitrate-nitrogen and nitrite-nitrogen. As for organic phosphorus, some models lump all organic nitrogen into a single state variable, whereas others divide organic nitrogen into two, three, or four state variables. Some modeling approaches use nitrogenous biochemical oxygen demand (NBOD) as a state variable. Mineralization to ammonia can be represented as first-order, or second order or saturating dependence on bacterial biomass.

Ammonia-nitrogen in the presence of nitrifying bacteria and oxygen is converted to nitrite then nitrate-nitrogen. The process of nitrification in natural water is complex, depending upon DO, pH, total inorganic carbon, alkalinity, *Nitrosomonas* and *Nitrobacter* bacteria, and flow conditions.

Most models represent the reaction with a first-order, temperature-corrected rate constant.

Some models treat nitrate and nitrite-nitrogen as a single lumped variable. Some models allow spatial variations calibrated by the user or empirical DO limitation terms. Obviously, a process-based predictive function for this rate would be quite valuable.

Denitrification is the reduction of nitrate to ammonia and nitrogen gas. Primarily a benthic reaction, it is included in some models as a loss rate of nitrate. It is modeled as a first order reaction, sometimes multiplied by a modified Michaelis-Menten term to suppress the reaction in the presence of a small amount of oxygen. Un-ionized ammonia may also be degassed and is of additional importance due to its toxicity.

Both ammonia and nitrate are taken up by phytoplankton at the stoichiometrically modified growth rate. Some models include a preference function for ammonia uptake when its concentration is high enough. Grazing causes transfer of phytoplankton nitrogen up the food chain. Upon respiration and death, biomass nitrogen is recycled to the various forms of organic nitrogen and ammonia at user-specified ratios.

2.5.2.4. The Carbon-Dissolved Oxygen Balance

Organic carbon is composed of a variety of materials in estuaries, both dissolved and particulate. Some models lump all organic carbon into a single state variable expressed in units of oxygen--carbonaceous biochemical oxygen demand (CBOD). Other models represent various fractions of organic carbon, with their separate oxidation and settling rates. Oxidation is

generally modeled as a first order temperature-corrected rate. Some models allow spatial variations calibrated by the user.

Traditional models of organic waste do not compute inorganic carbon and the associated variables of pH and alkalinity. This carbonate system could be important for simulating the effects of acidic wastes on unionized ammonia concentrations or potential carbon dioxide limitation in low alkalinity, high nutrient waters. Models that include the carbonate system calculate total inorganic carbon as the sum of bicarbonate, carbonate, and carbon dioxide. These species are in equilibrium controlled by the equilibrium constants of the dissociation reactions and the pH of the water. Carbon dioxide (and thus total inorganic carbon) is produced by respiration, consumed by algal growth, and replenished by atmospheric exchange.

Carbonate alkalinity is the sum of bicarbonate concentration plus twice the carbonate concentration plus the hydroxide concentration minus the hydrogen ion concentration. Addition of acids and nitrification lowers the pH and reduces alkalinity. Nitrate uptake by phytoplankton produces hydroxide and increases alkalinity.

DO is depleted by oxidation of organic carbon, nitrification, and respiration. Benthic reactions depleting oxygen are usually modeled as a spatially variable flux of sediment oxygen demand. Respiration effects may be combined for simplicity or separated into components such as respiration by bacteria, plankton, macrophytes, fish, etc. The respiration of decomposers that utilize organic matter is referred to as decomposition. Oxygen is used during some chemical transformations, such as nitrification and the oxidation of reduced substances (e.g. sulfide, methane, reduced iron, and reduced manganese).

Biochemical oxygen demand (BOD) is a measure of the materials present in a sample which may be oxidized by biochemical processes. The BOD exerted is determined by the change in oxygen concentrations of a sample over time under specific analytical conditions. The modeling problem with BOD is that it combines the effects of several oxygen consuming processes into one variable; this approach may be too simple for modeling some systems.

The more realistic approach is to separate oxygen demands into various components, such as biodegradable organic (carbonaceous) demands, nitrogenous demands, and oxidation of other substances (e.g., reduced metals, sulfide, etc.). Biodegradable organic demands may be due to dissolved and particulate matter in the water column and bottom sediments.

Some models separate water column organic matter into particulate and dissolved forms, referred to as POM and DOM. Because some forms of organic matter decay at faster rates than others, organic matter may be further divided into those that decay at a fast rate (labile) and those that decay at a slower rate (refractory). As labile organic matter decomposes, a portion is transferred to the refractory state. A similar approach can be used for organic sediments. Sources of organic matter include external waste loads and excretions and mortality of living substances.

DO is replenished by phytoplankton growth (photosynthesis) and by reaeration. Many reaeration formulas exist as well as in-situ measurement techniques. Reaeration formulas based solely on velocity and depth applicable to tidal rivers and estuaries include O'Connor-Dobbins (1958, for slower, deeper rivers), Churchill (1962, for moderately deep, faster streams) and Owens et al. (1964, for shallow streams) (see Thomann and Mueller 1987).

The Tsvoglou and Wallace method (1972) calculates reaeration in rivers and streams from the slope and travel time. Relationships that include the effects of bed roughness, secondary flow and wind are under development. Numerous relationships exist for wind-induced reaeration. Wind induced reaeration may be dominant in many estuaries due to the presence of off-sea breezes and the large fetch near the ocean outlet. However, a comprehensive approach to estuarine reaeration has not been developed. There remains a need for critical review and assimilation of all the formulas.

2.5.2.5. Benthic-Water Interactions

The decomposition of organic material in benthic sediment can significantly affect the concentrations of oxygen and nutrients in the overlying waters. Areal fluxes from the sediment due to diagenetic reactions can be substantial nutrient sources or oxygen sinks. The occurrence of anoxia may dramatically increase nutrient fluxes.

Most traditional models described these benthic fluxes as spatially variable source and sink terms. Some recent models have included benthic compartments in which state variables are simulated. Particulate nitrogen, phosphorus, and carbon are added to the bed by settling and lost by scour or sedimentation (burial). Dissolved species of nitrogen, phosphorus, carbon, and oxygen exchange with overlying water by pore water diffusion. Benthic oxidation rates are generally assumed first-order, with low rate constants producing ammonia and consuming organic carbon and oxygen equivalents (functionally, reduced organic

species that are oxidized at the water interface). Recently, efforts have been made to simulate the diagenetic reactions and resulting fluxes more realistically (DiToro 1986). These efforts hold great promise for more accurate and predictive modeling of organic and nutrient wastes. Discussions of the processes impacting benthic fluxes as well as modeling and measurement techniques may be found in Hatcher (1986).

See Supplement III for greater detail on organic wastes, dissolved oxygen and nutrients. This Supplement is found on page 2-20 at the end of this chapter.

2.6. Synthetic Organic Chemicals

2.6.1. Concepts

Synthetic organic chemicals include a wide variety of toxic materials whose waste loads are allocated based upon threshold concentrations as well as tolerable durations and frequencies of exposure. These pollutants may ionize and different forms may have differing toxicological effects. The transport of the materials also may be affected by sorption and they can degrade through such processes as volatilization, biodegradation, hydrolysis, and photolysis.

2.6.2. Fate Processes

2.6.2.1. Ionization

Ionization is the dissociation of a chemical into multiple charged species. Ionization can be important because of the different toxicological and chemical properties of the unionized and ionized species.

2.6.2.2. Sorption

Sorption is the bonding of dissolved chemicals onto solid phases such as benthic and suspended sediment, biological material, and sometimes 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 processes as volatilization and base hydrolysis, or enhance other reactions including photolysis and acid-catalyzed hydrolysis.

A common assumption is that equilibrium sorption is linear with dissolved chemical concentrations, and the distribution is controlled by a partition coefficient and the amount of solids present. 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.

2.6.2.3. Settling, Deposition, and Scour

Suspended particles carrying sorbed chemicals can settle through the water column and deposit on the underlying bed.

Benthic particles carrying sorbed chemicals can scour and become suspended in the water column. Mass fluxes for settling, deposition, and resuspension are controlled by the settling, deposition, and scour velocities, and the concentrations of suspended and benthic sediment (See Section 2.4).

2.6.2.4. Loss Kinetics

Chemical concentrations and resulting observed toxic effects often decline over time due to physical and chemical processes. The loss processes considered in most chemical fate models include volatilization, hydrolysis, photolysis, and bacterial degradation. Chemical oxidation and reduction are sometimes included as well.

Volatilization is the flux of a chemical across the air-water interface. The volatilization rate is proportional to the gradient between the dissolved concentration in the water and the concentration in the overlying atmosphere. For most chemicals, the partial pressure in the atmosphere is negligible and the equation describing volatilization reduces to a first-order form with the removal rate coefficient.

The conductivity, or rate of transfer between the atmosphere and water column, 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). Toxic chemical models either require the user to input a value for the transfer rate (k_v) or internally compute a value using the two-film theory first proposed by Lewis and Whitman (1924). This theory assumes that the rate of transfer is controlled by diffusion through laminar layers in the air and water at the interface in which the concentration gradients driving transfer are localized.

Hydrolysis is a reaction in which cleavage of a molecular bond occurs in the chemical and there is formation of a new bond with either the hydrogen or the hydroxyl component of a water molecule. 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 concentration (Wolfe 1980).

Photodegradation (photolysis) is the transformation or degradation of a compound that results directly from the adsorption of light energy. Its rate 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.

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.

See Supplement IV for more detail on synthetic organic chemicals. This Supplement is found on page 2-27 at the end of this chapter.

2.7. Metals

2.7.1. Concepts

Metals are found naturally in the earth's crust. As a result of irrigation in some regions, metals may be solubilized and transported to surface waters. Metals are also present in municipal treatment plants and industrial effluents, in landfill leachates and in nonpoint source runoff from urban areas.

2.7.2. Fate Processes

Upon entry to a surface water body, metal speciation may change due to complexation, precipitation, sorption, and redox reactions. Metals concentrations are diluted further by additional stream flow and mixing.

Physical loss can be caused by settling and sedimentation, whereas a physical gain may be caused by resuspension.

32.7.2.1. Metal Complexation, Precipitation

Heavy metals can form complexes with organic and inorganic ligands and precipitate or dissolve. At equi-

librium, the distribution of metals among the possible complexes is controlled by the amount of metals and ligands present, the reaction coefficients and solubility products. In natural waters, sorption also affects the distribution by reducing the amount of metal available for complexation and precipitation.

Complexation reactions can affect transport by either increasing or decreasing the soluble fraction. Sometimes one chemical species is known to be much more toxic than another for a given heavy metal. This is especially important because some states and EPA have been moving towards "site-specific water quality standards," in which chemical speciation will be considered on a site-by-site basis. For example, a site that is known to have a great deal of naturally occurring dissolved organics may not require as stringent a water quality standard because the dissolved organic material may complex the heavy metal and render it non-toxic to biota.

2.7.2.2. Sorption

Heavy metals frequently adsorb or "bind" to solid surfaces. The mechanism of sorption or attachment is via: 1) physical adsorption to solid surfaces, 2) chemical sorption or binding by ligands at the solid-water interface, or 3) ion exchange with an ion at the solid water interface. In addition, if the heavy metal is complexed in solution by an organic ligand, it could sorb into the organic solid phase much like an organic pollutant. The mathematical formulation for describing the partitioning of a heavy metal between the solid phase and the aqueous phase is the same as for organic chemicals except the K_{pi} is usually called the "distribution coefficient" for heavy metal (although it may be referred to as the partition coefficient or the binding constant in some cases). In most measurements and simulation

models, all soluble complexes are lumped with the free ion to give the dissolved metal concentration. Precipitated metal is lumped with all sorbed species to give the total particulate metal concentration. A spatially variable, lumped distribution coefficient K_D describes the distribution between the two phases. There is no general consistency in reported K_D values for particular methods in the natural environment, so site-specific values should be used when possible.

2.7.2.3. Redox Reactions

Metals can change oxidation states through various oxidation and reduction reactions. Under some conditions, the kinetics of oxidation or reduction may be important to simulate.

See Supplement V for greater detail on metals as they relate to estuarine models. This Supplement is found on page 2.31 at the end of this chapter.

2.8. Model Structure

Mathematical models vary widely in their ability to simulate the circulation and mixing processes as well as the processes impacting DO variations, eutrophication, synthetic organic chemicals, and metals as described in this Section. Some of the models that are presently available for use in estuarine waste load allocation studies and criteria for their selection are discussed in the following section (Section 3.0).

SUPPLEMENT I: FACTORS AFFECTING CIRCULATION AND MIXING MODEL EQUATIONS

I. Model Equations

The processes affecting circulation and mixing discussed in Section 2.2 may be described using equations based on laws of conservation of mass and momentum. The fundamental equations generally include: (A) the conservation of water mass (continuity), (B) conservation of momentum, and (C) conservation of constituent mass. The equations for the mean components are provided in Table 2-1.

A. Continuity Equation

The continuity equation expresses the fundamental principal that the sum of all volume transfers must equal

zero. For example, for a given control volume the inflow minus outflow must equal the change in storage over time. This expression alone, when used in conjunction with measured data such as outflows, surface elevation changes, and constituent concentrations, has formed the basis for estimating flows used to transport water quality constituents (using Equation 2.5) in many water quality studies. This type of solution is of greatest utility for describing flows in very simple systems and is often of limited use in estuarine studies with the possible exception of one-dimensional tidally averaged analyses. To predict flows, the continuity equation is usually coupled with momentum equations to form the basis of hydrodynamic models.

Table 2-1. Fundamental Model Equations

A. Conservation of Water Mass (Continuity)

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad (2.1)$$

(1) (2) (3)

B. Conservation of Momentum

x - direction:

$$\frac{\partial u}{\partial t} + \frac{\partial(uu)}{\partial x} + \frac{\partial(uv)}{\partial y} + \frac{\partial(uw)}{\partial z} = -\frac{1}{\rho} \frac{\partial P}{\partial x} + fu + g + \frac{\partial}{\partial x} \left[\frac{E_x \partial u}{\partial x} \right] + \frac{\partial}{\partial y} \left[\frac{E_y \partial u}{\partial y} \right] + \frac{\partial}{\partial z} \left[\frac{E_z \partial u}{\partial z} \right] \quad (2.2)$$

(4) (5) (6) (7) (8) (9) (10) (11) (12) (13)

y - direction:

$$\frac{\partial v}{\partial t} + \frac{\partial(vu)}{\partial x} + \frac{\partial(vv)}{\partial y} + \frac{\partial(vw)}{\partial z} = -\frac{1}{\rho} \frac{\partial P}{\partial y} + fv + g + \frac{\partial}{\partial x} \left[\frac{E_x \partial v}{\partial x} \right] + \frac{\partial}{\partial y} \left[\frac{E_y \partial v}{\partial y} \right] + \frac{\partial}{\partial z} \left[\frac{E_z \partial v}{\partial z} \right] \quad (2.3)$$

(4) (5) (6) (7) (8) (9) (10) (11) (12) (13)

z - direction:

$$\frac{\partial w}{\partial t} + \frac{\partial(wu)}{\partial x} + \frac{\partial(wv)}{\partial y} + \frac{\partial(ww)}{\partial z} = -\frac{1}{\rho} \frac{\partial P}{\partial z} + fw + g + \frac{\partial}{\partial x} \left[\frac{E_x \partial w}{\partial x} \right] + \frac{\partial}{\partial y} \left[\frac{E_y \partial w}{\partial y} \right] + \frac{\partial}{\partial z} \left[\frac{E_z \partial w}{\partial z} \right] \quad (2.4)$$

(4) (5) (6) (7) (8) (9) (10) (11) (12) (13)

C. Conservation of Constituent Mass (Transport)

$$\frac{\partial C}{\partial t} + \frac{\partial(uC)}{\partial x} + \frac{\partial(vC)}{\partial y} + \frac{\partial(wC)}{\partial z} = \frac{\partial}{\partial x} \left[\frac{K_x \partial C}{\partial x} \right] + \frac{\partial}{\partial y} \left[\frac{K_y \partial C}{\partial y} \right] + \frac{\partial}{\partial z} \left[\frac{K_z \partial C}{\partial z} \right] + \Sigma S \quad (2.5)$$

(14) (15) (16) (17) (18) (19) (20) (21)

where the numbered equation terms are:

- (1 to 3) = the velocity gradients in the x, y and z direction
- (4) = local acceleration
- (5 to 7) = are convective acceleration terms in the x, y and z direction
- (8) = pressure gradient
- (9) = the Coriolis force
- (10) = gravitational acceleration
- (11 to 13) = parameterization of the Reynold's stresses in the x, y and z direction
- (14) = rate of change in concentration

- (15 to 17) = advective terms
- (18 to 20) = turbulent diffusion
- (21) = constituent source/sink term (e.g. kinetics and transfers, boundary loadings)

Equation variables are defined as:

- t = time
- P = pressure
- g = gravitational acceleration
- ρ = density
- f = Coriolis frequency
- E_x, E_y, E_z = turbulent diffusion coefficient for momentum in the x, y and z direction
- u, v, w = mean velocity components in the x, y and z direction
- x, y, z = rectangular coordinates, where x and y are horizontal coordinates and z is vertical
- K_x, K_y, K_z = turbulent diffusion coefficient for mass in the x, y and z direction
- C = concentration of water quality constituent
- S = Constituent source/sink term

B. Conservation of Momentum

The conservation of momentum equation is derived from Newton's second law of motion, which states that the sum of all forces acting on a system is equal to the time rate of change of linear momentum of the system, where momentum is mass times velocity. The factors affecting changes in momentum are illustrated by Figure 2-1 for a given control volume. The terms in the conservation of momentum equation are expressions of: (4) local acceleration, (5-7) convective acceleration, (8) pressure forces, (9) coriolis force, (10) body force, and (11-13) turbulent stress terms. The equations as written in Table 2-1 assume that the fluid is incompressible, that the velocities are Reynold's averages, that turbulent diffusion is much greater than molecular diffusion, and that turbulent transfer of mass and momentum is directly related to concentration and velocity gradients (Boussinesq assumption). The equations may be found in the literature in a number of equivalent forms, differing due to mathematical manipulations or assumptions with regard to the system's geometry or boundary conditions. Unknowns in the equation include the velocities (u, v and w), the pressure (P), and the eddy viscosity coefficients (E_x, E_y, E_z).

The local acceleration (4) terms refer to the rate of change of velocity with respect to time. They are also referred to as the local inertia terms.

The convective acceleration (5-7) or convective inertia terms express the effects on the momentum balance of spatially varying velocities.

The pressure force (8) describes the effect of pressure gradients on the velocity field. For a homogeneous water body, i.e. one with no density differences, the pressure gradients are proportional to the slope of the water surface and the equal pressure surfaces are parallel to the water surface throughout. Flows induced by the water surface slope are referred to as barotropic flow. Changes in density in non-homogeneous water bodies establish pressure gradients inducing flows which are referred to as baroclinic.

An empirical relationship is generally used to establish the relationship between water density, temperature, and salinity and the relationship is generally referred to as the "equation of state." The equation of state provides a means of linking water quality and hydrodynamic models. The relationship is given by

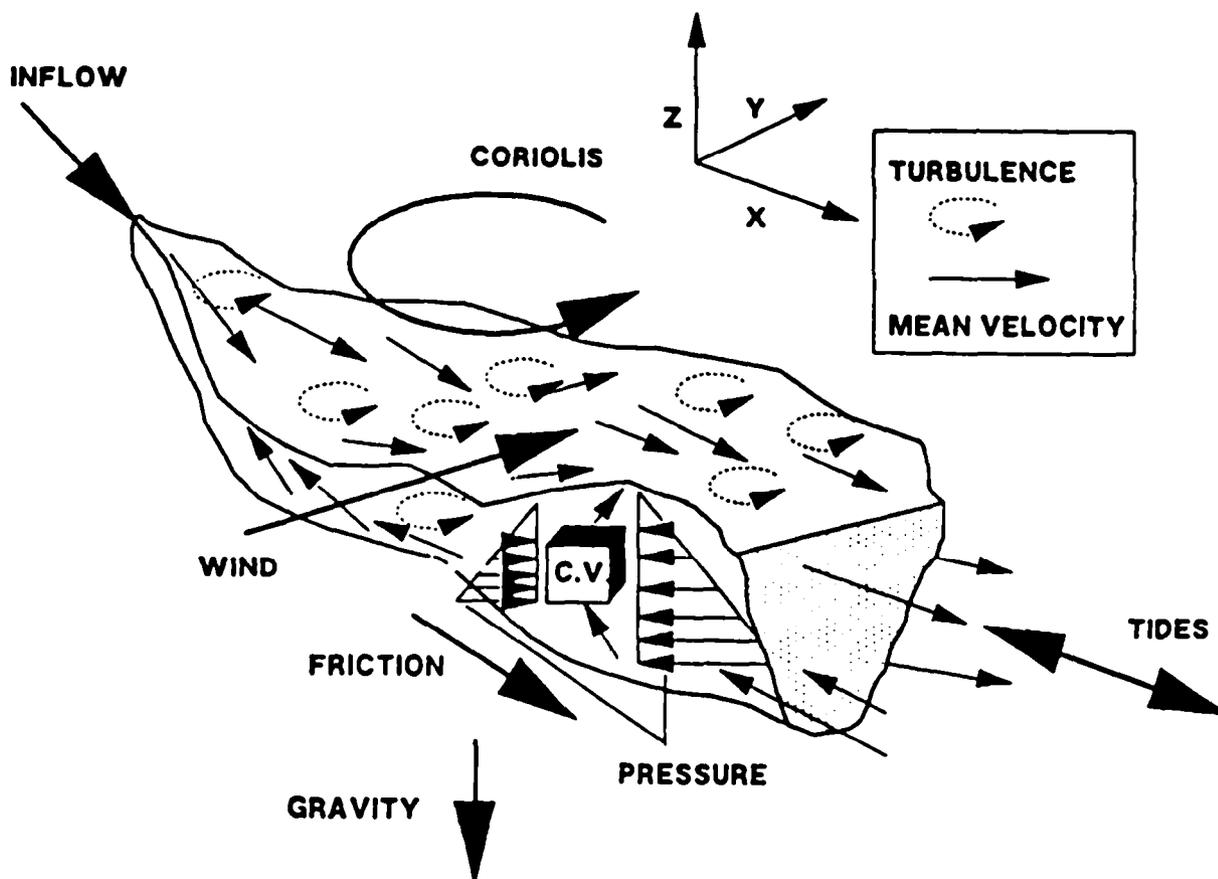


Figure 2-1. Factors affecting changes in momentum.

$$\rho = \rho_T + \Delta\rho_S + \Delta\rho_{SS} \quad (2.6)$$

where ρ is the water density (kg m^{-3}), ρ_T is the density as a function of temperature, and $\Delta\rho_S$ and $\Delta\rho_{SS}$ are the changes in density due to dissolved and suspended solids, respectively.

An empirical relationship between density and temperature is given by (Gill 1982)

$$\begin{aligned} \rho_T = & 999.8452594 + 6.793952 \times 10^{-2} T \\ & - 9.095290 \times 10^{-3} T^2 + 1.001685 \times 10^{-4} T^3 \\ & - 1.120083 \times 10^{-6} T^4 + 6.536332 \times 10^{-9} T^5 \end{aligned} \quad (2.7)$$

where T is the temperature ($^{\circ}\text{C}$) and the change in density due to salinity is (Gill 1982)

$$\begin{aligned} \Delta\rho_S = & C_{SL} (0.824493 - 4.0899 \times 10^{-3} T \\ & + 7.6438 \times 10^{-5} T^2 - 8.2467 \times 10^{-7} T^3 \\ & + 5.3875 \times 10^{-9} T^4) + C_{SL}^{1.5} (-5.72466 \\ & \times 10^{-3} + 1.0227 \times 10^{-4} T - 1.6546 \times 10^{-6} T^2) \\ & + 4.8314 \times 10^{-4} C_{SL}^2 \end{aligned} \quad (2.8)$$

where C_{SL} is salinity (kg m^{-3}). The relative affect of temperature and salinity on water density is illustrated in Figure 2-2. The effect of suspended solids may also be considered using (Gill 1982)

$$\Delta\rho_{SS} = C_{SS} (1 - 1/SG) \times 10^{-3} \quad (2.9)$$

where $\Delta\rho_{SS}$ is the change in density due to suspended solids, C_{SS} the suspended solids concentration (g m^{-3}), and SG the specific gravity of the solid. Some models include terms for the effects of spatial variations in the atmospheric pressure on the velocity fields.

Some estuary models with vertical resolution, such as the laterally averaged model CE-QUAL-W2 (Environmental and Hydraulics Laboratory 1986) and CELC3D, assume that the vertical acceleration is negligible compared to the vertical pressure gradient and gravitational acceleration (the hydrostatic approximation; i.e. the magnitude of terms 4-7, 9 and 11-13 of the vertical momentum equation, Equation 2.4, are negligible compared to terms 8 and 10). The hydrostatic assumption reduces the vertical momentum equation to

$$\frac{1}{\rho} \frac{\partial P}{\partial z} = g \quad (2.10)$$

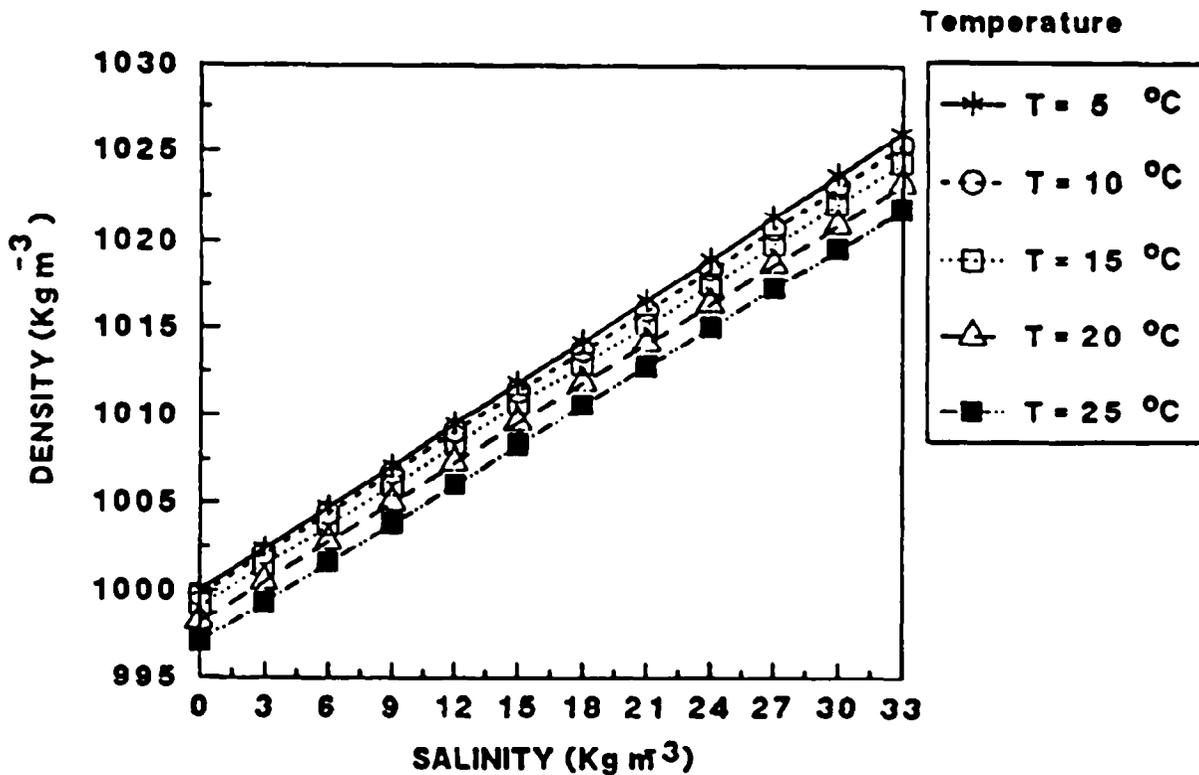


Figure 2-2. Relationship between water density, salinity, and temperature.

The formulation for the mean pressure, P , is performed in one of two ways, either as a free surface calculation or a rigid lid computation (i.e. the water surface elevation does not vary). For the more complex estuarine application, the free surface formulation is required due to the importance of tidal oscillations as a system forcing function. Free surface versions of estuary models often exploit the hydrostatic pressure equation to make an implicit relation between free surface elevation and the pressure field (Bedford 1985). Models which solve for the free surface implicitly are attractive due to less restrictive time step formulations (Paul and Nocito, 1983).

The Coriolis force (6) describes the effect of the earth's rotation which acts to deflect the motion of fluids to the right (left) in the northern (southern) hemisphere. The Coriolis force is an apparent force to allow a frame of reference to be used that is relative to the rotating earth. The force is usually described as a function of the angular velocity of the earth (Ω) and the latitude of the estuary. The Coriolis frequency (f) is estimated from

$$f = 2 \Omega \sin(\Phi) \quad (2.11)$$

where Ω is the angular velocity of the earth, Φ is the latitude, and the time scale for rotational effects is approximately of the order $1/f$ and ranges from about 15 hours in Washington State to 30 hours in southern Florida.

The eddy viscosity terms (11-13) arise from time-averaging the turbulent fluctuations of velocity components. The velocity components may be written as

$$U = u + u' ; V = v + v' ; W = w + w' \quad (2.12)$$

where u, v, w are the mean velocity components and u', v', w' are the fluctuations relative to the mean velocities. The time-averaging of the velocities gives rise to turbulent correlation terms of the form:

$$\overline{u'u'} \quad \overline{u'v'} \quad \overline{u'w'} \quad (2.13)$$

The Boussinesq analogy assumes that the turbulent stresses are proportional to the mean velocity and the turbulent stresses are often rewritten in the form shown in Equations 2.2-2.4 (terms 11-13)

$$\overline{u'u'} = E_x \frac{\partial u}{\partial x} ; \quad \overline{u'v'} = E_y \frac{\partial u}{\partial y} ; \quad (2.14)$$

$$\overline{u'w'} = E_z \frac{\partial u}{\partial z}$$

referred to as the eddy viscosity formulation. This formulation is generally applicable where large scale turbulence is of importance. These terms are unknown quantities and represent what is referred to as the closure problem in hydrodynamic modeling. Rewriting

the quantities in terms of eddy viscosity does not eliminate the problem but has put the terms in a form that has proved useful in practical calculations. A variety of procedures have been developed for turbulence closure, described as zero-equation, one-equation, two-equation, and higher order methods and have been reviewed by Rodi (1980), Bedford (1985) and others.

The horizontal eddy viscosity is often held constant in models ($E_x = E_y$). Procedures for estimating the magnitude of the eddy viscosity are described in Section 5 (Supplement III).

The vertical eddy viscosity at the interfaces of water segments for models with vertical resolution is often described as a constant or a function of the decay of surface shear. The shear at the surface boundary is generally described as a function of wind shear such as

$$\rho_o E_z \left(\frac{\partial u}{\partial z}, \frac{\partial v}{\partial z} \right) = \rho_a C_{da} (u_w^2 + v_w^2)^{0.5} (u_w, v_w) \quad (2.15)$$

in the x and y directions, respectively, where ρ_o is the surface water density, ρ_a the air density, C_{da} the drag coefficient, and u_w and v_w are the wind velocities in the x and y directions at some height above the water surface. This computation requires that representative data be available for both wind speed and direction. The vertical stress at the bottom boundary is usually described as a function of bottom friction, such as in the quadratic stress formulation

$$\rho E_z \left(\frac{\partial u}{\partial z}, \frac{\partial v}{\partial z} \right) = \rho C_d (u_b^2 + v_b^2)^{0.5} (u_b, v_b) \quad (2.16)$$

where C_d is a drag coefficient and u_b and v_b are the horizontal velocities at some point above the bottom. A constant drag coefficient has been used in modeling studies.

The drag coefficient has also been related to the Chezy coefficient (C_z) as

$$C_d = g/C_z^2 \quad (2.17)$$

or the Manning's roughness coefficient, n ,

$$C_d = \frac{g n^2}{R^5} \quad (2.18)$$

where R is the hydraulic radius (m). Guidance on the selection of bottom roughness coefficients is provided in Section 5 (Supplement I).

The vertical eddy viscosity is reduced significantly by stable stratification. Some formulations to account for

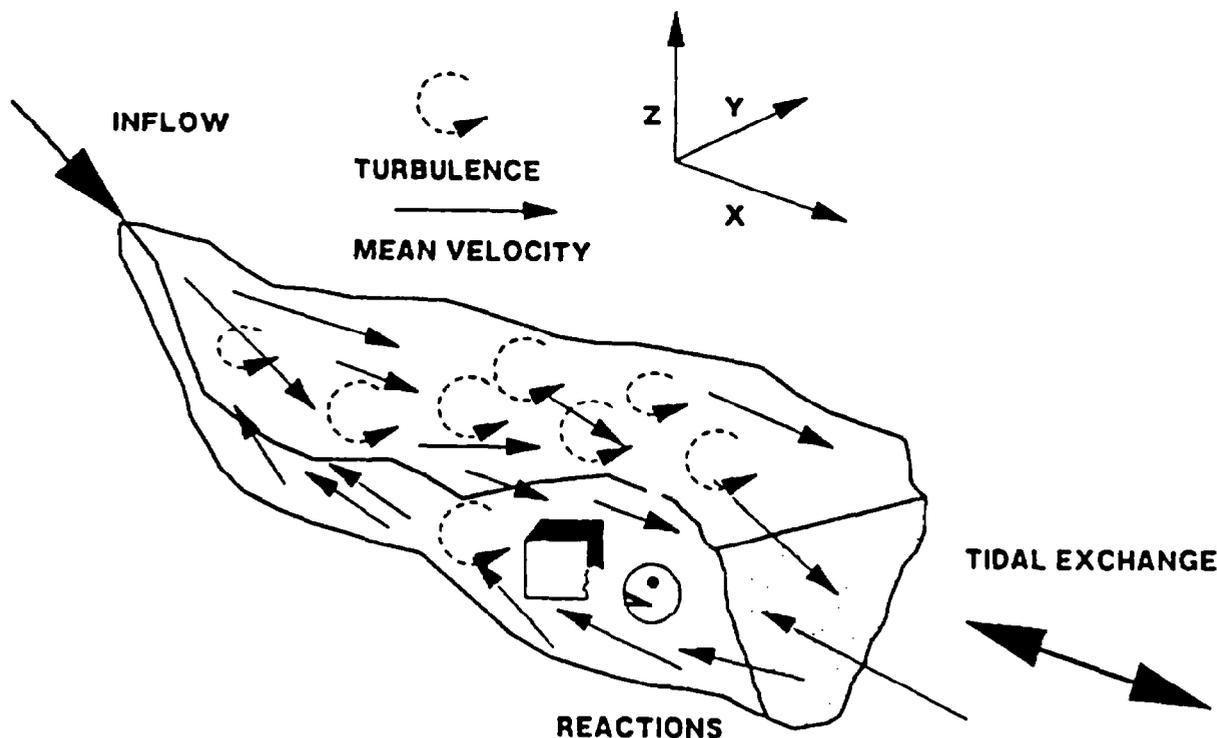


Figure 2-3. Factors affecting change in constituent mass.

this effect contain empirical relationships between vertical eddy viscosity and the Richardson number (Ri), an index of stratification stability given by

$$Ri = -\frac{g}{\rho} \frac{\partial \rho / \partial z}{(\partial v / \partial z)^2} \quad (2.19)$$

The most widespread of these formulations was developed by Munk and Anderson (1948) where

$$E_z = E_{z,0} (1 + 10 Ri)^{-0.5} \quad (2.20)$$

where $E_{z,0}$ is the value of E_z for neutral stratification (i.e. the estuary is unstratified).

Boundary conditions, such as water surface elevations and flows, provide the forcings which are propagated through the model solutions as computed variations in velocities and surface elevations.

C. Conservation of Constituent Mass

The conservation of constituent mass or transport equation forms the basis for estimating variations in water quality over space and time. The equation is a statement that the time rate of change of concentrations, or material accumulation, (14) is equal to the material entering or leaving the system due to advective transport (15-17) or turbulent diffusion (18-20) plus the change due to physical, chemical, or biological transformations (21) as illustrated by Figure 2-3. The

advection of constituents can be estimated from field measurements, computations using tracers and continuity, or hydrodynamic models. The diffusion coefficients are related to turbulence. For three-dimensional mass transport models using small time steps (on the order of a few minutes) the governing equations contain only turbulent diffusion terms. However, if the equations are temporally or spatially averaged then dispersion will result, and the magnitude of the dispersion term will depend upon how the averaging is done (Harleman, R.F., in his review of this document).

The eddy viscosity and mass dispersion coefficient are related by the turbulent Prandtl/Schmidt number (i.e. the ratio of transfer of momentum and mass). A complete review of dispersion relationships is found in Fischer et al. (1978). Guidance on the selection of the dispersion coefficient is provided in Section 5 (Supplements III and V).

II. Model Complexity

The solution of the equations for circulation and mixing (Equations 2.1-2.4) is generally based upon simplifications and assumptions regarding the spatial and temporal complexity of the system and its boundary conditions. These basic assumptions make it less difficult to solve the governing equations. Generally, simplifying assumptions may be made regarding the

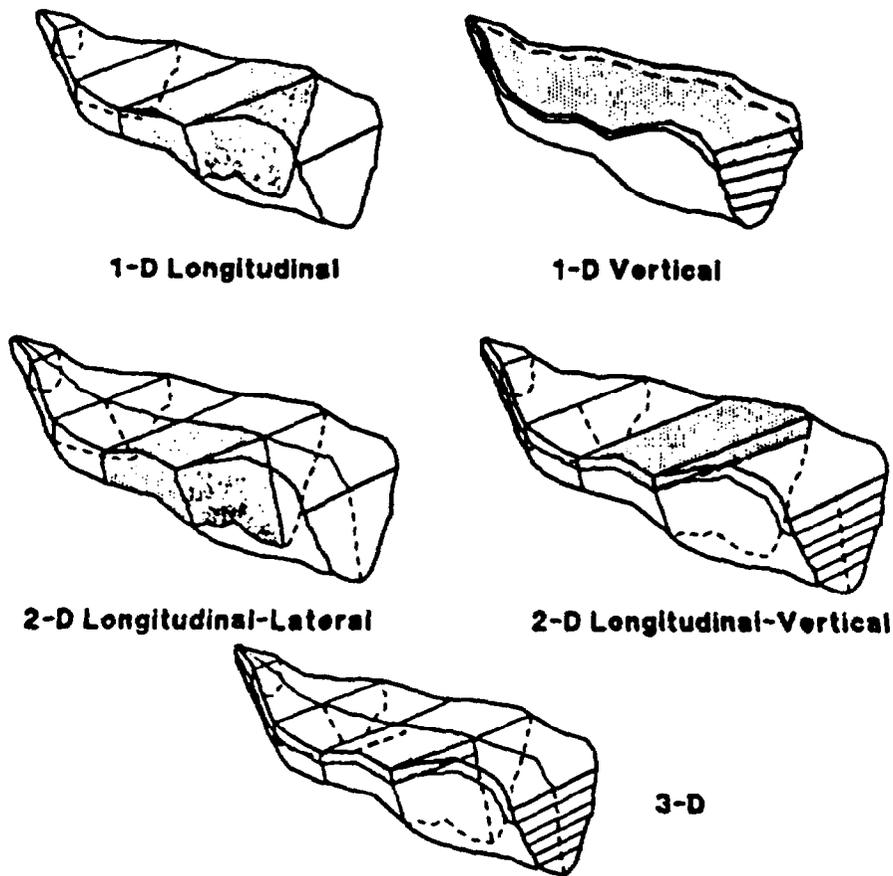


Figure 2-4. Model dimensions.

hydrodynamic complexity of the system, its dimensionality, temporal resolution, and kinetic resolution.

A. Spatial and Temporal Resolution

With regard to spatial resolution, models may be one, two or three dimensional. Most practical hydrodynamic models are either one, two (vertically or laterally averaged) or quasi-three dimensional, as illustrated by Figure 2-4. This often prevents their application to near-field problems where a high degree of turbulence occurs. For example, a model which does not include vertical momentum could not resolve momentum transfer due to a submerged jet. Nihoul and Jamarf (1987) describe available three-dimensional models. Similarly, mass transport models may be one, two or three dimensional. Tidally varying one-dimensional models are useful for tidal flow in narrow, relatively uniform channels, such as the long braided network of sloughs sometimes found in deltas or tidal rivers (Fischer et al. 1978). In wide and irregular channels, two or three dimensional models may be required.

With regard to temporal resolution, estuarine mass transport problems are usually characterized as inter-tidal or intra-tidal. Intra-tidal computations, which consider variations within a tidal cycle, generally require application of coupled hydrodynamic and water quality models in order to obtain real time predictions.

For inter-tidal computations, a variety of simplified methods are available to estimate circulation and mass transport. Simplified modeling approaches are often based on using either measured flows or flows estimated using continuity (Equation 2.1) for use with models based on constituent mass balance equations. The most simple models solve only the transport equation (Equation 2.5), usually assuming steady-state ($\partial C/\partial t = 0$) to obtain average conditions. Models of intermediate complexity estimate flows based on field data or use simplified methods to describe circulation, generally tidally averaged.

Mills et al. (1985) describes some simplified methods for calculating estuarine circulation, including fraction of freshwater methods, modified tidal prism method and Pritchard's Box model for a two-dimensional estuary.

The freshwater and tidal prism method are described further in Section 6 of Part 2 of this manual. Officer (1976, 1977) described analytical solutions to decoupled hydrodynamic and mass transport equations. Lung and O'Conner (1984) developed a tidally averaged method for two-dimensional (longitudinal-vertical) estuaries that allows analytical computation of horizontal and vertical velocities and vertical eddy viscosity terms.

Hydrodynamic models, based on the solution of the equations for circulation and mixing (Equations 2.1-2.4), are linked with water quality models, based on the constituent mass balance equation (Equation 2.5), when time varying predictions are required of both flows and water quality, such as for intratidal variations. Some models directly link solutions for the hydrodynamic and constituent transport equations with equations of state allowing variations in water quality to be considered in flow predictions. In other cases the hydrodynamic predictions are separate from water quality and may be averaged over space and time to allow use of coarser time or space scales in water quality modeling. This time and space averaging is often difficult to accomplish since important advective and diffusive information is lost in direct proportion to the length of the spatial and temporal averaging period and there are no quantitative guidelines for multidimensional models to indicate the extent of the information lost (Harleman, D., in review). Thus, empiricisms are often introduced as a result of the averaging. Studies on the interfacing problem have been conducted by Ford and Thornton (1979), Walters (1980), Imboden et al. (1983), Wang and Harleman (1984), Shanahan and Harleman (1984) and others which are applicable to estuarine conditions as well as studies conducted on Chesapeake Bay.

B. Kinetics

Descriptions or predictions of estuarine circulation may be coupled with detailed descriptions of constituent transformations. For a "conservative material" (one not subject to transformations, i.e. salinity and some tracers) the last term (S) in Equation 2.5 is equal to zero. However, the constituents of interest in estuarine WLA studies rarely behave conservatively. For most materials of interest, such as DO, nutrients, synthetic organics and metals, their physical, biological, and chemical transformations must be estimated. The

factors influencing those transformations is the subject of the remainder of this section (Sections 2.3-2.6).

C. Additional Considerations

A tendency may be to select the resolution (spatial, temporal and kinetic) for a particular waste load allocation study on the scale of interest for the model output rather than the physics, biology and chemistry of the system. An additional tendency may be to base model selection on those techniques which are perceived to be the simplest to use. However, the relationship between model simplicity and simplicity of application is not straightforward.

For example, inappropriate spatial and temporal averaging for hydrodynamic computations can result in a model that is far removed from the physics of the system. Inappropriate averaging may necessitate the introduction of empiricisms which must then be calibrated to data, and may result in increased rather than decreased data requirements to support the modeling studies. For example, averaging may introduce dispersion terms whose magnitude depends on how the averaging is done. Harleman (D.R.F., in his review) suggests that the data required to support a two-dimensional laterally averaged model is often more than that for a three-dimensional model, while the amount of synoptic data required to support a one-dimensional model (averages over a cross section) may be enormous. Therefore, if the physics of the system is not adequately considered, the data required to support a modeling study may increase with increasing "simplicity".

Similarly, the clumping of kinetics terms for "simpler" models may, if not carefully done, introduce empiricisms which have little relationship to the chemistry and biology of the system. Thus, the empirical coefficients may often be determined only through calibration, often to inadequate data, and the coefficients *must often be varied over space and time to get the "best" calibration*. Alternatively, the uncertainty of model predictions increases nonlinearly with the addition of uncertain parameters. Therefore, the Principle of Parsimony should apply: that is that it should be attempted to obtain a model calibration and validation with the fewest possible parameters (R.V. Thomann, in review of this document).

SUPPLEMENT II: SEDIMENT TRANSPORT AND SEDIMENT/WATER QUALITY INTERACTIONS

I. Source and Sink Term Processes

The processes affecting sediments are illustrated in Figure 2-5. Using the segmentation scheme illustrated, constituent mass balance equations (Equation 2.5) would be written for each vertical water segment. The advective and diffusive transport terms were described previously. The remainder of the processes would be described in the source/sink term (S). The source/sink term would typically be represented as

$$S = \frac{A}{V} \beta C \quad (2.21)$$

where A is area, V volume, C solids concentration and β is a coefficient with units of velocity (e.g. settling or resuspension velocity).

II. Settling

For settling the coefficient β is dependent upon Brownian motion, turbulent diffusion, and fall velocities. Brownian motion is negligible for most particles of interest in water quality modeling. The fall velocities (w_s) can be estimated from Stokes law, which is

$$w_s = \frac{g d^2}{18 \mu} (\rho_p - \rho_f) \quad (2.22)$$

where g is gravitational acceleration, d is particle diameter, ρ_p the particle density, ρ_f the fluid density and μ the dynamic viscosity of the fluid. Stokes settling or fall velocities for a range of materials are tabulated in Section 5 (Supplement VIII). The silts and clays carrying pollutants typically range in diameter from 0.002 to 0.02 mm, with densities of 2 to 2.7 g/cm³.

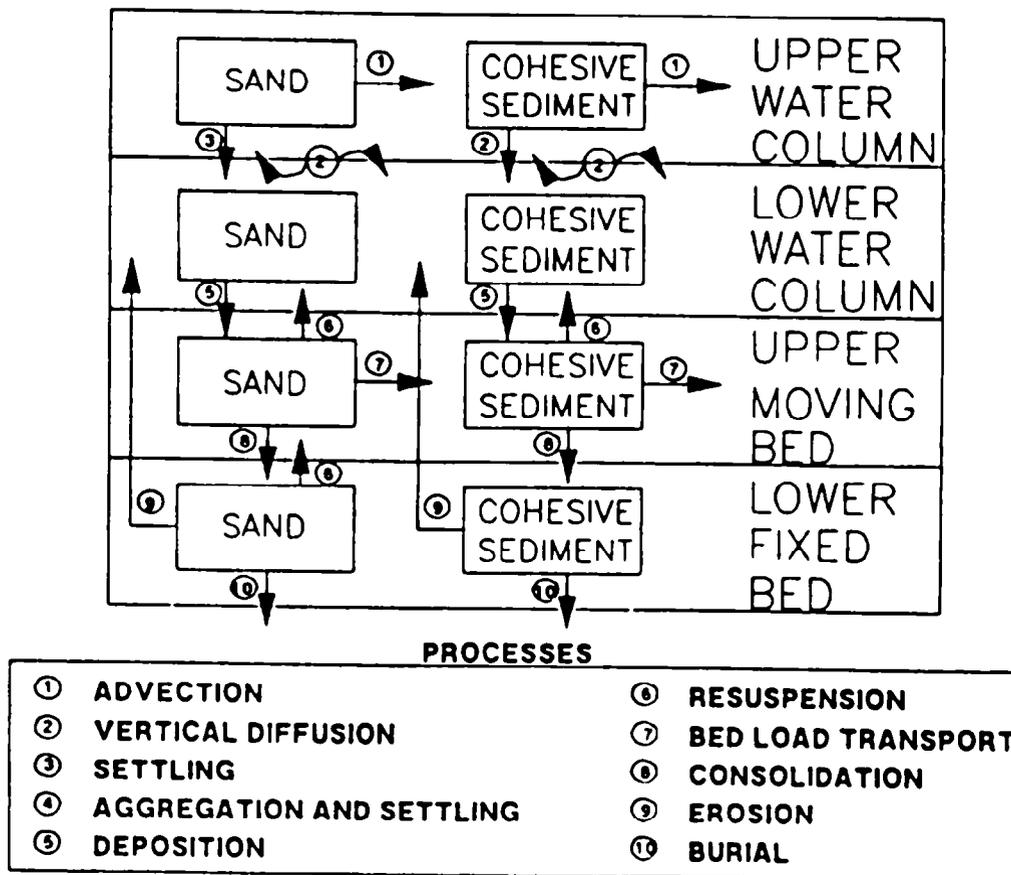


Figure 2-5. Sediment variables and processes.

Stokes law is valid for Reynolds numbers ($Re = \rho_1 w_s d/\mu$) less than about 0.1.

Collisions between small cohesive particles tend to lead to coagulation and the formation of flocs. Flocculation rates are dependent upon the size distribution and relative composition of the clays and electrolytes and upon local boundary shear stresses (Mills et al. 1985) as well as salinity. Turbulence increases the collisions while salinity increases the cohesion between particles (Sheng 1983). The effective density of the floc may vary considerably from that of the individual particles, making prediction of settling velocities difficult and requiring site-specific model calibration (Stefan, Ambrose and Dortch 1988).

III. Deposition

The deposition of sediments onto the surface sediment layer is a process by which suspended sediments leave the water column, either temporarily or permanently, and become part of the bottom sediments (Sheng 1983). In order to be deposited the particles must overcome resistances due to turbulent transport in the water column, resistances due to the thin viscous layer at the interface, and resistances due to chemical or biological activity after they reach the bottom. The deposition velocity depends on the extent to which settling is affected by turbulence. Sheng (1983) indicated particles of diameters less than approximately 100 μm will completely follow the eddy motions. The deposition velocity can be estimated as the product of the settling velocity and the probability of deposition on contact with the bed, which can vary from 0 for very turbulent systems to 1 for stagnant pools, and deposition velocities will generally vary from 0 to 5 m/day (Ambrose et al. 1988; Stefan, Ambrose and Dortch 1988).

IV. Entrainment

Entrainment or resuspension occurs when the flow induced shear stress at the sediment-water interface exceeds the cohesive forces of the surficial sediments (Sheng 1983). For granular non-cohesive materials the relationship between bed shear and entrainment is "explosive" in nature. Very low or no resuspension occurs until a threshold shear stress is reached. Then resuspension rates increase in proportion to some power of the excess shear stress. Powers of one have been found in estuarine studies, but powers of four and five have been found for granular river material according to a review by Akiyama and Fukushima (Wang et al. 1986). The rate of resuspension can be balanced by the rate of deposition. At that point, vertical concentration profiles above the bed show a balance of downward fluxes of sediment by settling and upward fluxes by turbulence as summarized by Vanoni (1975).

According to Rouse (see Vanoni 1975), the dimensionless parameter $V_s(Ku^*)^{-1}$ (where V_s = particle fall velocity, $K = 0.4$ and u^* = bed shear velocity = $\sqrt{\tau_b/\rho}$ with τ_b = shear and ρ = water density) determines for flow over flat bottoms the degree for which vertical sediment distribution will be uniform. It will be uniform within ± 10 percent when $V_s(Ku^*)^{-1}$ is less than about 0.02.

Rates of entrainment of non-cohesive materials have been specified in numerous alternative forms by Ariathurai (1982), Ariathurai and Krone (1976), and others (see Wang et al. 1986; Mehta 1986). Akiyama and Fukushima (in Wang et al. 1986) specified a dimensionless resuspension rate parameter E_s as:

$$E_s = 3 \times 10^{-12} Z^{10} (1 - 5/Z)$$

for $5 < Z < 13.4$

$$E_s = 0.3 \text{ for } Z > 13.4 \quad (2.23)$$

where

$$Z = \frac{u^*}{V_s} R_p$$

$$R_p = (g' D)^{1/2} D/\nu$$

$$g' = g(\rho_s/\rho - 1)$$

reduced acceleration of gravity of submerged particles; D = particle diameter; and ν = kinematic viscosity. The entrainment (or resuspension, scour or erosion) rate depends not only upon the shear stress on the benthic surface, and the sediment size but also on the state of consolidation of the surficial benthic deposits. Site-specific calibration is necessary to refine initial estimates of scour (Stefan, Ambrose and Dortch 1998).

Entrainment of cohesive sediments is less well understood. Unfortunately, cohesive sediments are of primary interest in water quality studies. For cohesive sediments, the resuspension rate is affected by bottom shear stress, salinity, sediment type, and the time history of bottom sediments (Sheng 1983). Lick et al. (1987) indicated that, as a result of cohesion and the resulting compaction, only a finite amount of cohesive sediment may be resuspended at a given shear stress as opposed to non-cohesive sediments which have a uniform rate of resuspension. Lick suggested that the amount of cohesive sediment that can be entrained is a function of the time after deposition, the shear stress, and an effective critical stress which needs to be determined experimentally for particular sediments.

V. Burial

Burial refers to the net sedimentation velocity, or the velocity by which deposited sediments are buried by additional deposits. Burial, compaction, and the cohesive forces between sediment particles result in varying sediment properties (e.g. density and porosity) with depth below the upper mixed sediment zone.

SUPPLEMENT III: ORGANIC WASTES, DISSOLVED OXYGEN AND NUTRIENTS

I. Important Processes and Variables

The basic variables and processes used in the prediction of DO and nutrient concentrations are illustrated in Figures 2-6 and 2-7, where separate constituent mass balance equations are generally written for each variable indicated by the boxes (constituents, C in Equation 2.5). The processes affecting those variables and the interactions between variables are indicated by arrows, and comprise the source/sink terms in the constituent mass balance equation (S, Equation 2.5). These processes are often modeled as zeroth-order,

$$S = K \alpha_h \quad (2.24)$$

where K is a constant with units of concentration/time; first-order,

$$S = K_{1st} C \quad (2.25)$$

where C is concentration and K is a rate term with units of 1/time; or higher-order (nonlinear) processes where the rate term is dependent upon variations of other variables or constituents. The variables are also affected by advective and dispersive transport, as described by Equation 2.5. Transport and reaction rates are affected by temperature as described below.

II. Temperature

Temperature affects transport through density terms (as described by the equation of state, Equation 2.5) as well as reaction kinetics. Temperature effects on reaction processes are usually computed as the product of a temperature adjustment factor and the rate term measured at some reference temperature, where the temperature adjustment factor (X_T) is estimated from

$$X_T = \theta^{T - T_r} \quad (2.26)$$

where θ is a coefficient, T is temperature, and T_r is a reference temperature.

Temperature variations may either be modeled or specified in water quality models (see Thomann and Mueller 1987). The temperature (thermal energy) equa-

tion can be obtained from the conservation of mass equation (Equation 2.5) by replacing concentration (mass/volume) by the heat/volume (i.e. $\rho C_p T$). Dividing through replaces C (concentration) with T (temperature) and the source/sink term (S, Equation 2.5) may be given as

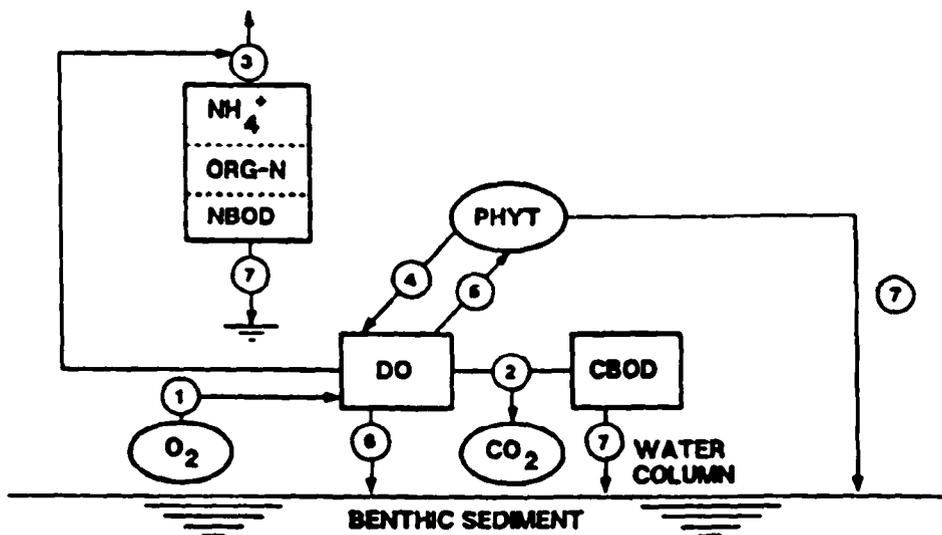
$$S = \frac{HA}{V C_p \rho_o} \quad (2.27)$$

where A is area (m^2), V volume, H the total heat flux ($Watts/m^2$), C_p is the specific heat of water ($Joule/Kg^{\circ}C$), and ρ_o the density of water at the given temperature (Kg/m^3).

The total heat flux includes fluxes due to conduction or sensible heat transfer, evaporation, long wave back radiation from the atmosphere, back radiation from the water surface, and absorption of short wave radiation. All predictive approaches to temperature modeling are based on one or more empirical functions that must be specified, such as the wind speed function. Guidance on the selection of the wind speed function is provided in Section 5 (Supplement VI).

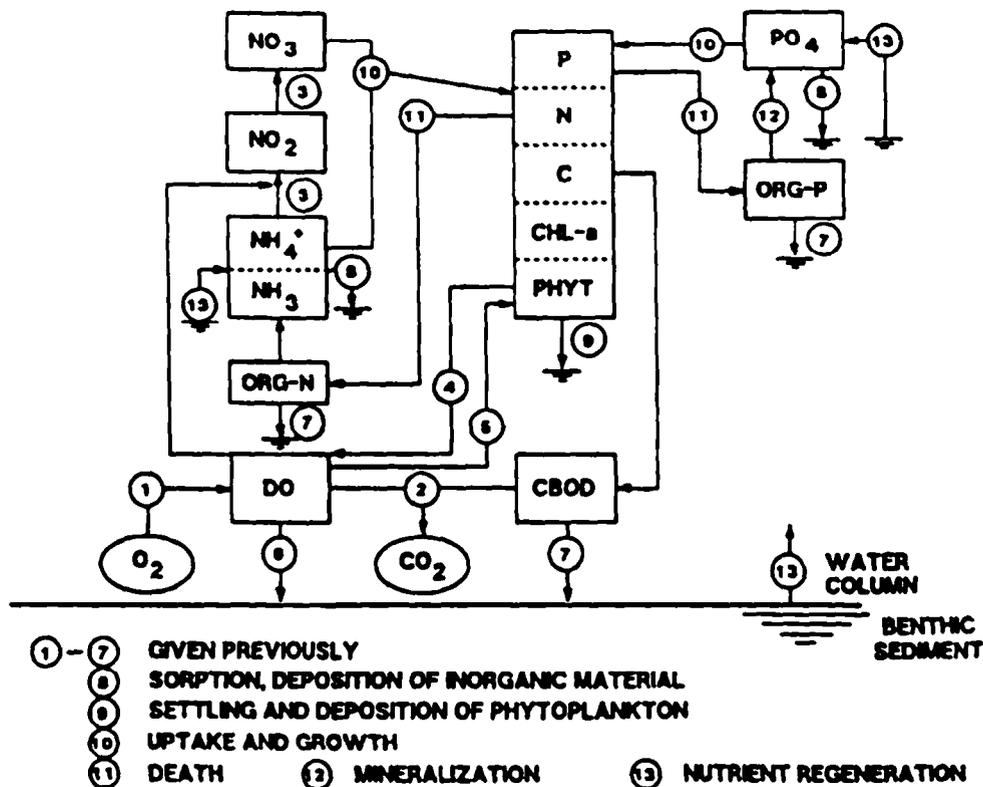
III. Indicator Bacteria

The bacteria of interest in WLA studies dealing with organic wastes of human origin include total or fecal coliforms, where the coliforms may be pathogenic in some cases or are used as indicators of the presence of pathogenic bacteria. Coliform bacteria generally can not reproduce in aerobic natural waters and are modeled using first-order kinetics, where the rate term represents a die-off rate. However, coliforms can reproduce in sediments and be resuspended in the water column. Guidance on the selection of die-off rates and their reference temperature (T_r) for temperature adjustments of the rate (Equation 2.26) is provided in Section 5 (Supplement VII). Coliform die-off may also vary with light and salinity as well as temperature. Thomann and Mueller (1987) provide additional discussion of modeling considerations for indicator or pathogenic bacteria.



- ① REAERATION
- ② CARBONEOUS DEOXYGENATION
- ③ NITROGENOUS DEOXYGENATION (NITRIFICATION)
- ④ PHOTOSYNTHESIS
- ⑤ RESPIRATION
- ⑥ SEDIMENT OXYGEN DEMAND
- ⑦ SETTLING AND DEPOSITION OF ORGANIC MATERIAL

Figure 2-6. Basic variables and processes for dissolved oxygen.



- ① - ⑦ GIVEN PREVIOUSLY
- ⑧ SORPTION, DEPOSITION OF INORGANIC MATERIAL
- ⑨ SETTLING AND DEPOSITION OF PHYTOPLANKTON
- ⑩ UPTAKE AND GROWTH
- ⑪ DEATH ⑫ MINERALIZATION ⑬ NUTRIENT REGENERATION

Figure 2-7. Standard variables for eutrophication and DO.

IV. Organic Material and Dissolved Oxygen.

DO is depleted by oxidation of organic carbon, nitrification, and respiration and is replenished by surface exchange and primary production (Figure 2-6). More complex interactions considering the effects of eutrophication have been considered (Figure 2-7).

Historically, deoxygenation by decomposition of organic material has been modeled using coupled equations for DO and Biochemical Oxygen Demand (BOD), where BOD is a measure of the oxidizable matter due to biochemical processes expressed in oxygen units. BOD has typically been divided into two components, Carbonaceous BOD (CBOD) and Nitrogenous BOD (NBOD) due to the difficulty of predicting variations in total BOD (CBOD + NBOD). CBOD removal processes usually included in model formulations include decomposition or oxidation by organisms, and settling. In addition, CBOD can be entrained or resuspended. The source/sink term for CBOD can be written as

$$S = (K_d + K_s) L + L_a \quad (2.28)$$

where K_d is the water column deoxygenation rate coefficient, K_s is the settling rate, L the ultimate CBOD and L_a a zero order CBOD resuspension rate. For DO, the loss rate due to deoxygenation is $K_d L$. Further information and guidance on the selection of rate terms is provided in Section 5 (Supplement XI).

The utility of CBOD is limited since it lumps the effects of a number of processes into one variable. Some modeling approaches will separate oxygen consuming reactions into various components. CBOD is essentially the only variable presently written into most WLA permits for the control of DO.

DO may also be depleted due to benthic demand. Discussions of the processes impacting sediment oxygen demand as well as modeling and measurement techniques may be found in Hatcher (1986).

V. Phytoplankton

Primary productivity by phytoplankton produces oxygen while respiration consumes oxygen. In addition, phytoplankton are often of primary interest in assessing eutrophication and in predicting nutrient interactions.

For simplistic DO models, as illustrated by Figure 2-6, it may be sufficient to describe the effects of phytoplankton using simple zeroth order terms for primary productivity and community respiration. These terms may often be estimated from field studies using measurements of variations in carbon isotopes,

oxygen or carbon dioxide. This approach is often of limited utility where changes in productivity are expected to occur in response to waste loadings. Most estimates of primary productivity in common mathematical models involve coupling algal growth equations with stoichiometric equations for photosynthesis in order to relate primary productivity to oxygen and nutrient production/consumption.

Modeling of specific algal species is usually not attempted. Instead major groups, such as diatoms, greens, blue-greens and dino-flagellates are simulated. Algal losses due to settling and grazing are also often simulated. Some of the more complex models include equations for zooplankton groups in order to predict variations in grazing losses (Figure 2-8).

The growth rate of phytoplankton (G) is usually formulated as the product of the maximum 20 °C species or group specific growth rate (under optimum light and nutrient conditions) with a temperature adjustment factor (X_T), a light adjustment factor (X_L), and a nutrient limitation factor (X_N).

$$G = G_{max} X_T X_L X_N \quad (2.29)$$

The temperature adjustment factor (X_T) is normally computed using an expression similar to Equation 2.26. Light attenuation functions (X_L) generally follow the analysis by Steele (1962), accounting for the effects of supersaturating light intensities and light attenuation through the water column, and lead to

$$X_L = \frac{2.718f}{\eta d} \left[\exp\left(-\frac{I_0}{I_s} \exp(-\eta d)\right) - \exp\left(-\frac{I_0}{I_s}\right) \right] \quad (2.30)$$

where d is the depth (m), η is the light extinction coefficient including self shading (m), f is the photoperiod correction, I_0 is the incident light intensity just below the surface (langley day⁻¹), and I_s is the algal saturation light intensity at the maximum photosynthetic rate. The above formulation is for a surface layer and a more general formulation is given by Chapra and Reckhow (1983).

Smith (1980) developed a framework for calculating I_s based upon the maximum growth rate, the quantum yield of chlorophyll, the extinction coefficient per unit of chlorophyll, and the ratio of carbon to chlorophyll in the phytoplankton. This framework allows for adaptation by changing the carbon to chlorophyll ratio. Recent developments in phytoplankton kinetics models use photosynthetically active radiation (PAR) ($\mu\text{Em}^{-2}\text{day}^{-1}$) instead of total energy I_s (langley day⁻¹). They also apply Haldane kinetics in place of Steele's equation (Megard et al. 1984).

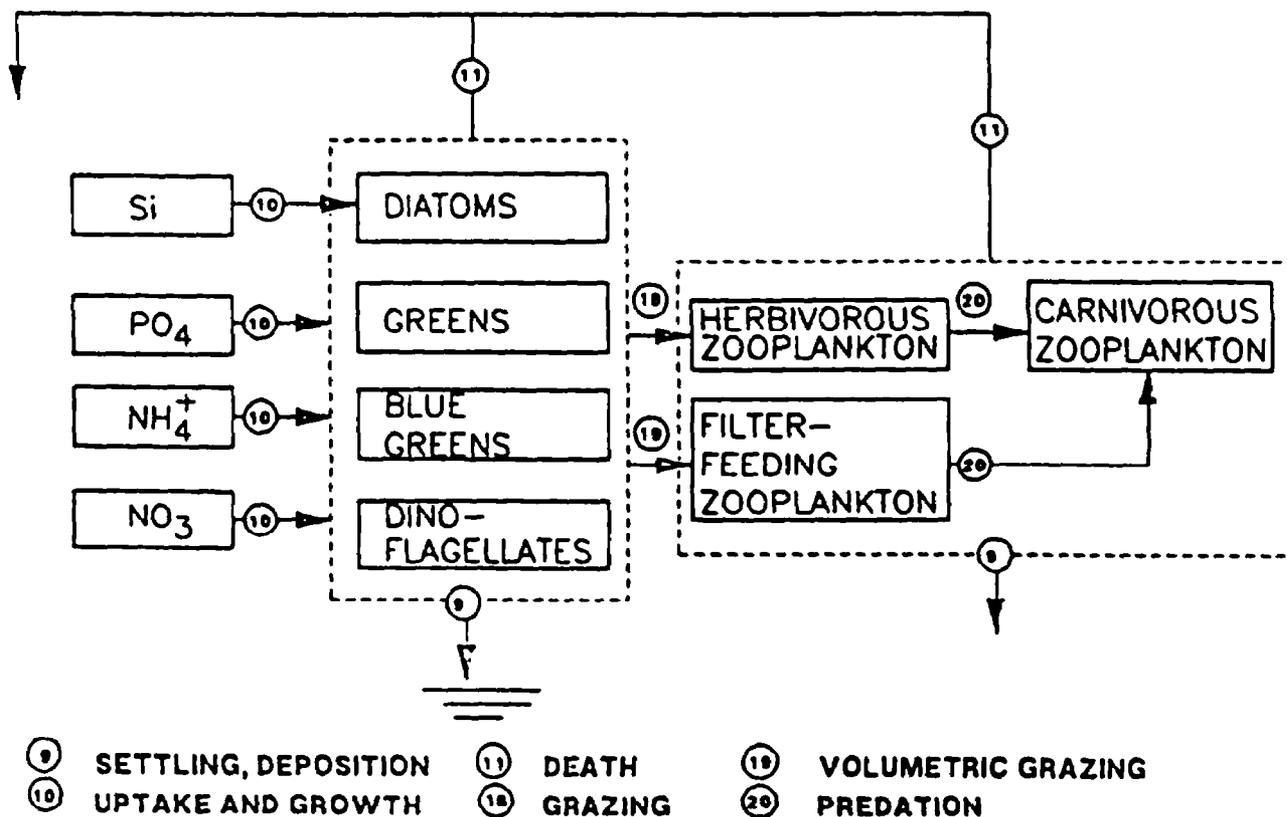


Figure 2-8. Additional variables and processes for trophic interactions.

The nutrient limitation factor is based on the assumption that phytoplankton follow Monod kinetics with respect to the important nutrients. Generally, the minimum function for inorganic nitrogen and phosphorus is used:

$$X_N = \text{Min} \left[\frac{C_{IN}}{K_{MN} + C_{IN}}, \frac{C_{IP}}{K_{MP} + C_{IP}} \right] \quad (231)$$

where C_{IN} is inorganic nitrogen ($\mu\text{g/l}$), C_{IP} is inorganic phosphorus ($\mu\text{g/l}$), K_{MN} is the Michaelis half-saturation constant for nitrogen ($\mu\text{g/l}$), and K_{MP} is the Michaelis half saturation constant for phosphorus ($\mu\text{g/l}$). Occasionally, X_N is expressed as the product of the nitrogen and phosphorus terms. Additional terms may include separation of nitrogen into ammonia-nitrogen and nitrate-nitrogen. Dissolved available silica is included where simulation of diatoms is required.

Phytoplankton "death" rates are conventionally expressed as the sum of the endogenous respiration rate, the death rate, and the grazing rate. The first two are generally modeled as the first order temperature corrected rates. Grazing may be expressed as first order, or second order if the herbivorous zooplankton population is specified or simulated. To capture the phytoplankton population dynamics properly,

zooplankton may have to be simulated. If average phytoplankton levels are adequate, then the first order approach is acceptable.

The relationship between phytoplankton kinetics and variations in DO and nutrients is expressed using stoichiometric relationships. Proper specification of average stoichiometry is necessary to accurately model these interactions. The ratios of phytoplankton carbon to phytoplankton nitrogen, phosphorus, and chlorophyll-a vary among species and in time. Few applied modeling frameworks account for the dynamics of stoichiometry. The user is forced to specify average values or those characteristic of stressed systems.

Guidance on the selection of parameters and coefficients for modeling phytoplankton nutrients and settling is provided in Section 5.

VI. Nutrients

Simulation of nutrients is critical to eutrophication models and to some DO models which include mechanistic descriptions of phytoplankton kinetics. Simulation of ammonia-nitrogen is also necessary in studies involving ammonia-toxicity. Sources of nutrients include bottom sediments, point source load-

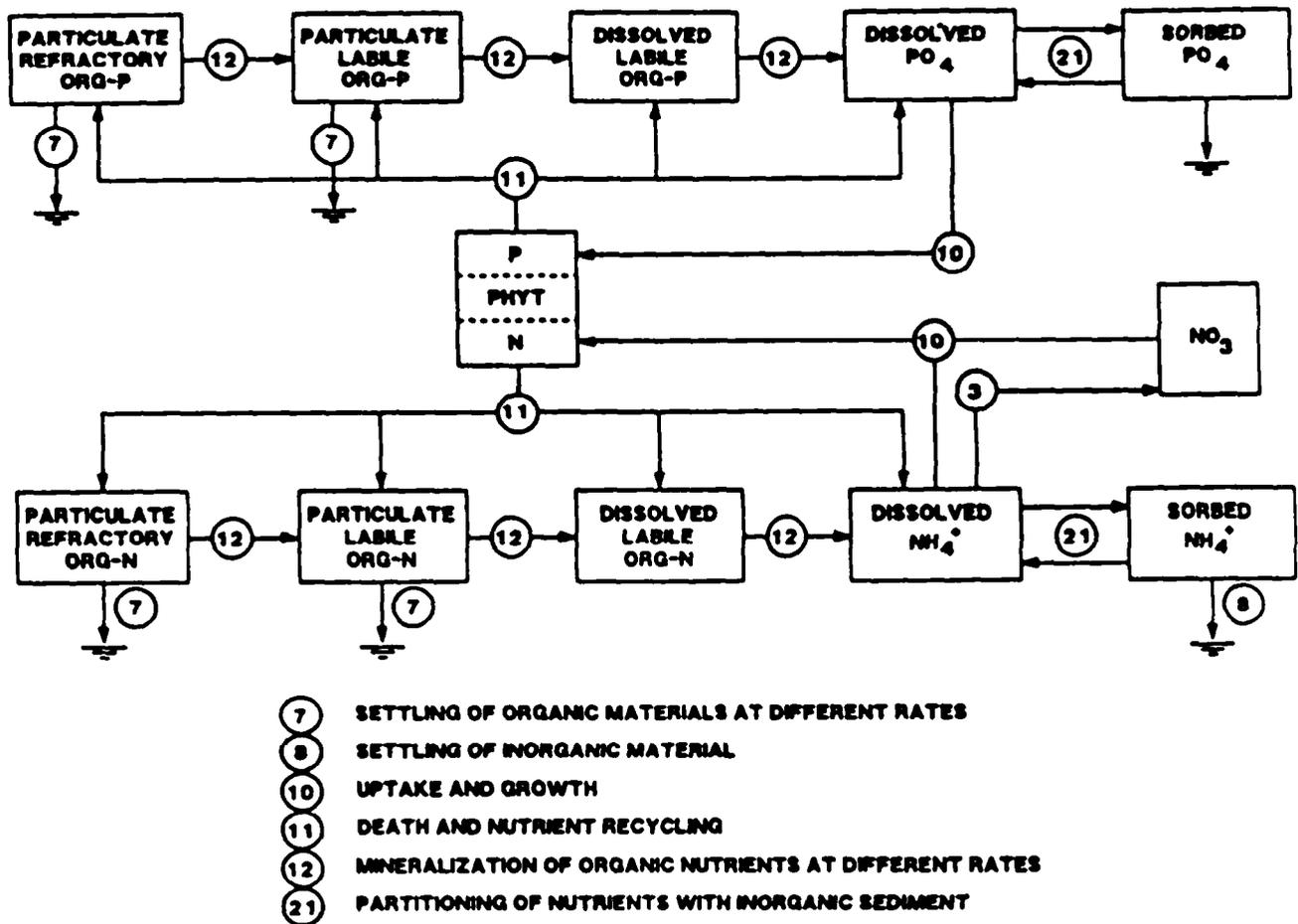


Figure 2-9. Additional variables and processes for nutrient interaction.

ings, non-point loadings from the watershed, and atmospheric deposition.

Atmospheric deposition has been implicated as a major source of nutrients in some large estuaries.

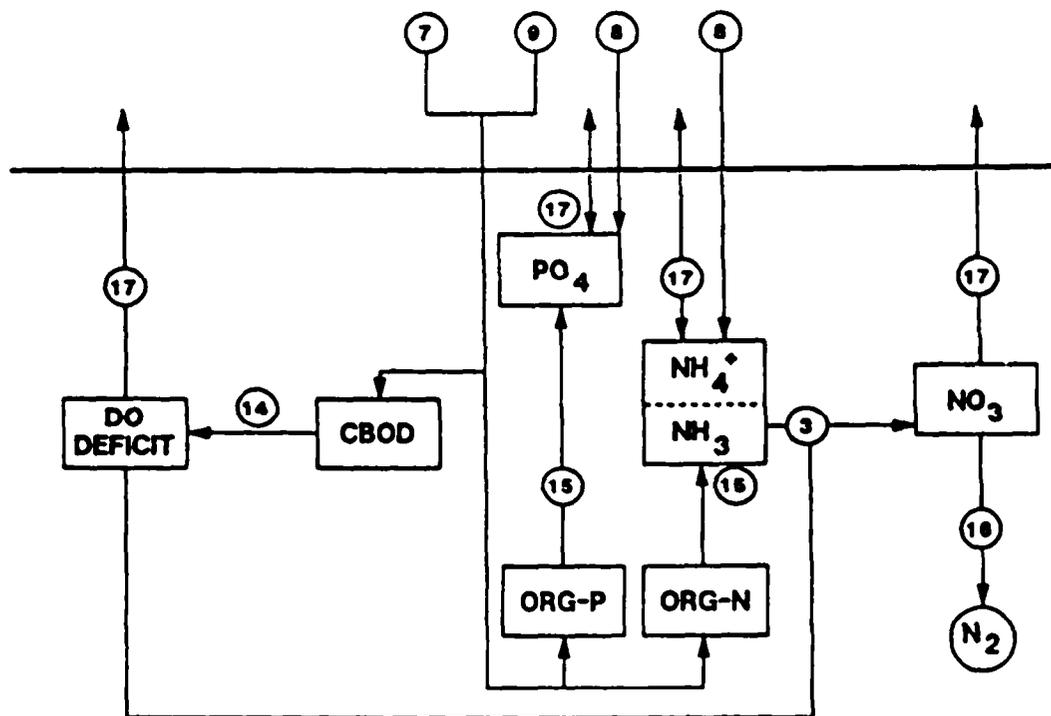
For the simplified DO-BOD modeling, as illustrated by Figure 2-6, it may be sufficient to consider only nitrogenous oxygen demand (NBOD). Similarly to CBOD, NBOD is modeled as a first-order process, where NBOD is expressed in oxygen units. Guidance on first-order nitrification rate constants is provided in Section 5 (Supplement X).

Models which include nutrient cycles vary in their complexity, as illustrated by the nutrients considered in the eutrophication model illustrated in Figure 2-7 as compared to that illustrated in Figure 2-9. The primary nutrients considered to impact eutrophication are nitrogen, phosphorus, and silica.

Nitrogen is present in particulate and dissolved, organic and inorganic forms (Figure 2-9). Nitrogen is

consumed by algae during growth, where the nitrogen loss rate is stoichiometrically related to the algal growth rate (Equation 2.29). During algal respiration and death, some nitrogen is returned directly to the inorganic nitrogen pool, while particulate organic nitrogen may be lost due to settling. Organic nitrogen undergoes bacterial decomposition whose end product is ammonia-nitrogen. Nitrification may then result in the oxidation of ammonia-nitrogen to nitrate-nitrogen and finally to nitrate-nitrogen. Denitrification by bottom sediments may be a major loss mechanism in some systems. Guidance on selection of rate terms for the various processes impacting nitrogen concentrations is provided in Section 5 (Supplement XI).

Simulation of nitrogen is also of importance due to the toxicity of unionized ammonia (NH_3). Direct simulation of ammonia speciation requires the simulation of pH. However, if pH is not expected to vary it may often be sufficient to simulate the nitrogen cycle in order to predict total ammonia concentrations. Knowing the equilibrium relationship between the two forms



- ⑭ BENTHIC DECOMPOSITION
- ⑮ BENTHIC REMINERALIZATION
- ⑯ DENITRIFICATION
- ⑰ DIFFUSION
- ⑦ DEPOSITION OF ORGANIC MATERIAL
- ⑧ SORPTION, DEPOSITION OF INORGANIC MATERIAL
- ③ NITRIFICATION
- ⑨ DEPOSITION OF PHYTOPLANKTON

Figure 2-10. Benthic interactions for nutrients and DO.

$$\frac{[NH_3][H^+]}{[NH_4^+]} = K_h \quad (2.32)$$

and that the total ammonia-nitrogen present or predicted (NH_T) is the unionized ammonia plus the ionized ammonia (NH_4^+), ($NH_T = NH_3 + NH_4^+$) the portion occurring as NH_3 can then be estimated from

$$NH_3 = \frac{1}{1 + [H^+]/K_h} NH_T \quad (2.33)$$

Some caution needs to be exercised concerning the reporting of units of nitrogen (i.e. as nitrogen or as ammonia). Speciation is also effected by temperature and the distribution of cations and anions. The aqueous ammonia calculations are discussed in detail by Thurston et al. (1974) and Emerson et al. (1975), as well as the effects of temperature and pH on calculations assuming zero salinity. These calculations are also summarized by Bowie et al (1985). Whitfield (1974) provided guidance on the effects of seawater on ammonia speciation. The speciation of ammonia may also be estimated using equilibrium speciation models such as MINTQA1 (Brown and Allison 1987).

Phosphorus may also occur in the water column in organic or inorganic, particulate or dissolved forms (Figure 2-9). Phosphorus is released during phytoplankton respiration and death in either organic or inorganic form. Phosphorus is utilized in algal growth as indicated in Equation 2.29. Dissolved inorganic phosphorus sorbs to suspended particulate matter in the water column, coming to an equilibrium expressed either with a partition coefficient or as a calibrated fraction dissolved:

$$f_{DIP} = \frac{1}{1 + K_{PIP} SS} \quad (2.34)$$

where f_{DIP} is the fraction inorganic phosphorus dissolved, SS is the suspended sediment concentration (kg/L), and K_{PIP} is the partition coefficient in (L/kg). Subsequent settling of the solids and sorbed phosphorus can provide a significant loss mechanism of phosphorus from the water column to the benthos. Process based functions that accurately calculate the phosphorus partition coefficient would improve prediction of this important variable significantly. Phosphorus loss mechanisms are generally described using first-

order kinetics, and guidance on rates is provided in Section 5 (Supplement XII).

VII. Sediment Interactions

Sediment processes may have profound effects on DO and nutrients in some systems. The decomposition of deposited organic material releases nutrients and results in an oxygen demand. Denitrification by sediments is often a major loss mechanism for nitrogen (Figure 2-10). Sediments may continue to have impacts on water quality long after sources of organic materials and nutrients have been eliminated.

Although often of critical importance, the predictive capability of most presently available models of sediment interactions is limited. Description of these impacts is often reduced to field measurements followed by use of zeroth order rate terms based on those measurements in models to describe their effects on other variables and processes. Guidance on selection of rate terms is provided in Section 5 (Supplement XV).

VIII. Surface Exchange

The surface exchange of dissolved oxygen, is typically modeled based on Whitman's two-film model (Lewis

and Whitman 1924) assuming resistance in the liquid controls. This reduces the source/sink (S , Equation 2.5) term for surface exchange to

$$S = K_2 (C - C_s) \quad (2.35)$$

where K_2 is a reaeration rate, C is the water concentration, and C_s the saturation concentration. The saturation concentration for dissolved oxygen is typically computed using empirical expressions including the effects of temperature and dissolved solids. The reaeration rate has been computed using a variety of formulations. Guidance on the selection of reaeration coefficients for dissolved oxygen is provided in Section 5 (Supplements XIII and XIV).

For other gases, such as unionized ammonia and many toxic materials, the gas film rather than the liquid film may control gas transfer, which must be reflected in the formulation of the rate term.

Additionally, the method for computing saturation concentrations will vary (see Supplement IV, Volatilization).

SUPPLEMENT IV: SYNTHETIC ORGANICS

I. Loss Rates

Synthetic organic concentrations are described using the constituent mass balance equation (Equation 2.5) similarly to other materials. The processes impacting their physical, chemical and biological transformations differ, as illustrated by Figure 2-11. Physical losses occur through mechanisms such as volatilization, settling, and sedimentation, while physical gains can occur through resuspension. Chemical transformations may result from hydrolysis, photolysis, oxidation and reduction and ionization. Biological transformation and loss can result from bacterial degradation and accumulation in biota. Additional differences result where materials do not mix, or only partially mix, with the mean flow, such as some oils. The mathematical treatment of immiscible or only partially miscible oils often requires specialized modeling techniques, such as those used in oil-spill modeling.

For constant environmental conditions, the overall chemical loss rate of synthetic organics is often approximated as a first-order reaction:

$$S = -K_T C \quad (2.36)$$

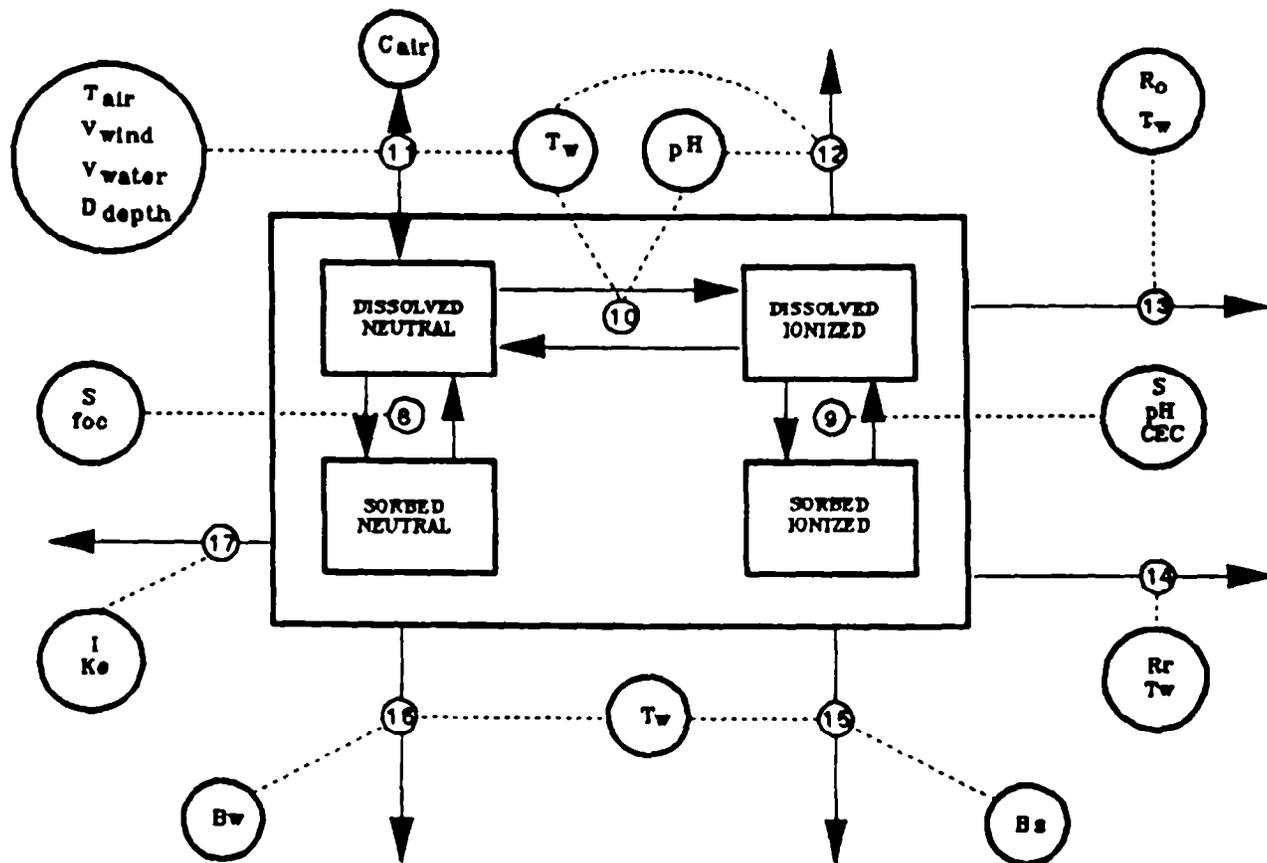
where K_T is the observed loss coefficient (day^{-1}), C is the total chemical concentration (g/m^3) and, and S is the source/sink term of the constituent mass balance equation (Equation 2.5). The value K_T represents a single set of environmental conditions only. Changes in temperature, velocity, depth, sunlight, wind, sediment concentrations, or pH can affect the total loss rate in ways that can not be considered using this approach. Alternatively, each of the processes impacting the transformations may be simulated.

An overview of methods used to describe these transformation processes is provided below. Additional information is provided by Chapra and Reckhow (1983), Thomann and Mueller (1987) and elsewhere.

A method to complement field survey data is the chemical process approach. This approach combines laboratory-measured chemical constants with field-measured environmental properties to estimate site-specific rate coefficients, $K_i(x,t)$, for several loss processes "i":

$$K_i(x,t) = K_i E_i(x,t) \quad (2.37)$$

where K_i is a laboratory measured second order rate constant and $E_i(x,t)$ is the intensity of the relevant



PROCESSES

- | | | | |
|---|---------------------------------|---|------------------------|
| ⑧ | HYDROPHOBIC SORPTION/DESORPTION | ⑬ | OXIDATION |
| ⑨ | IONIC SORPTION/DESORPTION | ⑭ | REDUCTION |
| ⑩ | IONIZATION | ⑮ | BENTHIC BIODEGRADATION |
| ⑪ | VOLATILIZATION | ⑯ | WATER BIODEGRADATION |
| ⑫ | HYDROLYSIS | ⑰ | PHOTOLYSIS |

PARAMETERS

- | | | | |
|-------------|-----------------------------|-------|---------------------------------------|
| T_{air} | = air temperature | T_w | = water temperature |
| V_{wind} | = wind speed | R_o | = concentration of oxidant |
| V_{water} | = water velocity | CEC | = cation exchange capacity |
| D_{depth} | = water depth | R_r | = concentration of reductant |
| C_{air} | = atmospheric concentration | B_s | = bacterial concentration in sediment |
| S | = Solids concentration | B_w | = bacterial concentration in water |
| f_{oc} | = fraction organic carbon | I | = incident light |
| | | K_e | = extinction coefficient |

Figure 2-11. Basic variables and processes for reactive organic chemicals.

environmental parameter. If more than one loss process is active for a chemical in an environment, the overall loss coefficient can be estimated by summing the individual rate constants. Combining the chemical process approach with the field survey approach should increase the reliability of modeling estimates, allowing extrapolation to a much wider range of environmental conditions.

II. Physical Loss Mechanisms

A. Volatilization

Volatilization in most models is treated similarly to surface oxygen exchange (Equation 2.35) where the loss due to volatilization (S_v) is equal to the difference in chemical concentrations multiplied by a transfer coefficient, as

$$S_v = k_v (C_w - C_a) \quad (2.38)$$

where k_v is the transfer rate, C_w the dissolved concentration of the chemical in water, and C_a the saturation dissolved concentration, dependent upon the atmospheric partial pressure and Henry's Law constant for the material.

A common assumption is that the atmospheric concentration is much less than the water concentration, allowing simulation of the transfer as a pseudo-first order rate. Where the toxicant mass balance expression (Equation 2.5) is written for the total concentration (dissolved plus particulate), the concentration must also be adjusted for the fraction dissolved (f_d) as

$$S_v = k_v f_d C_{tw} \quad (2.39)$$

where C_{tw} is the total concentration in water.

The transfer rate is usually computed as the reciprocal of the resistances in the two films (gas and liquid), as

$$k_v = (R_L + R_G)^{-1} \quad (2.40)$$

where R_L is the liquid phase resistance and R_G the gas phase resistance.

The liquid and gas transfer coefficients are dependent on turbulence at the interface, on temperature, and on properties of the chemical such as diffusivity. Empirical correlations have been developed relating transfer coefficients either directly to physical parameters such as wind velocity and the density and viscosity of the water (MacKay et al. 1983; Southworth et al. 1979a), plus the molecular weight and diffusivity of the chemical or to the field-measured transfer coefficients of oxygen and water vapor (Liss and Slater 1974).

O'Connor (1983) has presented a theoretical development for the liquid transfer coefficient applicable to a

wide range of hydrodynamic conditions, but application requires estimates of several coefficients that are not easily obtained.

B. Sorption

Many toxic materials sorb strongly onto particulates. Estimates of sorption are required in modeling toxic materials since processes impacting dissolved and particulate fractions differ. Sorption is the bonding of dissolved chemicals, C , onto solid phases, S_i , such as benthic and suspended sediment, biological material, and sometimes dissolved or colloidal organic material resulting in the formation of the chemical-sediment bond, $C-S_i$.

$$S_i + C = C - S_i \quad (2.41)$$

Sorption reactions are usually fast relative to other environmental processes, and equilibrium may be assumed. For environmentally relevant concentrations (less than 10^{-5} M or one-half water solubility), equilibrium sorption is linear with dissolved chemical concentration (Karickhoff 1984) or:

$$C_i = K_{pi} C_d \quad (2.42)$$

where C_i is chemical concentration in the solid phase I (mg/kg), C_d is dissolved chemical concentration (mg/L), and K_{pi} is the sorption partition coefficient between the two phases (L/kg). At equilibrium, then, the distribution among the phases is controlled by the partition coefficient, K_{pi} . The total mass of chemical in each phase is controlled by K_{pi} and the amount of solid phase present.

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. Normalization of the partition coefficient by the organic-carbon content of the sediment has been shown to yield a coefficient, K_{oc} , that is relatively independent of other sediment characteristics or geographic origin (Karickhoff 1981). Correlation of K_{oc} with the water solubility of the chemical or the octanol/water partition coefficient of the chemical has yielded successful predictive tools for incorporating the hydrophobicity of the chemical in an estimate of its partitioning. These correlations do poorly for chemicals with very low or very high hydrophobicity, however, because of deviations from hydrophobic adsorption.

Chemicals containing polar functional groups and low octanol/water partition coefficients tend to exhibit hydrophilic contributions to adsorption. Large non-polar molecules with high octanol/water partition coefficients generally require long time periods to reach

equilibrium resulting in low estimates of K_{OC} when sorption is measured over short time frames (Karickhoff 1984). The latter effect is particularly significant because it suggests that the assumption of instantaneous equilibrium used by the toxic chemical models may not be valid for those chemicals for which adsorption is the most important process (Ambrose et al. 1988).

In addition to the assumption of instantaneous equilibrium, implicit in the use of Equation 2.42 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 (1984) suggests that this effect may be the result of intraparticle kinetics in which the chemical is slowly incorporated into components of the sorbent. This phenomenon is not well understood and no quantitative modeling framework is available to characterize it (Ambrose et al. 1988).

Empirical evidence has suggested that the partition coefficient is inversely related to the particle concentration. A particle interaction model has been proposed by DI Toro (1985) which describes this relationship.

III. Chemical Loss Mechanisms

A. Hydrolysis

The overall hydrolysis rate constant in most toxic chemical models is calculated by:

$$K_H = \Sigma(k_{HAi} \cdot [H^+] + k_{HNi} + k_{HBi} \cdot [OH^-]) \quad (2.43)$$

where k_{HAi} is the acid hydrolysis rate constant for phase i ($L \text{ mole}^{-1} \text{ sec}^{-1}$), k_{HNi} is the neutral hydrolysis rate constant for phase i (sec^{-1}), k_{HBi} is the alkaline hydrolysis rate constant for phase i ($\text{mole}^{-1} \text{ sec}^{-1}$), $[H^+]$ is the hydrogen ion concentration (moles L^{-1}), and $[OH^-]$ is the hydroxide ion concentration in (moles/L). The models do not compute hydrogen or hydroxide ion concentrations. Instead these are input to the models assuming that their concentrations are unaffected by the hydrolysis reaction because of the low concentration of the toxic chemical present and reacting.

B. Photolysis

A quantitative framework that permits the prediction of direct photolysis from the incident light and the characteristics of the chemical (Zepp and Cline 1978) has been incorporated into several of the toxic chemical modeling frameworks. Use of this framework in natural water systems is complicated by the lack of a satisfactory model of UV-light penetration that incorporates the effects of both dissolved organics and particulate material in the water column. A comprehensive framework for photolysis also must include sensitized

photolysis. Unfortunately, the spectrum of compounds, particularly dissolved organics, involved in photochemical reactions is not known (Miller 1983). In addition, valid frameworks to predict free radical reactions have not been developed and the importance of these reactions remain undetermined (Zepp 1980).

A less rigorous method for predicting the photolysis rate coefficient K_p involves extrapolations of observed rates from one environmental condition to another:

$$K_p = K_{pG} [L] \Sigma \varphi P_i f_i \quad (2.44)$$

where K_{pG} is the observed rate coefficient (s^{-1}) for a reference light intensity, $[L]$ is the fraction of the reference light intensity averaged through the water column, φP_i is the relative yield for the chemical in phase i , and f_i is the fraction of the total chemical concentration in phase i . The reference light fraction $[L]$ accounts for depth, light extinction, cloud cover, latitude changes, and surface light variability.

C. Oxidation/Reduction

Chemical oxidation of organic materials 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. Oxidation is often modeled as a second order process dependent upon concentration of the oxidant and chemical.

D. Ionization

Consider a weak acid AH_3 or base BH_3 which may or may not react with water molecules to form charged anions and cations (ionize):



where K_a and K_b are the equilibrium first ionization constants for the reactions. These reactions are rapid. At equilibrium, the distribution of chemicals between the un-ionized and the ionized species is controlled by the pH of the water and the ionization constants (Ambrose et al. 1988). Stronger acids and bases may undergo further ionization, controlled by ionization constants K_{a2} , K_{a3} , K_{b2} , K_{b3} , the second and third ionization constants for the acid and base respectively. However, toxic organics are generally weak acids or bases. Examples of weak acids are the phenols (chlorophenol, dichlorophenol, trichlorophenol and pentachlorophenol), and a base is benzidine (Mills et al. 1985).

The ability to simulate ionization, the disassociation of a chemical into charged species, may be critical for chemicals that exhibit different chemical characteristics in different ionic states. For some chemicals, such as ammonia or hydrogen cyanide, it may be necessary to predict ionization in order to predict variations in toxic effects. Increases in observed toxicity of hydrogen cyanide (HCN) above pH 9 correlate well with the fraction in the anionic form (CN⁻), (Burns 1985). Ionization was described previously for ammonia (Supplement III, part V).

IV. Biological Loss Mechanisms

A. Biodegradation

Biodegradation is generally assumed to follow Michaelis-Menten enzyme kinetics. Values for the half saturation constant K_m and the maximum rate of degradation are not easily measured. Toxic chemical models generally assume the chemical concentration is much less than the half saturation constant and simplify the Michaelis-Menten equation to:

$$K_B = -B_{max} K_m^{-1} B = -k_B B \quad (2.47)$$

where K_B is the second order rate coefficient ($\text{mL cells}^{-1} \text{day}^{-1}$). The bacterial activity, B (cells mL^{-1}), is equal to

the reactant enzyme concentration (Ambrose et al. 1988). However, enzyme concentration cannot be measured in the field and the environmental and ecological effects on enzyme activity are difficult to estimate (Lewis et al. 1984). Consequently, other biological parameters are substituted, such as the concentration of bacterial cells.

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 well as the extrapolation of laboratory to field conditions questionable. As a result, toxic chemical models generally assume a constant biological activity rather than modeling the bacteria directly. Often, measured first order biodegradation rate constants obtained from experiments under field conditions as used rather than second order rates obtained from laboratory experiments that then require the additional estimation of field bacterial concentrations (Thomann and Mueller 1987).

SUPPLEMENT V: METALS

I. Modeling Techniques

The simulation of metals in aquatic systems has been approached from several levels of complexity. Presently, only approximate methods are available for estimating the dynamic mass transport of metals in complicated natural environments. The sorptive interactions of metals with particulate matter is the major process affecting the fate of toxic metals in the natural environment (Medine and McCutcheon 1989).

Modeling studies have been conducted using field derived or estimated, constant or varying, partition coefficients to describe the association of metals with solids, with associated transport due to settling and resuspension. For example, the riverine model MICHRIV (Large Lakes Research Station 1987) utilizes this approach and was used to analyze metal contamination in the Flint River, Michigan as described by Delos et al. (1984) and Mills et al. (1985). Thomann and Mueller (1987) described the simulation of sediment cadmium concentrations in the Sajó River, Hungary, using a partition coefficient which varied with suspended solids concentrations. Mills et al. (1985) describes several screening level approaches con-

sidering sorption. These methods may also be appropriate for some estuarine waste load allocations for metals. However, care should be exercised in using data to estimate sorption that does not reflect similar water chemistry and sediment characteristics to the system being modeled (Medine and McCutcheon 1989).

An alternative approach to using descriptive methods for partitioning may be required where sufficient field data are not available for estimating partition relationships, where chemical conditions are expected to change or where it is necessary to identify the form of the metal present in order to estimate its hazard. Equilibrium speciation models, such as MINTQA1 (Brown and Allison 1987) may provide estimates of equilibrium aqueous speciation, adsorption, gas phase partitioning, solid phase saturation states, and precipitation-dissolution for multimetal, multiligand systems. For waste load allocation purposes, equilibrium speciation models must then be run in conjunction with transport and transformation models, such as WASP4 (Ambrose et al. 1988).

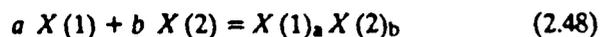
II. Process Descriptions

The form of the metal will be determined by the net result of interactions between complexation, chemical precipitation, adsorption, and oxidation-reduction. The combined effects of these interactions are computed using computer programs such as MINEQL (Westhall et al. 1986), MINTEQA1 (Brown and Allison 1987) and others which compute equilibrium composition in a multimetal, multiligand system, using mass balance and mass action equations and considering the effects of chemical precipitation, redox, and sorption.

A. Complexation.

Complexation refers to the reaction of a metal (e.g. Ag, Cd, Cu, Pb, Zn, etc.) with organic and inorganic ligands (e.g. OH⁻, CO₃²⁻, SO₄²⁻, Cl⁻, F⁻, NH₃, S²⁻, amino acids, humates, fulvates, etc.) in water, to form a third species (the metal-ligand complex).

To compute the form of a particular metal is likely to be in, it is usually necessary to consider all of the dominant sets of reacting ligands and competing metals. This involves the simultaneous solution of a series of non-linear equations. To develop these equations in a general form, we may first represent the components of a dissolved complex (metals and ligands) as X(j), where X(j) is the activity for the component j of the complex (or molar concentration if ionic strength is zero). For example, if "a" moles of component X(1) reacts with "b" moles of component X(2) to form a complex, the reaction may be written as



Assuming equilibrium, the reaction may be written as

$$K(i) = \frac{C(i)}{X(1)^a X(2)^b}$$

and then

$$C(i) = K(i) X(1)^a X(2)^b \quad (2.49)$$

where C(i) is the activity of the complex (X(1)_aX(2)_b) and K is a stability constant. If we further let the stoichiometric coefficients be represented as a(i,j) for the complex i and component j (for example above a = a(i,1) and b = a(i,2)) then the reaction may be written in more general form as

$$C(i) = k(i) \prod_{j=1}^N X(j)^{a(i,j)} \quad (2.50)$$

where N is the total number of components (metals and ligands) in complex i (2 in the above example), and a(i,j) is the stoichiometric coefficient for the jth component of the ith complex.

A mass balance may be written for any given component distributed among all of the complexes. For example the amount of a component X(j) in a complex C(i) is a(i,j)C(i). The total amount of the component among all complexes may be written as

$$X_T(j) = \sum_{i=1}^M a(i,j) C(i) \quad (2.51)$$

where M is the total number of complexes. Substituting from Equation 2.50, Equation 2.51 may be rewritten as

$$X_T(j) = \sum_{i=1}^M a(i,j) k(i) \prod_{j=1}^N X(j)^{a(i,j)} \quad (2.52)$$

The solution procedure, used in such models as MINEQL (Westhall et al. 1986) and MINTEQA1 (Brown and Allison 1987), is to make an initial guess as to the activity (or concentration) of each of the j components. The concentration of the individual species is then computed, using Equation 2.50, and the total of each component calculated (Equation 2.52, X_T(j)). This total is then compared to the known total (T(j)), as

$$D(j) = X_T(j) - T(j)$$

for all components and if the difference (D(j)) is greater than some criteria, a second guess estimate of the activities is made. The solution procedure is iterated until the known totals for each of the components and computed totals converge to within some specified difference. The procedure is accomplished numerically using techniques such as the Newton-Raphson method for solving simultaneous non-linear equations.

B. Precipitation and Dissolution.

In some cases, the transport and fate of metals is affected by chemical precipitation and dissolution, either through direct precipitation of metal solids (e.g. CdS, CuSO₄) or through coprecipitation where a major ion precipitate is formed which binds metals in the process (Medine and McCutcheon 1989). The possible concentrations of metal ligand complexes are constrained by their solubility, as expressed by the solubility product for the lth complex, K_{sp}(l). However, determination of the solubility requires consideration of all possible reactions and equilibria (Stumm and Morgan 1981). Chemical equilibrium models such as MINTEQA1 can examine the process of precipitation of pure metals forms in aqueous systems, assuming equilibrium conditions.

C. Redox Reactions.

Metals can change oxidation states through various oxidation and reduction reactions, expressed as



where M^{++} is oxidized metal, M^+ is reduced metal, e^- is an electron, and K_i is the equilibrium coefficient for reaction i . Oxidation-reduction reactions exert significant controls on the chemistry of major ions and trace metals and their mobility, particularly between suspended and bed solids forms (Medine and McCutcheon 1989). Reduction reactions, such as in the formation of sulfides in sediments, may strongly affect the dissolved concentrations and ecotoxicity of trace metals. Redox reactions are generally included in chemical equilibrium models, such as MINTEQA1.

D. Sorption.

The modeling of metal adsorption to metals is receiving considerable interest due to its importance in regulating metal movement in aquatic systems (Medine and McCutcheon 1989). However, sorption is strongly affected by the interactions between metals forms. Sorption is strongly affected by pH, often varying from 0 to

100 percent adsorption over a narrow range of pH (often less than 2 units).

A standard relationship for metals sorption may be written as

$$M + S_m = MS_m \quad (2.54)$$

and

$$K_{AM} = \frac{(MS_m)}{[M](S_m)} \quad (2.55)$$

where K_{AM} is a standard adsorption constant and S_m an adsorbing surface of type m and M is the free metal ion concentration. Other models proposed to describe adsorption and included in the MINTEQA1 code are activity Langmuir sorption, activity Freundlich, ion exchange sorption, constant capacitance and triple-layer surface complexation models (Medine and McCutcheon 1989, Brown and Allison 1987).

2.9. References

- Akiyama, J. and Stefan, H.G. 1985. Turbidity Current with Erosion and Deposition, ASCE, Jour. of Hydraulic Engineering, 111(HY12).
- Ambrose, R.B. Jr., Connoly, J.P., Southerland, E., Barnwell, T.O. Jr., and Schnoor, J.L. 1988. Waste Allocation Simulation Models. J. Water Poll. Contr. Fed. 60(9), pp. 1646-1656.
- Ariathurai, R. 1982. Two and Three-Dimensional Models for Sediment Transport, RMA 1980, Resources Management Associates, Lafayette, CA.
- Ariathurai, R. and Krone, R.B. 1976. Finite Element Model for Cohesive Sediment Transport. J. Hydraulic Division, ASCE, 102(HY3), pp. 323-338.
- Bedford, K.W. 1985. Selection of Turbulence and Mixing Parameterizations for Estuary Water Quality Models, Miscellaneous Paper EL-85-2, USAE Waterways Experiment Station, Vicksburg, MS.
- Bowden, K.F. 1967. Circulation and Diffusion, In Estuaries (G.H. Lauff, ed.) AAAS Publ. No. 85, Washington, DC. pp 15-36.
- Bowie, G.L. et al. 1985. Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling (second ed.), U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-85/040.
- Brown, D.S. and Allison, J.D. 1987. MINTEQA1, An Equilibrium Metal Speciation Model: User's Manual, U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-87/012.
- Chapra, S.C. and Reckhow, K.H. 1983. Engineering Approaches for Lake Management, Vol. 2: Mechanistic Modeling, Butterworth Publishers, Woburn, MA.
- Chen, R.L., Brannon, J.M., and Gunnison, D. 1984. Anaerobic and Aerobic Rate Coefficients for Use in CE-QUAL-R1, Waterways Experiment Station, Miscellaneous Paper E-84-5, July 1984.
- Churchhill, M.A., Smith, D.J., and Lee, S. 1962. The Prediction of Stream Reaction Rates, ASCE, J. Sanitary Engr. Div. 88(SA4), pp 1-46.
- Delos, C.G., Richardson, W.L., DePinto, J.V., Ambrose, R.B., Rogers, P.W., Rygwelski, K., and St. John, J.P. 1984. Technical Guidance Manual for Performing Waste Load Allocations: Book II Streams and Rivers, Office of Water Regulations and Standards, U.S. Environmental Protection Agency, Washington, D.C.
- Dietrich, W.E. 1982. Settling Velocities Of Natural Particles, Water Resources Research, 18(6), p. 1615-1626.
- Di Toro, D.M. 1985. A Particle Interaction Model of Reversible Organic Chemical Sorption, Chemosphere 14(10), pp. 1503-1538.
- Di Toro, D.M. 1986. A Diagenetic Oxygen Equivalents Model of Sediment Oxygen Demand, in Sediment Oxygen Demand: Processes, Modeling, and Measurement, editor K.J. Hatcher, Univ. of Georgia, Athens, GA., pp. 171-208.

- Emerson, K., Russo, R.C., Lund, R.E., and Thurston, R.V. 1975. Aqueous Ammonia Equilibrium Calculations: Effect of pH and Temperature, *J. Fish. Res. Board Canada*, 32(12): 2379-2383.
- Environmental and Hydraulics Laboratories. 1986. CE-QUAL-W2, A Numerical Two-Dimensional Model of Hydrodynamics and Water Quality, User's Manual, Instruction Report E-86-5, USAE Waterways Experiment Station, Vicksburg, MS.
- Fischer, H.B. et al. 1978. *Mixing in Inland and Coastal Waters*. Academic Press, N.Y. 483 pp.
- Ford, D. and Thornton, K.W. 1989. Time and Length Scales for One-dimensional Assumptions and its Relationship to Ecological Models, *Water Resources Research* 15(1).
- Gantzer, C.J., Kolig, H.P., Rittmann, B.R., and Lewis, D.L. 1988. Predicting the Rate of Trace-organic Compound Removal by Natural Biofilms, *Water Research*, 22(2), pp. 191-200.
- Gibbs, R.J., Matthews, M.D., and Link, D.A. 1971. The Relationship Between sphere Size and Settling Velocity, *Jour. Sedimentary Petrology*, 41(1).
- Gill, A.E. 1982. Appendix 3, Properties of Seawater, in *Atmospheric-Ocean Dynamics*, Academic Press, New York, pp. 599-600.
- Golterman, H.L., Sly, P.G., and Thomas, R.C. 1983. Study of the Relationship Between Water Quality and Sediment Transport, UNESCO, Tech. Papers in Hydrology No. 26.
- Hansen, D.V. and Rattray, M. 1966. New Dimension in Estuary Classification. *Limnology and Oceanography* 11, 319-325.
- Hatcher, K.J. (ed.) 1986. *Sediment Oxygen Demand: Processes, Modeling, and Measurement*, Univ. of Georgia, Athens, GA.
- Imboden, D.M. et al. 1983. Mixing Processes in Lakes: Mechanisms and Ecological Relevance, *Schweiz. Z. Hydrol.* 45(1).
- Ives, K.J. 1973. *The Scientific Basis of Filtration*, Nato Advanced study Inst., Cambridge, UK, D. Reidel Publishing Co., 1973.
- Karickhoff, S.W. 1981. Semi-Emperical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils, *Chemosphere* 10, pp 833-846.
- Karickhoff, S.W. 1984. Organic Pollutant Sorption in Aquatic Systems, *Jour. Hydraulic Engineering, ASCE*, 110(6), pp. 707-735.
- Lal, D. 1977. The Oceanic Microcosm of Particles, *Science*, 198(4321), pp. 997-1009.
- Large Lakes Research Station. 1987. Users's Manual for the Transport and Fate Model MICHRIX, USEPA Large Lakes Research Station, Grosse Ile, MI.
- Lewis, W.K. and Whitman, W.C. 1924. *Principles of Gas Adsorption*, Industrial & Engineering Chemistry, 16.
- Lewis, D.L. et al. 1984. Application of Single and Multi-phase Michaelis-Menten Kinetics to Predictive Modeling for Aquatic Ecosystems, *Environ. Tox. Chem.*, 3(4), pp. 563-574.
- Lick, W., Ziegler, K., and Tsai, C. 1987. Resuspension, Deposition and Transport of Fine-grained Sediments in Rivers and Near-shore Areas, Prepared for the USEPA Large Lakes Research Station, Grosse Ile, MI.
- Liss, P.S. and Slater, P.G. 1974. Flux of Gases Across the Air-Sea Interface, *Nature*, 247, pp. 181-184.
- Lung, W.S. 1987. Advective Acceleration and Mass Transport in Estuaries, *ASCE J. Hydraulic Engr.* 112(9), 874-878.
- Lung, W.S. and O'Connor, D.J. 1984. Two-Dimensional Mass Transport in Estuaries, *ASCE J. Hydraulic Engr.* 110(10), 1340-1357.
- Lung, W.S. and Testerman, N. 1989. Modeling Fate and Transport of Nutrients in the James Estuary, *ASCE J. Environ. Engr. Div.* (In Print).
- Lung, W., Mackay, D., and Yeun, A.T.K. 1983. Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water, *Environ. Sci. Technol.*, 17(4), pp. 211-217.
- Medine, A.J. and McCutcheon, S.C. 1989. Fate and Transport of Sediment-Associated Contaminants, in *Hazard Assessment of Chemicals* (ed. J. Saxena), Hemisphere Publ. Corp., New York, pp. 225-291.
- Megard, R.O., Tonkyn, D.W., and Senft, W.H. II. 1984. Kinetics of Oxygen Photosynthesis in Planktonic Algae, *Jour. of Plankton Research*, 6(4), pp. 325-337.
- Mehta, A., ed. 1986. *Estuarine Cohesive Sediment Dynamics*, Springer Verlag, 486 pp.
- Miller, S. 1983. Photochemistry of Natural Water Systems, *Environ. Sci. Technol.*, 19(12), pp. 568-570A.

- Mills, W., et al. 1985. *Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants*, Parts 1 and 2. US EPA Athens, Ga, EPA/600/6-85/002.
- Morel, F.M.M. 1983. *Principles of Aquatic Chemistry*. Wiley, New York.
- Munk, W. and Anderson, E.R. 1948. Notes on a Theory of the Thermocline. *J. Marine Res.* 7, 276-295.
- Nihoul and Jamarf. 1987. *Three-Dimensional Models of Marine and Estuarine Dynamics*. Elsevier Scientific, Amsterdam.
- O'Connor, D.J. and Dobbins, W.E. 1958. Mechanisms of Reaeration in Natural Streams, *ASCE Transactions*, pp 641-684, paper 2934.
- O'Connor, D.J. 1983. Wind Effects on Gas-liquid Transfer Coefficients, *Jour. Environmental Eng., ASCE*, 109(3), pp. 731-752.
- Officer, C.B. 1976. *Physical Oceanography of Estuaries*, John Wiley and Sons, New York.
- Officer, C.B. 1977. Longitudinal Circulation and Mixing Relations in Estuaries, *Estuaries Geophysics and The Environment* (Ed. C.B. Officer), National Academy of Sciences, Washington, DC, pp 13-21
- Orlob, G.T. and Selna, L.G. 1970. Temperature Variations in Deep Reservoirs, *ASCE, Jour. Hydraulic Div.*, 96(HY2), pp 391-410.
- Orlob, G.T. 1983. *Mathematical Modeling of Water Quality in Streams, Lakes and Reservoirs*. Wiley and Sons, 518 pp.
- Owens, M., Edwards, R.W., and Gibbs, J.W., 1984. Some Reaeration Studies in Streams, *International Jour. of Air and Water Pollution*, 8, pp. 469-486
- Paul, J.F. and Nocito, J.A., 1983. Numerical Model for 3-D Variable-Density Hydrodynamic Flows: Documentation of the Computer Program. U.S. EPA Environmental Research Lab, Duluth, Minnesota.
- Pritchard, D.W. 1967. Observations on Circulation in Coastal Plain Estuaries. in *Estuaries* (G.H. Lauff, ed.) AAAS Publ. No. 85, Washington, DC, pp 15-36
- Rodi, W. 1980. Computation of Turbulent Flow, *Ann. Review of Fluid Mechanics*, 8, pp. 183-208.
- Rodney, M. and Stefan, H. 1987. Conceptual Model for Wind-generated Sediment Resuspension in Shallow Ponds, *Proceedings, 1987 National Symposium on Mining, Hydrology, Sedimentology and Reclamation*, Univ. of Kentucky, Lexington.
- Shanahan, P. and Harleman, D.R.F. 1984. Transport in Lake Water Quality Modeling, *ASCE J. Environ. Engr.* 110(1).
- Sheng, Y.P. 1983. *Mathematical Modeling of Three-dimensional Coastal Currents and Sediment Dispersion: Model Development and Application*, Technical Report CERC-83-2, USAE Waterways Experiment Station, Vicksburg, MS.
- Southworth, G.R. et al. 1979a. The Role of Volatilization in Removing Polycyclic Aromatic Hydrocarbons from Aquatic Environments, *Bull. Environ. Contam. Toxicol.*, 21, pp. 507-514.
- Southworth, G.R. et al. 1979b. Transport and Transformation of Anthracene in Natural Waters, in *Aquatic Toxicology*, L.L. Marking and R.A. Kimerle (eds.), American Society for Testing and Materials, Philadelphia, PA, ASTM STP 667, pp. 359-380.
- Steele, J.H. 1962. Notes on Some Theoretical Problems in Production Ecology, in *Primary Production in Aquatic Environments*, Goldman, C.R. ed., pp. 383-398, Univ. of California Press, Berkeley.
- Stefan, H., Ambrose, R., and Dortch, M. 1988. *Surface Water Quality Models: Modeler's Perspective*. Proceedings of the June 19-23 International Symposium on Water Quality Modeling of Agricultural Non-Point Sources, Utah State University, Logan, Utah.
- Stumm, W. and Morgan, J. 1981. *Aquatic Chemistry. An Introduction Emphasizing Equilibrium in Natural Waters*, John Wiley and Sons, 780 pp.
- Thomann, R.V. and Mueller, J.A. 1987. *Principles of Surface Water Quality Modeling and Control*, Harper and Row, 608 pp.
- Thurston, R.V., Russ, R.C., and Emerson, K. 1974. Aqueous Ammonia Equilibrium Calculations, Technical Report 74-1. Fisheries Bioassay Laboratory, Montana State University, Bozeman, Montana.
- Tsvoglou, E.E. and Wallace, J.R. 1972. Characterization of Stream Reaeration Capacity. U.S. Environmental Protection Agency, Washington, DC, EPA-R3-72-012.
- Vanoni V., ed. 1975. *Sedimentation Engineering*, Manual No. 54, ASCE 745 pp.
- Wang, S.Y., Shen, H.W., Ding, L.Z. 1986. River Sedimentation, *Estuarine and Coastal Sedimentation*.

School of Engineering, The University of Mississippi, University, MI, 1822 pp.

Wang, M. and Harleman, D.R.F. 1984. Modeling Phytoplankton Concentrations in a Stratified Lake, Proceedings of the Ecology Modeling Conference, Colorado State University.

Westhall, J.C., Zachary, J.L., and Morel, F.M.M. 1986. MINEQL, A Computer Program for the Calculation of the Chemical Equilibrium Composition of Aqueous Systems, Report 86-01, Department of Chemistry, Oregon State Univ., Corvallis, OR.

Whitfield, M. 1974. The Hydrolysis of Ammonium Ion in Seawater-A Theoretical Study, J. Marine Bio. Assoc. United Kingdom, 54, pp. 565-580.

Wolfe, N.L. 1980. Determining the Role of Hydrolysis in a Fate of Organics in Natural Waters, in R. Haque (ed.), Dynamics, Exposure, and Hazard Assessment of Toxic Chemicals, Ann Arbor Science, Ann Arbor, MI, pp. 163-17.

Zepp, R.G. and Cline, D.M. 1978. Rate of Direct Photolysis in Aquatic Environments, Environ. Sci. Technol., 11(4), pp. 359-366.

Zepp, R.G. 1980. Assessing the Photochemistry of Organic Pollutants in Aquatic Environments, in R. Haque (ed.), Dynamics, Exposure, and Hazard Assessment of Toxic Chemicals. Ann Arbor Science, Ann Arbor, MI, pp. 69-110.

3. Model Identification and Selection

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3.1. Introduction

The first steps in the modeling process are model identification and selection. Specific water quality problems are identified and study objectives are set. The goals are to identify the simplest conceptual model that includes all the important estuarine phenomena affecting the water quality problems, and to select the most useful analytical formula or computer model for calculating waste load allocations. Selection of too simple a model can result in inaccurate predictions of future water quality under hypothetical load reductions. This can happen even if the model calibration "fits" existing data. Inaccurate projection from present to future can be caused by a changing balance among important processes, such as carbonaceous, nitrogenous, and sediment oxygen demand. The result is a waste load allocation that is either too expensive or underprotective of water quality.

On the other hand, selection of too complex a model will most likely result in misdirected study resources, delays in the study, and increased cost. Predictive uncertainty may increase because of extra "free" model parameters that cannot be estimated with available data. Study costs will increase because of the additional data requirements and the expanded computer and manpower time needed for model runs, analysis, and sensitivity studies.

This chapter provides general guidance and some specific procedures for identifying an appropriate model. The term "model" in Section 3.2 is used in a general sense to identify the variables and equations solved, the dimensionality, and the space and time resolution. Specific analytical formulas and computer models are discussed in Section 3.3.

3.2. Model Identification

During model identification, available information is gathered and organized to construct a coherent picture of the water quality problem. The goals are to develop the most effective monitoring strategy and to select the most appropriate computer model.

There are four basic steps in model identification:

- Establish study objectives and constraints

- Determine water quality pollutant interactions
- Determine spatial extent and resolution
- Determine temporal extent and resolution

These steps are generally considered sequentially. They are related, however, and later steps may require refinement of earlier decisions. Indeed, after the study has been initiated, new data or model results may suggest changes in the conceptual model initially identified.

Following model identification, another important step is advised:

- Perform rapid, simple screening calculations

These calculations should help the modeler gain a better understanding of expected pollutant levels and the spatial extent of water quality problems. Analytical solutions are often used along with available data throughout the model identification stage. These techniques are discussed in Section 3.3.2.

3.2.1. Study Objectives and Constraints

The first step in identifying an appropriate WLA model for a particular site is to review the applicable water quality standards and the beneficial uses of the estuary to be protected. Local, state, and federal regulations may contribute to a set of objectives and constraints. Each may specify particular pollutants or classes of pollutants, and imply time and space scales that must be resolved by the model. For example, proscription of "toxic pollutants in toxic amounts" implies simulation of whole effluent toxicity dilution. Ammonia or metals standards imply simulation of those specific chemicals.

Regulations may specify an "allowable mixing zone" in the vicinity of the outfall. This requires that a model have sufficient spatial resolution to resolve near-field dilution and mixing processes. For example, the regulation for a thermal outfall may require that waters return to within 2 °C of the ambient temperature within 100 m of the outfall. This requires a model with an analytical solution, or a numerical model segmented on the order of 10 meters. By contrast, standards for minimum daily average dissolved oxygen require an

estuarine-wide, or far-field model that extends beyond the range of influence of the discharge.

The next step in identifying an appropriate WLA model for a site specific application is to review the existing data on waste loads, stream flows, and ambient water quality with respect to the beneficial uses of the estuary and the applicable water quality standards. These data should indicate whether standards violations or water quality problems are associated with diurnal fluctuations, storm events, flow variation, and/or season of the year. The modeler can use this information to determine the temporal resolution (steady-state, tidally averaged, real time) and the important pollution sources (point source, nonpoint source) that must be included in the selected model. The ambient water quality data should also indicate where violations or problems are occurring and whether significant spatial gradients in concentration exist. The combined information collected on the water quality problems will help determine which driving forces (freshwater inflow, tides, wind, etc.) must be represented in the model. In order to further define required model capabilities, future developments planned for the watershed should be identified. Projected new point source discharges or land use changes may require the WLA model to have different capabilities than the existing situation merits.

The final result of this step should be a clear understanding of the pollutants and water quality indicators, the areas, and the time scales of interest. The spatial and temporal scales for a range of standard water quality problems are suggested in Table 3-1. These are for general guidance, and must be interpreted more precisely for each specific waste load allocation.

3.2.2. Water Quality - Pollutant Interactions

After the pollutants and water quality indicators are identified, the significant water quality reactions must be determined. These reactions must directly or indirectly link the pollutants to be controlled with the primary water quality indicators. All other interacting water quality constituents thought to be significant should be included at this point. This can best be done in a diagram or flow chart representing the mass transport and transformations of water quality constituents in a defined segment of water. Figures 2-4 through 2-10 (Section 2) illustrated variables and processes important to the major water quality problems. Not all of these have to be included in the actual WLA model selected for use. Those excluded from a model, however, should be considered externally and parameterized in the coefficients. Figure 2-4 covered sediment transport. Figures 2-5 through 2-9 illustrated conventional pollutant interactions affecting dissolved oxygen, nutrient enrichment, and

Table 3-1. General Scales of Interest

Problem Context	Spatial Scale	Temporal Scale
Salinity	Estuarine-wide	Seasons
Sediment	Estuarine-wide	Days to Seasons
Bacteria	Mid/Far-field	Hours/Days
Heat	Near-field	Hours
D.O. Depletion	Far-field	Days to Seasons
Nutrient Enrichment	Far-field	Seasons to Year
Toxicity	Near-field	Hours to Days
Human Exposure		
-metals	Far-field	Weeks to Years
-volatile organics	Far-field	Days to Weeks
-hydrophobic organics	Far-field	Seasons to Years

eutrophication. Figure 2-10 dealt with toxicants, such as organic chemicals.

Each water quality constituent must be examined to determine the important forcing functions and boundaries, such as the air-water or water-benthic sediment interfaces. For example, dissolved oxygen is influenced strongly by reaeration across the air-water boundary. The nature of the reaeration function, then, should receive particular attention in the monitoring and modeling process. Constant or spatially-variable rate constants might be specified as calibration parameters. For estuaries dominated by flow or wind, reaeration rates might better be specified as function of velocity, depth, and wind speed. At the benthic boundary, sediment oxygen demand is usually specified as a spatially-variable flux, to be measured or calibrated. This flux, however, can be expected to change with future reductions in waste loads. There have been recent attempts to include benthic organic material as a model variable, with the flux computed internally. While satisfying conceptually, the benthic components of these models are difficult to calibrate because of the long time frames controlling benthic reactions. Good practice at present may be to include these reactions in the conceptual model, but calculate or estimate their effects external to the waste load allocation model. An example calculational framework was proposed by Di Toro (1986).

The final result of this step should be the assimilation of all the available knowledge of a system in a way that major water quality processes and ecological relationships can be evaluated for inclusion in the numerical model description. The conceptual model is the starting point from which systematic reductions in complexity can be identified that will provide an adequate representation of the system, while meeting the objectives of the study.

3.2.3. Spatial Extent and Scale

The general area affected by the waste load allocation and the significant water quality reactions were identified in steps 1 and 2. The purpose of this step is to specify the spatial extent, dimensionality, and scale (or computational resolution) of the WLA model. This may be accomplished by determining the effective dimensionality of the estuary as a whole, defining the boundaries of the study area, then specifying the required dimensionality and spatial resolution within the study area.

3.2.3.1. Effective Dimensionality

Real estuaries are, of course, three dimensional. There are gradients in hydrodynamic and water quality constituents over length, width, and depth. The effective dimensionality of an estuary includes only those dimensions over which these gradients significantly affect the WLA analysis. Justifiable reductions in dimensionality result in savings in model development, simulation, and analysis costs. Usually the vertical and/or lateral dimension is neglected. Eliminating a dimension from the WLA analysis implies acceptable uniformity of water quality constituents in that spatial dimension. For example, use of one dimensional longitudinal models implies acceptably small concentration deviations from the cross-sectional mean, both vertically and laterally. This judgment requires understanding both the transport behavior of estuaries and the specific goals of the WLA study.

For estuarine WLA modeling, the longitudinal (x) dimension can almost never be neglected. The analyst must decide whether the lateral (y) or vertical (z) dimensions must also be retained. The most frequent cause of variation in the vertical direction is density stratification. Lateral variations may be caused by large widths and slow lateral mixing. Vertical and lateral variations can be observed by plotting water quality concentration variations with width and depth. If such data are not available, vertical and lateral variations can be predicted in one of several ways:

- density, salinity, or temperature gradients,
- tidal or residual velocity reversals over width or depth,
- dye cloud splitting and differential advection,
- geomorphological classification.

A. Degree of Stratification.

Fisher et al. (1972) suggested a method to predict the degree of stratification in an estuary as a whole. Fresh-

water is lighter than saltwater. This produces a buoyancy of amount:

$$\text{Buoyancy} = \Delta \rho g Q_R \quad (3-1)$$

where

$\Delta \rho$ = the difference in density between sea and river water, (about 0.025 kg/m^3),

g = acceleration of gravity, (about 9.81 m/sec^2), and

Q_R = freshwater river flow, m^3/sec

The tide on the other hand is a source of kinetic energy, equal to:

$$\text{Kinetic energy} = \rho W U_t^3 \quad (3-2)$$

where

ρ = the seawater density, about 1.025 kg/m^3 ,

W = the estuary width, m, and

U_t = the square root of the averaged squared velocities, m/sec.

Width and velocities should be taken at a representative cross section of the estuary. The ratio of the above two quantities, called the "Estuarine Richardson Number," is an estuary characterization parameter which is indicative of the vertical mixing potential of the estuary:

$$R = \Delta \rho g Q_R / \rho W U_t^3 \quad (3-3)$$

If R is very large (above 0.8), the estuary is typically considered to be strongly stratified and the flow dominated by density currents. If R is very small, the estuary is typically considered to be well-mixed and the vertical density effects to be negligible.

Another desktop approach to characterizing the degree of stratification in the estuary is to use a stratification-circulation diagram (Hansen and Rattray, 1966). The diagram (shown in Figure 3-1) is based on measurements from a number of estuaries with known degrees of stratification. Its use requires the calculation of the

$$\text{Stratification Parameter} = \Delta S / S_0 \quad (3-4)$$

and the

$$\text{Circulation Parameter} = U_s / U_t \quad (3-5)$$

where

ΔS = time averaged difference between salinity levels at the surface and bottom of the estuary,

S_0 = cross-sectional mean salinity,

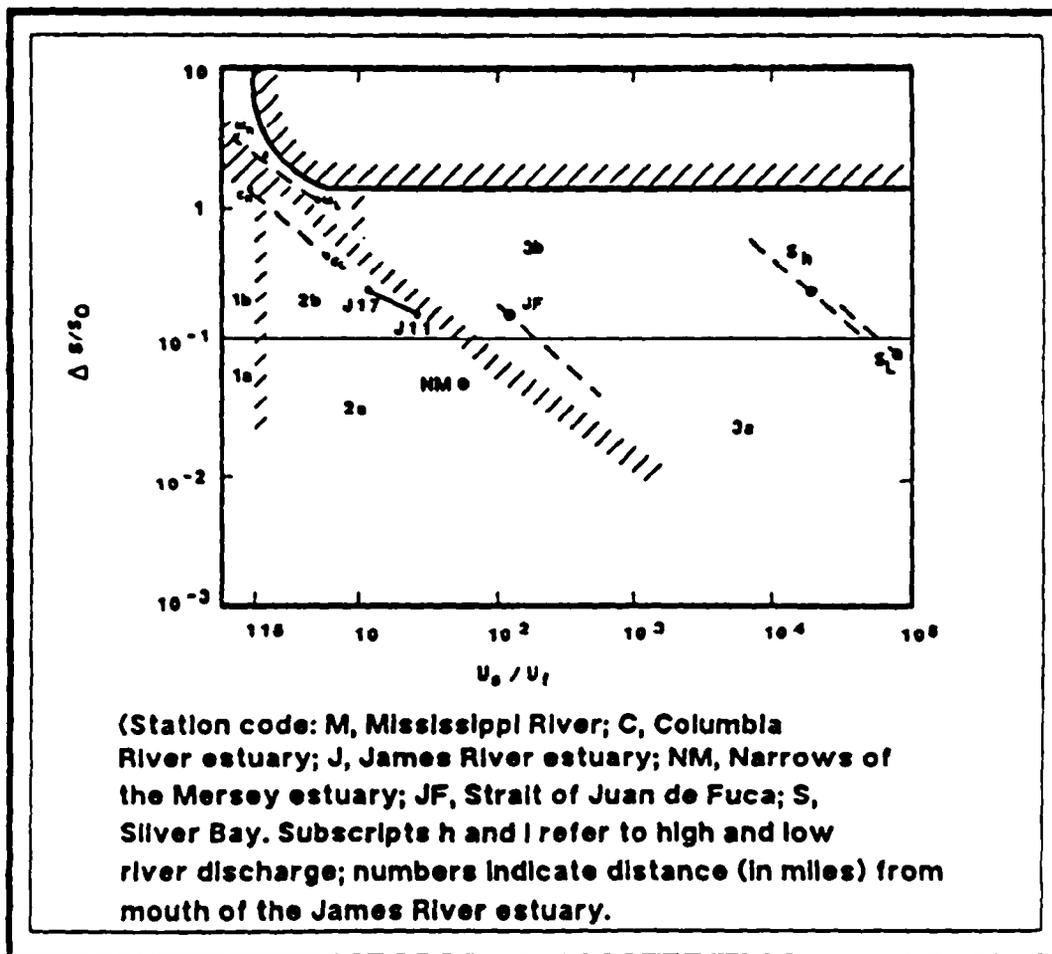
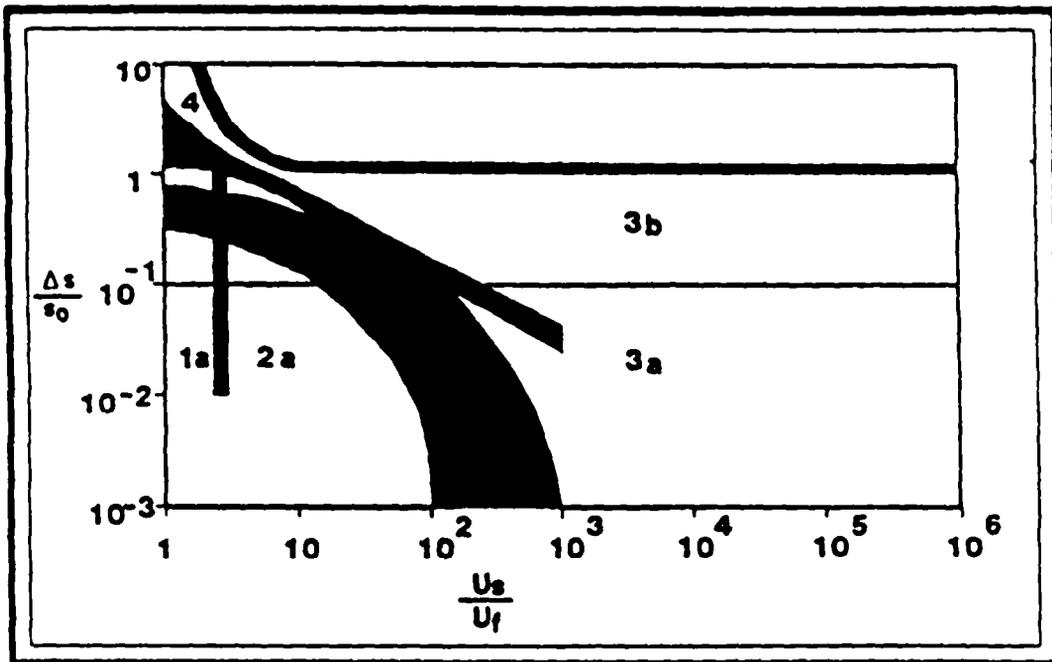


Figure 3-1. Stratification circulation diagram and examples.

U_s = net non-tidal surface velocity, and

U_f = mean freshwater velocity through the section.

For best results, mean salinity and velocity should represent averages over several tidal cycles. The stratification parameter is much less sensitive to tidal variations than the circulation parameter. To apply the stratification-circulation diagram, calculate the parameters of Equations 3-4 and 3-5, and plot the resulting point on the diagram. Type 1 estuaries have seaward flows at all depths, and the upestuary salt intrusion is due to tidal diffusion. Type 1a represents slight stratification as in a laterally homogeneous, well-mixed estuary. In Type 1b, there is strong stratification. Type 2 is partially well-mixed and shows flow reversals with depth. In Type 3a the transfer is primarily advective, and in Type 3b the lower layer is so deep, as in a fjord, that circulation does not extend to the bottom. Finally, Type 4 represents the salt-wedge type with intense stratification (Dyer, 1973). The purpose of the stratification-circulation analysis is to determine the degree of vertical resolution needed for a modeling study. If the estuary is well-mixed, the vertical dimension may be neglected, and all constituents in the water column are assumed to be dispersed evenly throughout. If the estuary is highly stratified, it is appropriate to model at least two layers. The approach for a partially-mixed system is not so clear and judgment must be exercised. For a recent toxics study (O'Connor et al., 1983), the James River, which is partially stratified, was treated as a 2-layer system.

A final desktop method for characterizing the degree of stratification is the calculation of the estuary number proposed by Thatcher and Harleman (1972):

$$E_d = P_t U_o^2 / U_d^2 T \quad (3-6)$$

where

E_d = estuary number,

P_t = tidal prism volume, m^3 ,

U_d = densimetric velocity, m/sec ,

$$= (g D \Delta \rho / \rho)^{1/2}$$

$\Delta \rho$ = the density difference between river water and sea water (about 0.025 kg/m^3),

ρ = density of sea water (about 1.025 kg/m^3),

U_o = maximum velocity at mouth of estuary, m/sec

D = depth, m ,

g = acceleration due to gravity (9.81 m/sec^2), and

T = tidal period, (about 44,700 sec).

Again, by comparing the calculated value with the values from known systems, one can infer the degree of stratification present.

The degree of stratification determined by one of the above methods may be translated into the following criteria for model selection:

- strongly stratified - include the vertical dimension in at least a 2 layer model
- moderately stratified - may include the vertical dimension in a multi-layered model, or
- vertically well-mixed - neglect vertical dimension, unless water quality processes dictate vertical resolution

B. Tidal or Residual Velocity Reversals.

Beyond the use of a stratification diagram, the analysis of vertical dimension reduction becomes more difficult and intuitive. However, the following criteria seem reasonable (Figure 3-2):

- tidal velocity reversals - should include vertical dimension in at least a 2-layer model,
- residual velocity reversals - may include the vertical dimension in a multi-layered model or may neglect vertical dimension if vertical variability is small,
- no observable reversals - may neglect vertical dimension.

C. Dye Studies.

Dye studies simply replace the Eulerian observations of current meters with the Lagrangian movement of a dye cloud study. Again, quantitative analyses are difficult, but the following criteria seem reasonable (Figure 3-3):

- Dye cloud separates and moves -cloud is responding to a vertical flow reversal and moves as 2 or more distinct units, indicating the vertical dimension should be included in at least a 2-layer model,
- Dye cloud spreads in non-Gaussian manner - some differential shearing is present and the system may be studied using a multi-layer model, or,
- Dye cloud moves downstream and diffuses in a Gaussian manner - little differential shearing is present and the system may be modeled neglecting the vertical dimension.

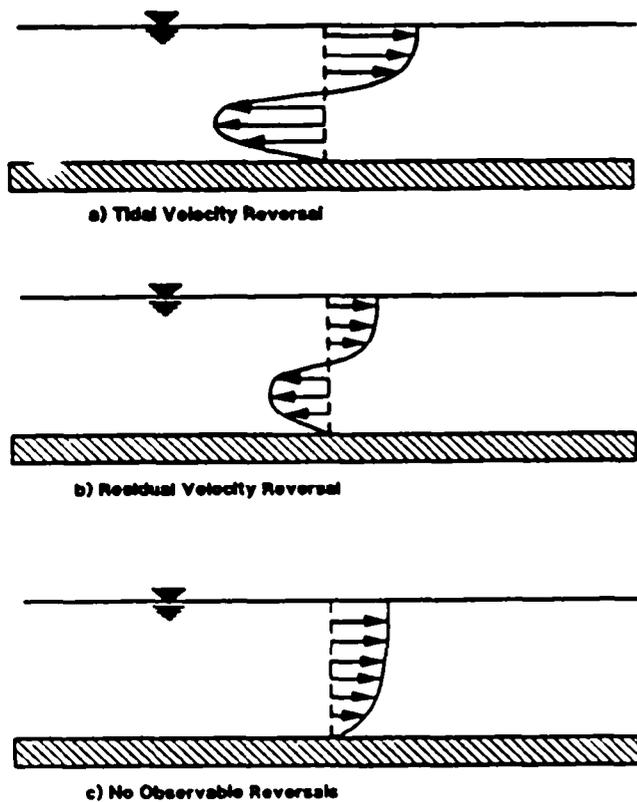


Figure 3-2. Vertical velocity profiles.

D. Geomorphological Classification.

Over the years, a systematic geomorphological classification of estuaries has evolved. If little or no data are available, one can try to categorize the estuary within the basic morphological definitions of Dyer (1973). Dyer (1973) and Fischer et al. (1979) identify four groups:

- Drowned river valleys (coastal plain estuaries)
- Fjords
- Bar-built estuaries
- Other estuaries that do not fit the first three classifications

Typical examples of North American estuaries are presented in Tables 3-2 and 3-3. The characteristics of each geomorphological classification were discussed in Section 2-1. Using these classifications, the approach is to estimate the degree of stratification from known conditions in a geomorphologically similar estuary and use the criteria given below under "degree of stratification".

3.2.3.2. Study Area Boundaries

After the effective dimensionality of the estuary has been determined, specific boundaries of the study area must be established. In general, the boundaries should be located beyond the influence of the discharge(s) being evaluated. Otherwise, proper specification of boundary concentrations for model projections is very difficult. Sometimes this guideline is not possible. One rule strictly applies - boundaries influenced by a discharge should be located far enough from the discharge so that errors in the boundary concentrations do not significantly affect predicted maxima or minima upon which the WLA is being based.

Beyond these rules, several common sense guidelines can help locate proper model boundaries. Boundaries should be located where flow or stage and water quality are well monitored. Upstream boundaries should be located at a fall line, or at a gaging station in free-flowing, riverine reaches. Downstream boundaries are best located at the mouth of an estuary, or even nearby in

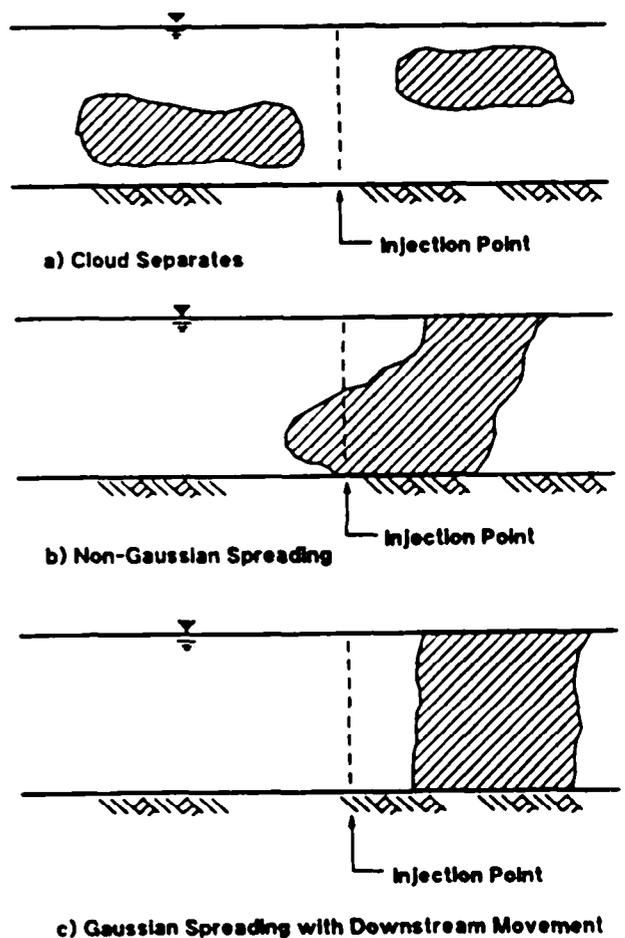


Figure 3-3. Vertical dye concentration profiles.

Table 3-2. Topographic Estuarine Classification

Type / Dominant Long Term Process	Vertical Degree of Stratification	Lateral Variability	Example
Coastal Plain / River Flow	Moderate	Moderate	Chesapeake Bay James River Potomac River Delaware Estuary New York Bight
Bar Built / Wind	Vertically Well Mixed	High	Little Sarasota Bay Apalachicola Bay Galveston Bay Albemarle Sound Palmico Sound Pugent Sound
Fjords / Tide	High	Small	Alberni Inlet Silver Bay
Other Estuaries/ Various	Various	Various	San Francisco Columbia River

the ocean. For large estuaries with relatively unaffected seaward reaches, the downstream boundary can be located within the estuary near a tidal gage and water quality monitoring station.

If these guidelines are not possible because of excessive computational elements, consideration should be given to nested grids. A crude grid could span the estuary and predict tidal flows and concentrations. Two or more internal elements in the coarse grid could serve as boundaries to a fine grid. This strategy may be particularly useful for assessing near-field effects in a strongly tidal estuary.

3.2.3.3. Study Area Resolution

If the study area constitutes all or most of the estuary, the model dimensionality should equal the effective estuarine dimensionality. If, however, the study area is a discrete segment of the estuary, then further simplifications in dimensionality may be possible. Data describing the spatial gradients of important water quality constituents within the study area should be examined. Dye studies can give important information

on the speed and extent of lateral and vertical mixing. The rate of mixing must be compared with water quality reaction rates to determine if lateral or vertical gradients are to be expected for particular constituents. For example, an estuarine reach that mixes laterally in 1 day can be laterally averaged for pollutants with characteristic reaction times of days (such as BOD). This same reach, however, should not be laterally averaged for pollutants with reaction times of hours (such as coliform bacteria or some organic chemicals).

Lateral mixing can be described by the convective length, L_c , over which the discharge plume is mixed laterally (Fischer et al., 1978, Holley and Jirka, 1986). Complete mixing is defined when the concentration is within 5 percent of its mean value everywhere in the cross section. For centerline and side discharges, respectively, the mixing length L_c is given by

$$L_c = 0.1 u W^2 / E_y \quad (3-7)$$

$$L_c = 0.4 u W^2 / E_y \quad (3-8)$$

where

u = mean downstream velocity, m/day

W = channel width, m

E_y = lateral diffusion coefficient, m^2/day

These formulas strictly apply to steady, unidirectional flow. Complete mixing is not achieved during ebb or flood tide if the lateral mixing time L_c/u is greater than 6 hours. Steady discharges can become laterally well mixed within the mixing length even if the lateral mixing time exceeds 6 hours due to tidal reversals. Lateral diffusion coefficients are best estimated by dye studies or other site specific data. Several general formulas are

Table 3-3. Stratification Classification

Type	Lateral Type	River Discharge	Example
Highly Stratified	Laterally Homogeneous	Large	Mississippi River Mobile River
Partially Mixed	Partially Mixed	Medium	Chesapeake Bay James Estuary Potomac River
Vertically Homogeneous	Moderate to High Variability	Small	Delaware River Raritan River Tampa Bay San Francisco Bay San Diego Bay

given in Bowie et al., (1985). The time required for complete lateral mixing (L_c/u) can be usefully compared to reaction half lives ($\Delta t_{1/2}$) to predict the degree of lateral mixing for various pollutants and water quality constituents. Half lives can be estimated from the first order reaction rate constant K:

$$\Delta t_{1/2} = 0.693/K \quad (3-9)$$

The convective mixing length should be compared to the study area dimensions to determine the relative importance of lateral mixing on the study area as a whole. If the effects are significant, or if regulations enforce water quality standards at the edge of the mixing zone, then a near-field model is required. Numerical models should be composed of computational elements with short length Δx and width Δy :

$$\Delta x \leq 0.2 L_c \quad (3-10)$$

$$\Delta y \leq 0.2 W \quad (3-11)$$

Smaller dimensions will give better precision, but at greater computational cost.

If near field effects are judged unimportant, then spatial resolution for the entire study area must be determined. Dye studies can give important information about the advective velocities and flushing times through the study area. The rate of downstream transport must be compared with water quality reaction rates to determine if longitudinal gradients are to be expected for particular constituents. Steeper water quality gradients require more detailed spatial resolution. The length of model computational elements should be significantly less than that required for concentrations to halve:

$$\Delta x < u \Delta t_{1/2} \quad (3-12)$$

The characteristic velocity can be either tidal or tidal-averaged, depending upon the type of simulation chosen. This decision is discussed in the next section.

Other considerations may affect the choice of spatial scale and the actual layout of the model network. One is the desired spatial resolution in critical areas to be protected, as along a public beach or around a water intake. Computational elements should be centered on these features, so that predicted concentrations can be related directly to appropriate standards or goals set to protect these resources. Likewise, computational elements should be centered on monitoring stations and important discharges. The model network may also have to account for unique features of the study area, such as embayments, marshes and tidal flats, channels, and islands. If the required spatial resolution is much larger than these features, they may be ignored. They should be accounted for when the required spatial resolution is of a similar size or less.

Another set of considerations affecting spatial scale is the required time resolution and the dynamics of the loading, transport, and kinetic processes. The need for monthly or seasonal average concentrations may allow quite large computational elements. If high or low tidal concentrations are needed, however, computational elements must be a fraction (say 20% or less) of the length of a tidal excursion. Predicting the effects of a steady discharge may allow large computational elements, while tracking the direct effects of batch discharges or storm runoff with characteristic times (Δt_E) constrains the computational lengths:

$$\Delta x \leq u \Delta t_E \quad (3-13)$$

Direct effects include such problems as acute toxicity and bacterial exposure. Indirect effects from unsteady discharges, such as the impact of nutrients on eutrophication and dissolved oxygen, generally don't constrain the computational lengths. An exception is when load is correlated with tidal transport, such as batch discharges into ebb tide only.

It is clear that choice of spatial scale and layout of the model network requires considerable judgment. Knowledge of the regulatory problem must be combined with knowledge of the loading, transport, and transformation processes and an understanding of the WLA model chosen to perform the simulations. Competing factors must often be balanced, such as precision and cost, or better fitting one section of the network versus another. For best results, the modeler should retain the flexibility to refine the model network during the calibration phase of the WLA study. Examples of 6 different model networks applied in actual case studies are given in Part 4 of this manual.

3.2.4. Temporal Extent and Scale

The WLA problem context and its general time scale were identified in step 1. The purpose of this step is to specify the duration and temporal resolution of the WLA model.

3.2.4.1. Duration of WLA Simulations

The duration of WLA simulations can range from days to years, depending upon the size and transport characteristics of the study area, the reaction kinetics and forcing functions of the water quality constituents, and the strategy for relating simulation results to the regulator's requirements. One basic guideline applies in all cases - the simulations should be long enough to eliminate the effect of initial conditions on important water quality constituents at critical locations. This will ensure that errors in the initial conditions do not significantly affect predicted concentrations upon which the WLA is being based.

The size and transport characteristics of the study area determine its flushing time. This is the time required to remove a parcel of water (along with associated dissolved non-reactive pollutants) from an upstream location in an estuary. Factors that control flushing include tidal action, freshwater inflow, and wind stress. All of these forcing functions are time variable. Flushing time calculations are usually based on average tidal range and average or low freshwater inflow, with wind effects neglected. Because estuarine flushing is inherently dispersive in nature, there is no unambiguous point at which the original water and pollutants are completely replaced. Flushing times can be defined for 90%, 95% or even 99% removal. Typical flushing times range from days in small estuaries or those dominated by tributary flow to months in large estuaries during low tributary flow conditions.

Several formulas have been used to estimate flushing times. The Fraction of Fresh Water Method, the Tidal Prism Method, and the Modified Tidal Prism Method are described in Mills, et al., (1985). These are screening calculations only and should not be considered accurate. Better estimates can be obtained directly from dye studies or simple box models calibrated to salinity or dye data.

Flushing times give the minimum duration for simulations of dissolved, non-reactive pollutants. Reaction kinetics affect the required duration for those pollutants and water quality constituents controlled by various physical, chemical, and biological transformations and removal processes. Pollutants controlled by rapid loss rates, such as fecal bacteria or some volatile organic chemicals, can generally be characterized by simulations that are shorter than the flushing time. For water quality constituents affected by transformation rates, the time required to complete the entire reaction chain or cycle must be considered. Some chemicals that interact extensively with benthic sediments may require simulations greatly exceeding flushing times because their removal is controlled by desorption and benthic diffusion kinetics. Examples include nutrients and hydrophobic organic chemicals. Sediment diagenesis models should be helpful in analyzing chemical dynamics and fate in such situations.

The dynamics of major loading and kinetic forcing functions may dictate longer simulations than flushing times and kinetic reactions suggest. Nonpoint sources may provide significant "background" loads that must be considered in a WLA study. These are highly intermittent, but seasonal in nature and may extend sediment, dissolved oxygen, and nutrient enrichment simulations from weeks to seasons. The annual sunlight and temperature cycles almost require that

eutrophication simulations range from seasons to years.

The final factor affecting the duration of simulations is the strategy for relating simulation results to the regulatory requirements. Sometimes a set of "design conditions" can be defined, allowing for shorter simulations. Care must be taken to ensure that a particular combination of design conditions, such as flow, temperature, and nonpoint source loads, does not reflect an unreasonably low probability of occurrence and thus an overly restrictive WLA.

Another strategy is to extend a simulation for many years, defining the variability of the major forcing functions as realistically as possible. Often, historical records of tide, flow, temperature, and rainfall are used to ensure the proper interaction among processes. Predicted concentrations are expressed as a frequency or probability of exceedance of water quality goals or standards. Critical combinations of factors leading to violations may be isolated and examined in more detail.

3.2.4.2. Temporal Resolution

The temporal resolution of WLA simulations falls into one of three categories - dynamic, quasidynamic, and steady state. Dynamic simulations predict hour to hour variations caused by tidal transport. Diurnal forcing may also be included, although not necessarily if output is to be time-averaged. Quasidynamic simulations predict variations on the order of days to months. The effects of tidal transport are time-averaged, and net or residual flows are used to drive advection. Other forcing functions such as freshwater inflow, pollutant loading, temperature, and sunlight may vary from daily to monthly. Steady state simulations predict monthly to seasonal averages. All inputs are time-averaged.

Two schools of thought have persisted regarding the utility of dynamic versus quasidynamic and steady state simulations. For some problems the choice is reasonably clear. Dynamic models are necessary for analysis of control options for complex situations in estuaries. Predicting the upstream migration of pollutants from an outfall to a beach or water supply intake requires a dynamic simulation. Predicting water quality effects from batch discharges into ebbing tide requires a dynamic simulation.

On the other hand, quasidynamic and steady state models are currently more practical for long term analysis of water quality response. Predicting the year to year eutrophication response or the accumulation of hydrophobic organic chemicals in the benthic sediments of large estuaries is best accomplished by quasidynamic simulations. In general, if the regulatory

need or kinetic response is on the order of hours, then dynamic simulations are required; if regulatory needs are long term averages and the kinetic response is on the order of seasons to years, then quasidynamic or steady simulations are indicated.

Between these two extremes lie many WLA problems that might be addressed by either dynamic or quasidynamic simulation. Some experts assert that even for long term analyses where only average predictions are needed, dynamic simulations are practical and more desirable. Dynamic simulations can be expected to more accurately account for interactions among the important tidal and diurnal forcing functions controlling average water quality conditions. Calculated maxima and minima at a location can account for the major tidal and diurnal processes; calculated concentrations, then, can be compared directly to water quality criteria expressed in terms of daily or hourly maxima and minima, or in terms of frequency or return intervals. Quasidynamic and steady state simulations require statistical calculations outside the model to relate predicted average concentrations with maxima or minima criteria. Further, quasidynamic and steady simulations require careful calibration to long term average salinity data rather than shorter slack water data. It is argued that data needs for calibrating dynamic models are actually less because extensive averaging over cross sections and time is not necessary.

Others prefer quasidynamic simulations when the choice is ambiguous. Some experts assert that for standard WLA analyses, dynamic models are often not necessary and are too formidable for two and three dimensional situations. Dynamic simulation requires fully calibrated hydrodynamic models to drive the water quality computations. It is argued that an extensive data base is necessary to calibrate the dynamic calculations. Quasidynamic simulations cost less because of their longer time steps and less use of hydrodynamic simulation. The lower costs allow for longer simulations than dynamic models, and thus greater ability to explore seasonal and yearly trends. The lower costs also allow for more water quality variables and processes to be simulated.

The computational time step used by the WLA model will depend upon the temporal resolution chosen as well as the spatial network, the transport characteristics of the estuary, and the numerical solution technique of the model. Most computer waste load allocation models use explicit schemes—that is, variables at the new time step are calculated using known values at previous time steps. This leads to several common conditions that must be satisfied to ensure model stability (i.e., solutions remain within bounds

and do not "blow up"). Furthermore, satisfying these conditions will often result in smaller time steps that would generally be needed from solution resolution conditions alone.

The conditions, or criteria, for one-dimensional models using explicit solution schemes are usually:

- a hydrodynamic criterion (Courant condition)

$$\Delta t \leq \Delta x / \sqrt{g h} \pm u \quad (3-14)$$

- mass transport, dispersion, and kinetic conditions

$$\Delta t \leq \frac{\Delta x (2\alpha - 1)}{u} + \frac{\Delta x^2}{2E_L} + \frac{1}{K} \quad (3-15)$$

where

u = maximum tidal velocity, m/sec

g = gravitational acceleration, 9.81 m/sec²

h = hydraulic radius, or depth, m

E_L = longitudinal dispersion coefficient, m²/sec

K = first order decay rate, 1/sec

α = finite difference weight, (1 for backward differences, 1/2 for central differences)

Similar conditions exist for 2 and 3-dimensional models, and other conditions, such as a friction term criterion, may also be required. Chemical and biological components of the WLA model may cause restrictions in the time step if reaction kinetics are rapid. In that case, the reaction is often written as an equilibrium relationship, which does not affect the time step. The most stringent condition is usually the Courant condition (unless vertical diffusion and/or momentum transfer is explicitly treated, in which case a criterion like Equation 3-15 is required with Δz replacing Δx). Many models solve for the mass transport equations in a separate model, or at a different time step than the hydrodynamic solution. In these cases, all the above criteria should be checked.

Dynamic models are governed by equations 3-14 and 3-15 where u is the maximum tidal velocity. Time steps are on the order of seconds to minutes for the hydrodynamic component or model, and minutes to an hour for the mass transport (and water quality) model. Quasidynamic models are governed by equation 3-15 where u and E_L are tidal-averaged values (u being smaller and E_L being larger than nonaveraged values). Time steps are on the order of one to several hours.

Some models, particularly current hydrodynamic programs, use an implicit technique to approximate the

governing equations. In these cases, the model may be unconditionally stable, which means that the choice of the time step is not limited by stability considerations. Here, the time step should be chosen to provide adequate resolution of temporal processes. Care should still be taken because even implicit schemes may have certain limiting time or space conditions.

3.3. Model Selection

The goal of model selection is to obtain a simulation model that effectively implements the conceptual model identified for the WLA. The available set of general purpose models may not always fully implement a specific conceptual model. In this case, calculations or assumptions may be made outside the model's computational framework, or model code may be refined. Models that are known to the user and that are easily modified provide valuable flexibility to the WLA study. In the final analysis, how a model is used is more important to the success of a WLA than exactly which model is used. Nevertheless, while selection of an appropriate model will not guarantee success, it will help. Selection of an inappropriate model will not guarantee failure, but will render a successful outcome more difficult.

Models may be classified in different and somewhat arbitrary ways. Some models may not quite fit in any category, or may fit well in several. In addition, models tend to evolve with use. The exact capabilities of the individual models described here may change. In particular, kinetic reactions may be modified and new variables inserted. Dispersion functions may be updated. Usually the computational framework and the basic transport scheme remain stable over time. For this reason, transport characteristics will provide the basis for the model classification scheme used here. Models selected for discussion here are general purpose, in the public domain, and available from or supported by public agencies.

The selection of an estuarine WLA model need not be limited to the models discussed in this document. Other models that are available to a project or organization should also be considered. The models summarized in this report represent the typical range of capabilities currently available. Other available computer programs can generally be grouped into one of the following categories:

- Variants of the models discussed here;
- Proprietary models held by consulting firms;
- Models developed for research purposes.

It is recommended that where project staffs do not have access to or familiarity with a wide range of computer programs, effort should be focused on those discussed in this document.

One important word of caution: it is highly likely that all computerized models discussed here contain a few undiscovered software and documentation errors. The user must be careful to verify that the models are implemented properly and are providing reasonable calculations. With support from EPA's Office of Water, the EPA Center for Exposure Assessment Modeling (CEAM), Athens, Georgia, maintains some of these models, providing their users with an information and error clearinghouse. These models may be obtained over the CEAM electronic bulletin board system, or by mailing in the appropriate number of diskettes.

3.3.1. Classification of Models by Transport Complexity

Estuarine WLA models consist of two components--hydrodynamic and water quality. In the simplest case, hydrodynamics may be represented in a model by user-supplied velocity and flow data. In a more complex model, hydrodynamics may be represented by numerical solution of the equations of motion and continuity. In either case, water quality conservation-of-mass equations are executed using the hydrodynamic output of water volumes and flows. The water quality component of the model calculates pollutant dispersion and transformation or decay, giving resultant concentrations over time. All the estuarine WLA models discussed in this report include as a minimum the first order decay of BOD and the prediction of DO concentrations. The more comprehensive models include nutrient-algal relationships and benthic source/sink terms. A few estuarine models that include reaction rate coefficients and transformation processes for toxic materials also are available.

Although the hydrodynamic submodel is independent of the water quality submodel, water quality depends on the advection, dilution, and dispersion controlled by hydrodynamics. As a result, estuarine WLA models can be classified as Level I to Level IV according to the temporal and spatial complexity of the hydrodynamic component of the model. The model classification scheme followed in this report was recommended by Ambrose et al. (1981).

Level I includes desktop screening methodologies that calculate seasonal or annual mean pollutant concentrations based on steady state conditions and simplified flushing time estimates. These models are designed to examine an estuary rapidly to isolate trouble spots for more detailed analyses. They should

be used to highlight major water quality issues and important data gaps in the early, model identification stage of a study.

Level II includes computerized steady state or tidally averaged quasidynamic simulation models, which generally use a box or compartment-type network to solve finite difference approximations to the basic partial differential equations. Steady state models use an unvarying flow condition that neglects the temporal variability of tidal heights and currents. Tidally averaged models simulate the net flow over a tidal cycle. These models cannot predict the variability and range of DO and pollutants throughout each tidal cycle, but they are capable of simulating variations in tidally averaged concentrations over time. Level II models can predict slowly changing seasonal water quality with an effective time resolution of 2 weeks to 1 month.

Level III includes computerized one-dimensional (1-d) and quasi two-dimensional (2-d), dynamic simulation models. These real time models simulate variations in tidal heights and velocities throughout each tidal cycle. One-dimensional models treat the estuary as well-mixed vertically and laterally. Quasi 2-d models employ a link-node approach that describes water quality in two dimensions (longitudinal and lateral) through a network of 1-d nodes and channels. The 1-d equation of motion is applied to the channels while the continuity equation is applied at nodes between channels. Tidal movement is simulated with a separate hydrodynamic package in these models. Although the Level III models will calculate hour-to-hour changes in water quality variables, their effective time resolution is usually limited to average variability over one week because tidal input parameters generally consist of only average or slowly varying values. In this case, model results should be averaged to obtain mean diurnal variability over a minimum of 1 week intervals within the simulated time period (Ambrose and Roesch 1982). The effective time resolution could be reduced to under 1 day given good representation of diurnal water quality kinetics and precise tidal input parameters. The required data and modeling effort are usually not mobilized in standard WLAs.

Level IV consists of computerized 2-d and 3-d dynamic simulation models. Dispersive mixing and seaward boundary exchanges are treated more realistically than in the Level III 1-d models. These models are almost never used for routine WLAs. While 2-d models are beginning to find regular use for some engineering applications, at the present time practical 3-d models and modeling techniques are still developing. The only 3-d models currently reported in the literature are hydrodynamic models that include simple first order decay rates for uncoupled nonconservative pollutants

(Swanson and Spaulding 1983) and box type models configured in three dimensions (HydroQual 1987). The effective time resolution of the Level IV models can be less than 1 day with a good representation of diurnal water quality and intratidal variations. The required data and modeling effort are usually not mobilized in standard WLAs.

The advantages of Level I and II models lie in their comparatively low cost and ease of application. The disadvantages lie in their steady state or tidally averaged temporal scale. When hydrodynamics and pollutant inputs are rapidly varying, steady state models are difficult to properly calibrate. Consequently, these models are less satisfactory in short estuaries or when waste load, river inflow, or tidal range vary appreciably with a period close to the flushing time of the water body. Steady state and tidally averaged models require calibration of a dispersion coefficient using field data. The calibrated value is applicable to the condition monitored and cannot be extrapolated to proposed modifications in estuary shape, tidal volume, or river discharge.

As Hinwood and Wallis (1975) explain, dispersion is caused by the combined action of turbulence and a nonuniform velocity profile. Nonuniform velocities elongate a wastewater slug, whereas turbulence, acting normal to the mean velocity, mixes the waste. Velocities at any section of the estuary vary due to shear at the bed and sides of the channel. In addition, irregularities in channel shape, salinity and temperature induced density currents, and wind-induced currents, cause nonuniform velocities. In a wide estuary, the Coriolis force and streams entering on one side of the channel also may produce nonuniform velocities.

Dispersion coefficients in the Level I through IV models represent different transport phenomena. The flux of matter through an estuary can be represented with the following simplified notation:

- Flux = Net advection from freshwater flow (1)
- + Tidal dispersion (2)
- + Net transverse gravitational circulation (3)
- + Net vertical gravitational circulation (4)
- + Transverse oscillatory shear (5)
- + Vertical oscillatory shear (6)
- + Turbulent or eddy diffusion (7)

One-dimensional, tidally averaged or steady state models calculate term 1 directly but represent terms 2

through 7 with a tidal average or steady state longitudinal dispersion coefficient. In contrast, the Level III 1-d, real time models calculate terms 1 and 2 directly and use the cross-sectional averaged longitudinal diffusion coefficient to represent terms 3 through 7. The Level IV 2-d, depth-averaged models represent even more terms directly. These models calculate terms 1,2,3 and 5 directly, using the depth-averaged longitudinal and lateral diffusion coefficients only to represent terms 4, 6 and 7.

As a model is simplified from Level IV to Level II, the dispersion coefficients become larger and more unique to each flow situation. The steady state or tidally averaged Level II models require the dispersion coefficient to include the effects of tidal mixing. As a result, the coefficient must be calibrated using salinity measurements, and it cannot be used to predict the water quality effects of projected changes in estuarine topography or river inflows. Due to shorter time scales, the Level III and IV dispersion coefficients do not have to include the effects of tidal mixing and can be more closely based on the physical properties of the channel (hydraulic radius and roughness coefficient). Changes in these properties can then be made in the model to predict the effect of proposed changes in channel geometry or freshwater inflows.

The dynamic models (Levels III and IV) have advantages over steady state and tidally averaged models in representing mixing in partially mixed estuaries because advection is so much better represented. Although shear effects and the effects of spatial averaging must still be accounted for, the effects of time averaging can be avoided.

The short time step of dynamic models allows them to be more sensitive predictors of the duration of violations of water quality standards. Dynamic models can provide a more accurate response to nonpoint source loads and pollutant spills, short term events that can produce water quality standard violations with a duration less than one tidal cycle in length. The success with which these models can predict transient violations depends upon both the accuracy and resolution of the loading and environmental data, and the model's treatment of short time scale kinetics such as desorption or diurnal fluctuations in temperature, pH, or sunlight. While dynamic models are capable of predicting diurnal and transient fluctuations in water quality parameters, the input data requirements are much greater. Lack of detailed data or process descriptions often render their real predictive resolution significantly longer than their computational time step.

The Level III, 1-d models can produce good estimates of tide heights, mean velocities, and pollutant con-

centrations for estuaries with fairly regular channels that are much longer than they are wide. Near points of waste injection, however, model predictions can be significantly in error due to lateral variations in concentrations. The quasi 2-d approach can solve this problem, but the difficulty in estimating effective dispersion coefficients still remains. The Level IV longitudinal and lateral 2-d models have the advantage of representing the lateral variations in velocity and waste concentrations that arise in all estuaries and bays because of the nonuniformity of cross-sections, embayments, branching channels, and bends (Hinwood and Wallis 1975). In addition, these models can include the effects of Coriolis and wind circulations. The remaining flaw is that the lateral-longitudinal models assume an estuary is vertically well-mixed. This assumption can lead to significant errors in predictions for stratified estuaries.

3.3.2. Level I Models

The purpose of modeling at Level I is to screen trouble spots for more detailed analysis. Level I desktop methodologies may be done with a hand held calculator and are based on steady state conditions, first order decay coefficients, simplified estimates of flushing time, and seasonal pollutant concentrations.

Level I screening of a given waterbody may entail selected analyses to answer individual questions (e.g., is the estuary stratified in a particular location; what is the flushing time of the estuary; what is the annual phosphorus loading), or it may entail a comprehensive examination of the estuary. A comprehensive analysis may be accomplished with models such as the Simplified Estuary Model (SEM) or the Water Quality Assessment Methodology (WQAM). SEM and WQAM both require only hand calculations and are used chiefly for preliminary assessments of estuarine water quality. Documentation on WQAM is available from CEAM.

3.3.2.1. Water Quality Assessment Methodology

WQAM is a steady state desktop model that includes both one-dimensional and two-dimensional box model calculations (Mills et al. 1985). Use of WQAM procedures requires classification of an estuary into one of three possible types: stratified, well-mixed, or partially mixed. Two methods are presented to determine the appropriate classification. The Hansen and Rattray method utilizes vertical salinity gradients, freshwater inflow velocities, and surface tidal current velocities averaged over a tidal cycle to characterize the system. The flow ratio calculation method classifies the estuary using a comparison of freshwater flow volume and tidal flood volumes (tidal prism) over a tidal cycle. Values

calculated from these input data are compared to ranges set for each estuarine classification.

WQAM includes calculations to estimate the transport of BOD, DO, pH, arbitrary conservative substances, thermal pollution, turbidity, sediment, and organic chemicals in an estuary. Pollutant distribution can be estimated using either a far field or a near field method of analysis. The near field technique predicts initial dilution of submerged discharges through the use of tabulated data from MERGE, a computerized plume model. For well-mixed estuaries, far field pollutant distributions can be predicted using the fraction of freshwater method, modified tidal prism method, or one-dimensional advection-dispersion equations. For partially mixed and stratified estuaries, WQAM far field analysis uses Pritchard's two-dimensional box model approach, which represents the estuary as a series of longitudinal segments with a surface and a bottom

layer. The analysis is performed by solving a system of simultaneous linear equations for pollutant concentrations in each layer. WQAM consists of a number of individual analyses, listed in Table 3-4 (Mills et al. 1985). The document is available from the Center for Exposure Assessment Modeling in Athens, Georgia.

3.3.2.2. Simplified Estuarine Model

SEM is a one-dimensional steady state desktop model capable of simulating water quality in tidal rivers and non-stratified estuaries (Hydroscience 1971). Coupled BOD-DO reactions, arbitrary conservative substances, and uncoupled nonconservatives with first order decay (nutrients and coliforms) are represented in SEM. The model is based on user-specified hydraulics that consider only longitudinal variations and handle only point source inputs. Advection is represented in the form of freshwater flow velocity and dispersion in the form of a

Table 3-4. Summary of Methodology for Estuarine Water Quality Assessment

Calculations	Methods	Type of Estuary
Estuarine Classification	* Hansen & Ratray	1 D/ 2 D
	* Flow ratio	1 D/ 2 D
Flushing Time	* Fraction of freshwater	1 D/ 2 D
	* Modified tidal prism	1 D
Pollutant Distribution	* Fraction of freshwater (conservative pollutants +)	1 D
	* Modified tidal prism (conservative or first-order decay pollutants)	1 D
	* Dispersion-advection equations (conservative, first-order decay pollutants + and dissolved oxygen)	1 D
	* Pritchard's Box Model (conservative pollutants +)	2 D
	* Initial dilution	1 D/ 2 D
	* Pollutant concentration at completion of initial dilution (conservative pollutants +, pH, dissolved oxygen)	1 D/ 2 D
	* Farfield distribution (conservative and first-order pollutants +, and dissolved oxygen)	2 D
Thermal Pollution	* ΔT of water passing through condenser	N/A
	* Maximum discharge temperature	N/A
	* Thermal block criterion	1 D/ 2 D
	* Surface area criterion	1 D/ 2 D
	* Surface temperature criterion	1 D/ 2 D
Turbidity	* Turbidity at completion of initial dilution	1 D/ 2 D
	* Suspended solids at the completion of initial dilution	1 D/ 2 D
	* Light attenuation and turbidity relationship	1 D/ 2 D
	* Secchi disk and turbidity relationship	1 D/ 2 D
Sedimentation	* Description of sediment movement	1 D/ 2 D
	* Settling velocity determination	1 D/ 2 D
	* Null zone calculations	2 D
* One dimensional (1D) means a vertically well-mixed system.		
A two dimensional (2D) estuary is vertically stratified.		
+ These methods apply to either conventional or toxic pollutants		

dispersion coefficient that accounts for the mixing and translation of the tides.

SEM uses a synthetic parameter called the estuary number (O'Connor, 1960) to determine the relative magnitude of advection and dispersion at a given location and to characterize the reach as either tidal river or estuarine segment. The estuarine number (N) is calculated from the values of the dispersion coefficient (E), the freshwater flow velocity (V) and the deoxygenation coefficient (K_d). If the estuarine number ($N = K_d E / V^2$) is less than 10, the reach is considered a tidal river and initial dilution is calculated using freshwater inflow and the effects of tidal dispersion. Above the breakpoint of 10, the reach is considered to behave in a purely estuarine fashion, and the initial dilution neglects freshwater inflow.

3.3.3. Level II Models

Level II includes computerized steady state and tidally averaged simulation models that generally use a box or compartment-type network. Steady state models are difficult to calibrate in situations where hydrodynamics and pollutant releases are rapidly varying. Consequently, these models are less appropriate when waste load, river inflow, or tidal range vary appreciably with a period close to the flushing time of the waterbody.

Both tidally averaged and steady state models use a dispersion coefficient calibrated from survey data. The network and time step used by these models add "numerical dispersion" to the calculations, which tends to spread out concentration profiles in a similar manner as dispersive mixing processes. Consequently, calibrated dispersion coefficients apply to the specific network and situation monitored; they cannot be extrapolated to major modifications in estuary shape, tidal volume, or river discharge.

A recent modeling strategy is to drive a Level II compartment model that has been configured in two or three dimensions with tidal-averaged or steady flows and volumes from a 2-d or 3-d hydrodynamic model. This strategy is briefly discussed under Level IV models. A variation of this strategy is to use compartment models with net advective flows calculated from measured vertical and longitudinal salinity distributions. An iterative calculation has been published by Lung and O'Connor (1984) and Lung (1986) for two-dimensional estuaries characterized by a horizontal seaward velocity in the upper layer and a net landward velocity in the lower layer. This analysis gives analytical solutions to the horizontal and vertical tidally-averaged velocities, as well as values of vertical eddy viscosity. This analysis has been applied to the Sacramento-San

Joaquin Delta, the James River Estuary, the Patuxent River Estuary, and the Hudson River Estuary.

The Level II models supported by CEAM are QUAL2E and the Water Quality Analysis Simulation Program (WASP4), with its associated toxic chemical and eutrophication programs TOXI4 and EUTRO4. Other models described here include HAR03, FEDBAK03, and AUTOQUAL.

3.3.3.1. QUAL2E

QUAL2E is a steady state one-dimensional model designed for simulating conventional pollutants in streams and well-mixed lakes. It has been applied to tidal rivers with minor adaptations to the hydraulic geometry and dispersion functions. Water quality variables simulated include conservative substances, temperature, bacteria, BOD, DO, ammonia, nitrite, nitrate, and organic nitrogen, phosphate and organic phosphorus, and algae. QUAL2E is widely used for stream waste load allocations and discharge permit determinations in the United States and other countries. It has a 15-year history of application and is a proven, effective analysis tool. QUAL2E Version 3 incorporates several uncertainty analysis techniques useful in risk assessment. This model can be obtained from the Center for Exposure Assessment Modeling, Athens, Georgia (requires 4 diskettes).

3.3.3.2. WASP4

WASP4 is a general, multi-dimensional model that utilizes compartment modeling techniques (DiToro et al. 1981; Ambrose et al. 1987). Operated in either the quasidynamic or steady state mode, the user must supply initial segment volumes, network flow fields, and inflow time functions. The user also must calibrate dispersion coefficients between compartments. Depending on the process model with which it is linked, WASP4 has the capability of simulating a range of conventional and toxic pollutants. Problems that have been studied using WASP4 include BOD, DO dynamics, nutrients and eutrophication, bacterial contamination, and toxic chemical movement (DiToro, 1981). WASP4, along with the associated programs TOXI4, EUTRO4, and DYNHYD4, can be obtained from the Center for Exposure Assessment Modeling, Athens, Georgia (requires 3 diskettes).

A. TOXI4

TOXI4 is a version of WASP4 that is designed to simulate organic chemicals and heavy metals (Ambrose et al. 1987). TOXI4 was created by adapting the kinetic structure of EXAMS-II to the transport framework of WASP4 and adding sediment balance algorithms. It can simulate up to three chemicals and three sediment

classes. In addition to segment volumes, flows, and dispersive exchanges, the user must supply sediment deposition and scour rates, bed sediment velocity, water column/sediment exchange coefficients, and sediment/pore water exchange coefficients.

In TOXI4 the total transformation rate of an organic chemical is based on the simple addition of the rate constants for individual photolysis, hydrolysis, biolysis, and oxidation reactions. These rate constants may either be specified by the user or calculated internally from second order rate constants and such environmental conditions as light intensity, pH, bacteria, oxidants, depth, velocity, and wind speed. Internal transport and export of organic chemicals occur via advective and dispersive movement of dissolved, sediment-sorbed, and biosorbed materials, and by volatilization losses at the air-water interface. Internal transport and export of heavy metals occur via advective and dispersive movement of dissolved, sediment-sorbed, and biosorbed materials. Sorption of both organic chemicals and heavy metals on sediments and biomass is calculated assuming local equilibrium using a constant partition coefficient and spatially varying environmental organic carbon fractions. TOXI4 has the capability of simulating up to two daughter products of organic chemical transformations. Exchange between the water column and the bed can occur by settling or resuspension of particulates, diffusion of dissolved pollutants between the water column and pore water, direct adsorption/desorption between the water column and bed, and percolation or infiltration. Within the bed, a pollutant can move vertically by diffusion, turnover, percolation and burial, and horizontally with bed load transport.

B. EUTRO4

EUTRO4 is a version of WASP4 that is designed to simulate conventional pollutants. EUTRO4 combines a kinetic structure adapted from the Potomac Eutrophication Model with the WASP transport structure. EUTRO4 predicts DO, carbonaceous BOD, phytoplankton carbon and chlorophyll a, ammonia, nitrate, organic nitrogen, organic phosphorus, and orthophosphate in the water column and, if specified, the underlying bed. In addition to segment volumes, flows, and dispersive exchanges, the user must supply deposition and resuspension velocities for organic solids, inorganic solids, and phytoplankton. The fraction of each water quality variable associated with these solids also must be given. Rate constants and half-saturation coefficients for the various biochemical transformation reactions must be specified by the user. Finally, the time and/or space variable environmental forcing functions, such as light intensity, light extinc-

tion, wind speed, cloud cover, temperature, and benthic fluxes must be input.

3.3.3.3. HAR03

HAR03 is a steady state, multi-dimensional model that utilizes compartment modeling techniques (Chapra and Nossa 1974). An orthogonal system of segmentation is used with each segment having up to six interfaces. The model includes the effect of net advection and dispersive tidal exchange. HAR03 models the BOD-DO deficit system as a coupled reaction with first order decay of BOD. With minor modifications, the program may also be used to model variables analogous to the BOD-DO system such as ammonia-nitrate. Zero order net photosynthetic and benthic oxygen demands can be user-supplied to the model and used in the DO balance.

3.3.3.4. FEDBAK03

FEDBAK03 is a steady state, multi-dimensional model that utilizes compartment modeling techniques (Nossa 1978). Each estuarine segment may have up to six interfaces. The model simulates net advection and dispersive tidal exchange. FEDBAK03 is written in general form so that it is applicable for any substances that undergo consecutive first order reactions with feedback. The model is thus capable of simulating nitrification and associated DO deficits as well as BOD-DO reactions. The program can be modified to allow for the input of net photosynthetic and benthic oxygen demands.

3.3.3.5. AUTOQUAL

AUTOQUAL and a later update AUTOQD are steady state and quasidynamic models for simulating conventional pollutants in streams and estuaries (Crim and Lovelace 1973, Lovelace 1975). Transport is calculated from user-specified flow and dispersion. Water quality variables simulated include carbonaceous BOD, nitrogenous oxygen demand, DO, total phosphorus, and total nitrogen.

3.3.4. Level III Models

Level III includes computerized 1-d and quasi 2-d models that simulate variations in tidal height and velocity throughout each tidal cycle. Level III models are generally composed of separate but compatible hydrodynamic and water quality models. These two models are run sequentially, and the output of the hydrodynamic model becomes part of the input to the water quality model. Level III models enable the characterization of phenomena rapidly varying within each tidal cycle, such as pollutant spills, stormwater runoff, and batch discharges. Level III models also are

deemed appropriate for systems where the tidal boundary impact, as a function of the hydrodynamics and water quality, is important to the modeled system within a tidal period.

The application of tidally varying (intratidal) models has found most use in the analysis of short-term events, in which the model simulates a period of time from one tidal cycle to a month. Some seasonal simulations have also been run. In most cases, the hydrodynamic model must be run for several tidal cycles before an actual event can be simulated. This will dampen out any errors in the initial conditions and achieve stability in the hydrodynamic simulation. Following this initial period, the model will simulate a cyclical steady-state in which the tidal characteristics are repeated for subsequent tidal periods. This approach can be applied when a particular design tide is used to simulate water quality. In this case, the hydrodynamic model is run and the cyclical steady state output saved as input to the water quality model. By running the two models in this fashion, multiple cases can be examined with the water quality model without the need to rerun the hydrodynamic model.

For simulating storm events where both loads and flows are rapidly varying, the hydrodynamic model is run for the entire simulation period. The first step is to run the hydrodynamic model to steady-state for the nonstorm period to obtain initial conditions for the storm simulation. The storm flows are specified as input to the hydrodynamic model, which must be run for a sufficient number of tidal cycles after the storm event to simulate the water quality response throughout the estuary. The water quality model, using the pollutant loads from an input file and the flows from the hydrodynamic model, simulates the same period (number of tidal cycles) as the hydrodynamic model. Although the storm may only last a few hours, the actual simulation time may be considerably longer (days or weeks) in order to characterize the full response of the system to the event.

In using Level III models, one must decide whether a simple 1-d link-node longitudinal system is sufficient, or whether a quasi 2-d model with branching networks or triangular/rectangular configuration is required to model the longitudinal and lateral variations in the estuary. For estuaries with channels longer than their width and which are reasonably well mixed across their width, a 1-d model may be chosen. If large differences exist in water quality from one side of an estuary to the other, then a quasi 2-d model would be appropriate.

The length of model segments or links will depend on the resolution required in the study, as discussed in Section 2.3.3. The length and position of segments

depends on the physical properties of the estuary. Homogeneity of physical characteristics should be the basis for defining segments. Where bends, constrictions, or other changes occur, smaller segments are generally defined to improve resolution.

In their treatment of conventional pollutants, Level I models deal mainly with biochemical processes. A Level III model considered here can simulate simple BOD-DO interactions. Most of these models also are formulated to simulate the reactions and interactions of organic phosphorus and orthophosphorus; organic nitrogen, ammonia, nitrite and nitrate; algal growth and respiration; and DO. These models also include settling rates and benthic flux rates for several different constituents such as phosphorus, nitrogen and sediment oxygen demand. Only one model is designed to simulate the physiochemical processes affecting organic chemicals and metals.

The Level III model supported by CEAM is the Water Quality Analysis Simulation Program (WASP4), with its associated hydrodynamic program DYNHYD4 and its toxic chemical and eutrophication programs TOX14 and EUTRO4. Other models described here include the Dynamic Estuary Model, EXPLORE-1, and the MIT Dynamic Network Model.

3.3.4.1. WASP4

The Water Quality Analysis Simulation program, WASP4, is a general multi-dimensional model that uses compartment modeling techniques (DiToro et al. 1981, Ambrose et al. 1987). Version 4 may be operated in the tidal dynamic mode through linkage with the associated hydrodynamic model DYNHYD4. DYNHYD4 is a link-node model that may be driven by either constantly repetitive or variable tides. Unsteady inflows may be specified, as well as wind that varies in speed and direction. DYNHYD4 produces an output file of flows and volumes that can be read by WASP4 during the water quality simulation.

Two water quality programs accompany WASP4. TOX14 simulates organic chemicals, metals, and sediment in the water column and underlying bed. EUTRO4 simulates DO, carbonaceous BOD, phytoplankton carbon, chlorophyll a, ammonia, nitrate, organic nitrogen, organic phosphorus, and orthophosphate in the water column and, if specified, the underlying bed. These programs are described more fully in Section 3.3.3.3. WASP4, along with the associated programs TOX14, EUTRO4, and DYNHYD4 can be obtained from the Center for Exposure Assessment Modeling, Athens, Georgia (requires 3 diskettes).

3.3.4.2. Dynamic Estuary Model, DEM

EM is a quasi 2-d model that represents tidal flow in the lateral and longitudinal directions with a branching link-node network (Feigner and Harris 1970). Two versions of the hydrodynamic component of DEM exist. One version is limited to steady inflows and constantly repetitive tide. The steady inflow version cannot explicitly handle short-term stochastic transients such as wind stress or large storm flushing and has difficulty in predicting long-term patterns such as the 2-week spring-neap-tide cycle or the seasonal freshwater inflow pattern. Consequently, this version is most reliable when predicting high and low values for diurnal or tidal cycles, or both, averaged over a relatively steady 2-week period (Ambrose and Roesch, 1982). Real time simulations of water quality are possible with the steady inflow version of DEM, but with some inaccuracies. Newer hydrodynamic versions of the model can handle variable inflows and can thus generate a more accurate real time prediction of water quality.

Several water quality submodels also have been used with DEM. All versions include nutrient modeling and algal growth, photosynthesis, and respiration. The following is a brief description of the versions of DEM currently available:

- DEM, Chen-Orlob version, is the most comprehensive version of the model currently available (Chen and Orlob 1972). The model has the capability of representing 22 coupled biotic and abiotic constituents including: temperature, pesticides, heavy metals, CBOD, DO, phosphate, ammonia, nitrite, nitrate, total dissolved solids, alkalinity, pH, carbon dioxide, phytoplankton, zooplankton, fish, benthic animals, suspended detritus, and sediment detritus.
- DEM, Pearl Harbor version, is limited to steady inflows and constantly repetitive tide (Genet et al. 1974). It incorporates the heat budget terms of the Tidal Temperature Model and simulates temperature, DO, CBOD, ammonia, nitrite, nitrate, total nitrogen, phosphate, chlorophyll-a, and total dissolved solids.
- DEM, Potomac version, is documented as handling only steady inflows and constantly repetitive tide, but a newer version is available that is capable of handling variable inflows (Roesch et al. 1979). The model simulates CBOD, DO, ammonia, nitrate, phosphate, and chlorophyll-a.

3.3.4.3. MIT Dynamic Network Model, MIT-DNM

MIT-DNM is a one-dimensional model that uses a finite element, branching network to simulate the flow regime of an estuary with unsteady tidal elevation and

upstream flow (Harleman et al. 1977). The model was originally developed for aerobic, nitrogen limited systems and includes detailed simulation of the nitrogen cycle as well as temperature, CBOD, DO, and fecal coliforms. Two versions of the model are currently available, and are described below.

- MIT-DNM, Potomac version, includes nutrient modeling and algal growth, photosynthesis, and respiration and represents bacterially mediated reactions for ammonia, nitrite, nitrate, phytoplankton-N, zooplankton-N, particulate organic N, and dissolved organic N (Najarian and Harleman 1975).
- MIT-DNM, St. Lawrence version, includes nutrient modeling and algal growth, photosynthesis, and respiration, and represents CBOD, DO, inorganic phosphorus, organic phosphorus, inorganic nitrogen, organic nitrogen, phytoplankton, and zooplankton (Thatcher et al. 1975).

3.3.4.4. EXPLORE-I

EXPLORE-I is a quasi 2-d model that represents tidal flow in the lateral and longitudinal directions with a branching link-node network (Chen and Orlob 1972). The full 1-d hydrodynamic equations are solved, but the water quality model excludes dispersive transport. EXPLORE-I has the capability of simulating DO, conservatives, toxic pollutants, coliforms, sedimentary phosphorus, soluble phosphorus, organic phosphorus, organic nitrogen, ammonia, nitrite, nitrate, total organic carbon, refractory organic carbon, phytoplankton, zooplankton, CBOD, and benthic BOD. Sedimentation and scour of organic matter is represented in the model as well as algal growth, photosynthesis, and respiration.

3.3.5. Level IV Models

Level IV includes a variety of computerized 2-d and 3-d intratidal models. These may be divided into three broad categories: 2-d vertically averaged (x-y), 2-d laterally averaged (x-z), and 3-d. While they are not routinely used in most WLAs, they are now finding use by experts in special studies.

Although many 2-d vertically averaged, finite-difference or finite-element hydrodynamic programs exist, relatively few contain a water quality program that simulates constituents other than salinity and/or temperature. Likewise, a number of 2-d, laterally averaged models (longitudinal and vertical transport simulations) treat mass transport of salt and temperature but very few include nonconservative constituents or water quality routines. Models in this category simu-

late vertical stratification but neglect lateral effects, including Coriolis effects. Last is the category of 3-d, finite-difference and finite-element models. These models allow all physical processes to be included, although many were developed for systems of constant salinity (lakes or oceans). A summary of 3-d marine and estuarine models is provided in Nihoul and Jamarf (1987).

A Level IV model would be used when finer spatial definition is required than is provided by a Level III model and when finer temporal definition is required than is provided by a Level II model that has been configured in two or three dimensions and driven by the averaged hydrodynamic output of a Level IV hydrodynamic model. In particular, these models will be selected for investigations where diurnal and tidal fluctuations are of prime importance to the study.

The quasi 2-d Level III model is applicable where there is a need to project lateral differences in water quality for wide estuaries. The quasi 2-d model, however, which uses 1-d equations of motion applied to the channels, cannot estimate longitudinal and lateral dispersion as effectively as the true 2-d model of Level IV. Although the quasi 2-d and the true 2-d model both assume that the estuary is vertically mixed, the true 2-d model can effectively represent lateral variation in velocity and constituent concentration for estuaries with nonuniform cross sections, branching channels, and embayments. The 2-d model also can account for the effect of Coriolis forces and wind circulation.

For a wide, stratified estuary the application of a 3-d model would be appropriate for intratidal simulations. There are no well documented intratidal 3-d models with coupled constituent interactions applicable to tidally driven estuaries. Fully 3-d models that can predict longitudinal, lateral, and vertical transport are the most complex and expensive to set up and run. Due to their cost and complexity, these models have not been widely used. For experts with access to supercomputers, these models are feasible for special applications.

A recent modeling strategy is to drive a Level II compartment model that has been configured in two or three dimensions with either averaged or tidally varying flows and volumes from a 2-d or 3-d hydrodynamic model. This strategy attempts to combine the transport rigor of Level IV models with the convenience, flexibility, and cost efficiency of compartment models. A recent and currently ongoing example is a study of the Chesapeake Bay. There, the averaged output of a finite difference stretch coordinate hydrodynamic model was linked to a specially adapted compartment model, AESOP and run to steady state (HydroQual,

1987). When running the water quality model at different time steps or on a coarser grid, the user must still calibrate horizontal and vertical dispersion coefficients to observed salinity or tracer data.

The criteria for the specification of time and space scales for Level IV models are similar to those discussed for Level III with the additional need to consider a vertical scale for a 3-d model application. For 2-d and 3-d models, the time step would be calculated as a function not only of the longitudinal space steps and longitudinal dispersion coefficient (as described by Equations 3-14 and 3-15), but also as a function of the lateral and vertical space steps and dispersion coefficients.

At present, no Level IV model is supported by CEAM. A variety of these models currently being used is described below.

3.3.5.1. H.S. Chen Model

The H.S. Chen model is a real time 2-d (x-y) model that simulates conventional pollutants (Chen, 1978). The hydrodynamic submodel considers inertial forces, convective forces, hydrostatic pressure, wind forces, Coriolis forces, bottom friction, and internal water column forces due to eddies. The parameters simulated by the model include the following: conservatives, coliforms, chlorophyll-a, organic nitrogen, ammonia, nitrite, nitrate, organic phosphorus, inorganic phosphorus, CBOD, and DO. Algal growth, photosynthesis, and respiration are represented in the model as well as benthic oxygen demand and bottom releases of ammonia and inorganic phosphorus. Equations are solved by a finite element technique.

3.3.5.2. FETRA

FETRA is a real time, 2-d (x-y) water quality model that utilizes a finite element solution technique to simulate toxic pollutants (Onishi 1981). Hydrodynamic data must be supplied by a separate model such as EXPLORE-I. FETRA consists of three submodels linked to simulate the transport and transformation of sediments and contaminants by the processes of advection, diffusion/dispersion, adsorption/desorption, and degradation/decay. The sediment transport submodel simulates advection and dispersion of sediments, fall velocity and cohesiveness, and deposition or erosion for the bed. Three sediment sizes are modeled, and calculations are made of bed elevation changes and the distribution of sediment sizes within the bed. The dissolved contaminant transport submodel predicts advection and diffusion/dispersion of dissolved pollutants, adsorption by both moving and stationary sediments, desorption from sediments, and degradation or radionuclide decay. The particulate contaminant

transport submodel includes advection and dispersion of sediment-attached contaminants, adsorption/desorption with sediment, degradation or radionuclide decay, and settling/resuspension.

3.3.5.3. TABS-2

TABS-2 is a generalized numerical modeling system for open-channel flows, sedimentation, and constituent transport developed and supported by the U.S. Army Engineers Waterways Experiment Station, Hydraulics Laboratory (Thomas and McAnally, 1985). It consists of more than 40 computer programs to perform modeling and related tasks. The major modeling components--RMA-2V, STUDH, and RMA-4--calculate two-dimensional, depth-averaged (x-y) flows, sedimentation, and dispersive transport, respectively. The other programs in the system perform digitizing, mesh generation, data management, graphical display, output analysis, and model interfacing tasks. Utilities include file management and automatic generation of computer job control instructions.

TABS-2 has been applied to a variety of waterways, including rivers, estuaries, bays, and marshes. It is designed for use by engineers and scientists who may not have a rigorous computer background.

3.3.5.4. WIFM-SAL

WIFM-SAL is a two dimensional depth-averaged (x-y) finite difference model that generates time-varying water surface evaluations, velocities, and constituent fields over a space staggered grid (Schmalz, 1985). This model was developed by the U.S. Army Engineers, Waterways Experiment Station. Units of measure are expressed in the English system (slug-ft-second). Results computed on a global grid may be employed as boundary conditions on more spatially limited refined grid concentrated around the area of interest. In addition, the user may select either of two distinct transport schemes. Scheme 1 is a flux-corrected transport scheme capable of resolving sharp front without oscillation. Scheme 2 is a full, three time level scheme directly compatible with the three time level hydrodynamics. The telescoping grid capability in conjunction with the user selectable constituent transport scheme is a powerful concept in practical transport problem solving.

3.3.5.5. FCSTM-H

FCSTM-H, by Earl Hayter at Clemson University, is a finite element modeling system for simulating two-dimensional depth-averaged (x-y) surface water flow and cohesive sediment transport consisting of three separate computer programs (Hayter, 1987). FEGRD is a two-dimensional finite element grid genera-

tion/modification program. FLWM-H is a hydrodynamic model that solves the depth-averaged equations of motion and continuity for model horizontal velocity components and flow depths. The effects of bottom, internal and surface shear stresses and the Coriolis force are represented in the equations of motion. CSTM-H is a cohesive sediment transport model that solves the advection-dispersion equation for nodal depth-averaged concentrations of suspended sediment and bed surface elevations. The processes of erosion, dispersion, aggregation, deposition and consolidation are simulated. A layered bed model is used in simulating bed formation, subsequent consolidation and erosion. An example problem, including input and output data, is included.

FLWM-H and CSTM-H are semi-coupled in the following manner. First, the flow field is calculated for the current time step using FLWM-H. Second, the predicted flow field is used in CSTM-H to calculate the transport of cohesive sediments during the same time step. The flow field may be updated due to erosion or deposition and/or unsteady boundary conditions.

The following sediment related properties are calculated for each element: sediment bed structure (bed density and shear strength profiles, bed thickness and elevation), net change in bed elevation over a given interval of time (e.g. over a certain number of tidal cycles), net vertical mass flux of sediment over an interval of time, average amount of time sediment particles are in suspension, and the downward flux of sediment onto the bed. These parameters are essential in estimating the bed-water exchange of chemicals adsorbed onto cohesive sediments.

The FCSTM-H modeling system may be used to predict both short term (less than one year) and long term (one year and longer) scour and/or sedimentation rates in vertically well mixed bodies of water. Because of the iterative routine used in the hydrodynamic model, long term simulations will require large (order of magnitude of one or more hours) CPU times, even on mainframe computers. Limited computer resources and budgetary constraints will often require extrapolation of short term simulations.

3.3.5.6. CE-QUAL-W2

CE-QUAL-W2 is a dynamic 2-d (x-z) model developed for stratified waterbodies (Env. and Hyd. Laboratories 1986). This is a Corps of Engineers modification of the Laterally Averaged Reservoir Model (Edinger and Buchak 1983, Buchak and Edinger, 1984a, 1984b). CE-QUAL-W2 consists of directly coupled hydrodynamic and water quality transport models. Hydrodynamic computations are influenced by vari-

able water density caused by temperature, salinity, and dissolved and suspended solids. Developed for reservoirs and narrow, stratified estuaries, CE-QUAL-W2 can handle a branched and/or looped system with flow and/or head boundary conditions. With two dimensions depicted, point and non-point loadings can be spatially distributed. Relative to other 2-d models, CE-QUAL-W2 is efficient and cost effective to use.

In addition to temperature, CE-QUAL-W2 simulates as many as 20 other water quality variables. Primary physical processes included are surface heat transfer, shortwave and longwave radiation and penetration, convective mixing, wind and flow induced mixing, entrainment of ambient water by pumped-storage inflows, inflow density current placement, selective withdrawal, and density stratification as impacted by temperature and dissolved and suspended solids. Major chemical and biological processes in CE-QUAL-W2 include: the effects on DO of atmospheric exchange, photosynthesis, respiration, organic matter decomposition, nitrification, and chemical oxidation of reduced substances; uptake, excretion, and regeneration of phosphorus and nitrogen and nitrification-denitrification under aerobic and anaerobic conditions; carbon cycling and alkalinity-pH-CO₂ interactions; trophic relationships for total phytoplankton; accumulation and decomposition of detritus and organic sediment; and coliform bacteria mortality.

3.3.5.7. EHSM3D

The EHSM3D model was developed by Y. P. Sheng at University of Florida calculates three-dimensional unsteady currents and sediment dispersion in estuaries and lakes (Sheng, et al., 1987, Sheng, 1989). Given proper boundary and initial conditions, the code can calculate the three-dimensional time-dependent distributions of flow, velocity, temperature, salinity, suspended sediment concentration, density, and dissolved species concentration. The status of the sediment dispersion model is preliminary since research is continuing with the development and validation of this portion of the model.

3.3.5.8. John Paul Hydrodynamic Model

This numerical model, developed by John Paul and colleagues at the U.S. EPA, is capable of realistically describing the hydrodynamics in lakes, embayments, nearshore marine coastal areas, and river and thermal outfall plumes (Paul and Nocito, 1989). The model is time-dependent, three dimensional, and variable density. Both rigid-lid and free-surface flows can be determined. The main assumptions used in the development of the model include hydrostatic pressure variation, Boussinesq approximation, and eddy coefficients to

account for turbulence. A new solution procedure, which is a modification of the simplified marker and cell method, is used. The procedure permits selected terms in the equations to be treated implicitly in time. A compatible 3-D, time dependent numerical physical transport model is available for use with this model.

3.3.6. Summary of Model Capabilities

The important features of the models selected for discussion in this manual are summarized in Tables 3-5 and 3-6. The information provided in these tables is primarily qualitative and sufficient to determine whether a model may be suitable for a particular application. For complete information, the potential user must consult the appropriate user's manuals, the supporting agency, and other experienced users.

Table 3-5 summarizes the basic features of the models. The time scales are dynamic (D), quasidynamic (Q), and steady (SS). Spatial dimensions are 1 (x), 2 (xy, xz, or xx for link-node networks), or 3 (xyz or B, for box models). Hydrodynamics are either input by the user (I) or simulated (S). Solution techniques are analytical (A), finite difference (FD) or finite element (FE). Finally, models are implemented on mainframes (M) or personal computers (PC).

Table 3-6 summarizes the water quality problems that may be directly addressed by the models. All models address salinity and bacteria either explicitly or by specifying appropriate boundaries, loads, and first order decay constants for another state variable. Sediment may be modeled using calibrated deposition and scour velocities (1), or by using functional relationships with shear stress and shear strength to predict these velocities (2). Dissolved oxygen may be modeled along with total BOD (1), with CBOD, NBOD, and prescribed sediment oxygen demand (SOD) and net photosynthetic production (2), or with CBOD nitrification, SOD, and simulated nutrients and phytoplankton (3). Nutrient enrichment and eutrophication may be simulated using total phytoplankton biomass (1), multiple phytoplankton classes (2), or multiple phytoplankton and zooplankton classes (3). Organic chemicals may be modeled with calibrated decay rates and partition coefficients (1), with predicted transformation rates and partition coefficients (2), or with predicted rates and coefficients for the original chemical plus reaction products (3). Metals may be modeled as dissolved and particulate fractions with calibrated partition coefficients (1), or as multiple species predicted with a thermodynamic data base and process models (2).

Table 3-5. Basic Model Features

Model	Time Scale	Spatial Dimension	Hydrodynamics	Solution Tech.	Computer
SEM	SS	x	I	A	-
WQAM	SS	x	I	A	-
HARO3	SS	B	I	FD	M
FEDBAKO3	SS	B	I	FD	M
QUAL2	SS	x	I	FD	M, PC
AUTOQUAL/QD	Q	x	I	FD	M, PC
WASP4:					
stand alone	Q	B	I	FD	M, PC
with DYNHYD4	D	xx	S	FD	M, PC
DEM	D	xx	S	FD	M
EXPLORE-I	D	xx	S	FD	M
MIT-DNM	D	x	S	FD	M
Chen	D	xy	S	FE	M
FETRA	D	xy	I	FE	M
CE-QUAL-W2	D	xz	S	FD	M
TABS-2	D	xy	S	FE	M
WIFM-SAL	D	xy	S	FE	M
FCSTM-H	D	xy	S	FE	M
EHSM3D	D	xyz	S	FD	M
J. PAUL	D	xyz	S	FD	M
O-dynamic	x-1 dimensional		I-hydrodynamics input	A-analytical solution	M-mainframe computers
Q-quasidynamic (tidal-averaged)	xy-2 dimensional, longitudinal-lateral		S-hydrodynamics simulated	FD-finite difference solution	PC-personal computers
SS-steady state	xz-2 dimensional, longitudinal-vertical xyz-3 dimensional B-compartment or box 3D xx-link node branching 2D			FE-finite element solution	

Table 3-6. Water Quality Problems Addressed

Model	Salinity Bacteria	Sedi- ment	DO	Eutro- phica- tion	Org. Chem.	Me- tals
SEM	X		2			
WQAM	X	1	2		1	
HARO3	X		2			
FEDBAKO3	X		2			
QUAL2	X		3	1		
AUTOQUAL	X		2			
WASP4:						
EUTRO4	X		3	1		
TOX4	X	1			1,2,3	1
DEM	X		3	1		
EXPLORE-I	X		3	3		
MIT-DNM	X		3	1		
Chen	X		3	1		
FETRA	X	2				1
CE-QUAL-W2	X	1	3	1		
TABS-2	X	2				
WIFM-SAL	X					
FCSTM-H	X	2				
EHSM3D	X	2				
J.PAUL	X					

3.4. References

- Ambrose, R.B., Najarian, T.O., Bourne, G., Thatcher, M.L. 1981. Models for Analyzing Eutrophication in Chesapeake Bay Watersheds: A Selection Methodology. USEPA, Office of Research and Development, Chesapeake Bay Program, Annapolis, MD.
- Ambrose, R.B. and Roesch, S.E. 1982. Dynamic Estuary Model Performance. Journal of the Environmental Engineering Division, American Society of Civil Engineers, 108(EE1).
- Ambrose, R.B. Jr. et. al. 1987. WASP4, A General Water Quality Model for Toxic and Conventional Pollutants. U.S. Environmental Protection Agency, Athens, Georgia.
- Blumberg, A.F. 1975. A Numerical Investigation into the Dynamics of Estuarine Circulation. Chesapeake Bay Institute, Johns Hopkins University, Baltimore MD. NTIS PB-248 435/OCP.
- Bowie, G.L. et. al. 1985. Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling

- (second ed.), U.S. Environmental Protection Agency, Athens, Ga. EPA/600/3-85/040.
- Buchak, E.M. and Edinger, J.E. 1984a. Generalized, Longitudinal-vertical Hydrodynamics and Transport: Development, Programming And Applications, Document No. 84-18-R, U.S. Army Corps of Engineers, WES, Vicksburg, Mississippi.
- Buchak, E. M. and Edinger, J.E. 1984b. Simulation of a Density Underflow into Wellington Reservoir using Longitudinal-vertical Numerical Hydrodynamics, Document No. 84-18-R, U.S. Army Corps of Engineers, WES, Vicksburg, Miss., March.
- Chapra, S. and Nossa, G.A. October, 1974. Documentation for HARO3, 2nd Edition. USEPA Region II, New York, NY.
- Chen, H.S., August 1978. A Mathematical Model for Water Quality Analysis. Proceedings of ASCE Hydraulics Division Specialty Conference on Verification of Mathematical and Physical Models in Hydraulic Engineering, American Society of Civil Engineers, New York, NY.
- Chen, C.W. and Orlob, G.T. December, 1972. Ecological Simulation for Aquatic Environments. NTIS Doc. PB 218828, Water Resources Engineers, Inc., Walnut Creek, California, for Office of Water Resources Research, U.S. Department of the Interior, Washington, D.C.
- Crim, R. and Lovelace, N.L. 1973. AUTO_QUAL Modeling System. U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-73-004.
- Di Toro, D.M., 1986. A Diagenetic Oxygen Equivalents Model of Sediment Oxygen Demand, In Sediment Oxygen Demand; Processes, Modeling, and Measurement, editor K. J. Hatcher, Univ. of Georgia, Athens, GA, pp 171-208.
- Di Toro, D.M., Fitzpatrick, J.J., and Thomann, R.V. 1981. Water Quality Analysis Simulation Program (WASP) and Model Verification Program (MVP)-Documentation. Hydrosience, Inc., Westwood, New Jersey, for U.S. Environmental Protection Agency, Duluth, MI.
- Dyer, K.R. 1973. Estuaries: A Physical Introduction. John Wiley and Sons, New York.
- Edinger, J.E. and Buchak, E.M. 1983. Developments in LARM2: A Longitudinal-vertical, Time-varying Hydrodynamic Reservoir Model, Technical Report E-83-1, USAE Waterways Experiment Station, Vicksburg, MS.
- Elliott, A.J. 1976. A Numerical Model of the Internal Circulation in a Branching Tidal Estuary. Chesapeake Bay Institute, Johns Hopkins University, Baltimore, MD, Special Report 54.
- Environmental and Hydraulics Laboratories. 1986. CE-QUAL-W2, A Numerical Two-Dimensional Model of Hydrodynamics and Water Quality, User's Manual. Instruction Report E-86-5, USACE Waterways Experiment Station, Vicksburg, MS.
- Feigner, K.D. and Harris, H.S. July, 1970. Documentation Report -FWQA Dynamic Estuary Model. Prepared for USEPA, Water Quality Office, Washington, D.C. NTIS No. PB 197 103.
- Fisher, J.S., Ditmars, J.D., and Ippen, A.T. 1972. Mathematical Simulation of Tidal Time-Averages of Salinity and Velocity Profiles in Estuaries. Ralph M. Parsons Laboratory, Massachusetts Institute of Technology, Cambridge, MA, MITSG-772-11, NOAA-72110204.
- Fischer, H.B. et al. 1978. Mixing in Inland and Coastal Waters. Academic Press, N.Y. 483 pp.
- Genet, L.A., Smith, D.J. and Sonnen, M.B. 1974. Computer Program Documentation for the Dynamic Estuary Model. Water Resources Engineers, Inc., Walnut Creek, California for U.S. Environmental Protection Agency, Systems Development Branch, Washington, D.C.
- Hamilton, P. 1975. A Numerical Model of the Vertical Circulation of Tidal Estuaries and its Application to the Rotterdam Waterway. Geophys. J. R. Astr. Soc., 40:1-21.
- Hansen, D.V. and Rattray, M. 1966. New Dimensions in Estuarine Classification. Limnology and Oceanography 11(3):319-316.
- Harleman, D.R., Daily, J.E., Thatcher, M.L., Najarian, T.O., Brocard, D.N., and Ferrara, R.A. January, 1977. User's Manual for the M.I.T. Transient Water Quality Network Model. EPA-600/3-77-010. USEPA Environmental Research Lab, Corvallis, Oregon.
- Hayter, E.J. 1987. Finite Element Hydrodynamic and Cohesive Sediment Transport Modeling System. Dept. of Civil Engineering, Clemson University, Clemson, SC.
- Hinwood, J.B. and Wallis, I.G. October 1975. Classification of Models of Tidal Waters, Journal of the Hydraulics Division, Proceedings of the American Society of Civil Engineers, 101(HY10).

- Holley, E. and Jirka, G. 1986. Mixing in Rivers. U.S. Army Corps of Engineers, Vicksburg, MS. COE TR-E-86-11.
- HydroQual, Inc. August, 1987. Steady State Coupled Hydrodynamic/Water Quality Model of Eutrophication and Anoxia Process in Chesapeake Bay. HydroQual, Inc. under contract to Battelle Ocean Sciences, Duxbury, MA for U.S. Environmental Protection Agency, Chesapeake Bay Program, Annapolis MD.
- Hydrosience, Inc. March, 1971. Simplified Mathematical Modeling of Water Quality. US Government Printing Office: 1971-44-367/392. Water Programs, U.S. Environmental Protection Agency, Washington, D.C.
- Lovelace, N.L. 1975. AUTO-QUAL Modelling System: Supplement I. Modification for Non-Point Source Loadings. U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-73-004.
- Lung, W.S. 1987. Advective Acceleration and Mass Transport in Estuaries, ASCE J. Hydraulic Engr. 112(9), 874-878.
- Lung, W.S. and O'Connor, D.J. 1984. Two-Dimensional Mass Transport in Estuaries, ASCE J. Hydraulic Engr. 110(10), 1340-1357.
- Mills, W.B., Dean, J.P., Porcella, D.B., Gherini, S.A., Hudson, R.J.M., Frick, W.E., Rupp, G.L. and Bowel, G.L. September, 1982. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants. EPA-600/6-82-004. USEPA Environmental Research Lab, Athens, Georgia.
- Mills, W.B., Porcella, D.B., Unga, M.J., Gherini, S.A., Summers, K.V., Lingfung, M., Rupp, G.L., Bowie, G.L., and Halth, D.A. 1985. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants. U.S. Environmental Protection Agency, Athens, GA, EPA/600/6-85/002a,b.
- Najarian, T.O. and Harleman, D.R. July, 1975. A Real-Time Model of Nitrogen Cycle Dynamics in an Estuarine System. R.M. Parsons Laboratory for Water Resources and Hydrodynamics, Massachusetts Institute of Technology.
- Nihoul, J. and Jamarf, Ed. 1987. Three-Dimensional Models of Marine and Estuarine Dynamics. Elsevier Scientific, Amsterdam.
- Nossa, G.A. November, 1978. FEDBAKO3 - Program Documentation and Users Guide, USEPA Region II, New York, NY.
- O'Connor, D.J. and Lung, W. 1983. Suspended Solids Analysis of Estuarine Systems. Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers. 107(EE1).
- Onishi, Y. 1981. Sediment-Contaminant Transport Model. Journal of the Hydraulics Division, American Society of Civil Engineers, 107(HY9).
- Paul, J.P. and Nocito, J.A. 1989. Numerical Model for Three-Dimensional, Variable-Density Hydrodynamic Flows: Documentation of the Computer Program. U.S. Environmental Protection Agency, Duluth MN (in press).
- Roesch, S.E., Clark, L.J., and Bray, M.M. 1979. User's Manual for the Dynamic (Potomac) Estuary Model. EPA-903/9-79-001. Technical Report 63. U.S. Environmental Protection Agency, Annapolis, MD.
- Schmalz, R.A. 1985. User Guide for WIFM-SAL: A Two-Dimensional Vertically Integrated, Time-Varying Estuarine Transport Model. U.S. Department of the Army, Waterways Experiment Station, Corps of Engineers, Vicksburg, MS.
- Sheng, Y.P. 1989. A Three-Dimensional Numerical Model of Hydrodynamics and Sediment Dispersion. University of Florida, Gainesville, FL for U.S. Environmental Protection Agency, Athens, GA (in press).
- Sheng, Y.P., Parker, S.F., and Henn, D.S. 1987. A Three-Dimensional Estuarine Hydrodynamic Software Model (EHSM3D). Aeronautical Research Associates of Princeton, Inc., Princeton, NJ, for U.S. Geological Survey, Contract 14-08-0001-21730.
- Swanson, C. and Spaulding, M. March, 1983. User's Manual for Three Dimensional Time Dependent Numerical Dispersion Model of Upper Narragansett Bay. Prepared for USEPA Region I, Boston, MA.
- Thatcher, M.L., Pearson, H.W. and Mayor-Mora, R.E. September, 1975. Application of a Dynamic Network Model to Hydraulic and Water Quality Studies of the St. Lawrence River. Presented at the Second Annual Symposium of the Waterways, Harbors and Coastal Engineering, ASCE, San Francisco, CA.
- Thatcher, M.L. and Harleman, D.R.F. 1972. Prediction of Unsteady Salinity Intrusion in Estuaries: Mathematical Model and Users Manual. Ralph M. Parsons Laboratory, Massachusetts Institute of Technology, Cambridge, MA, Technical Report 159.
- Thomas, W.A. and McAnally, W.H. Jr. 1985. User's Manual for the Generalized Computer Program System - Open Channel Flow and Sedimentation TABS-2. U.S.

Department of the Army, Waterways Experiment Station, Corps of Engineers, Vicksburg, MS.

Wang, J.D. and Connor, J.J. 1975. Mathematical Modeling of Near Coastal Circulation. MIT Sea Grant Program, Massachusetts Institute of Technology, Cambridge, MA, Report MIT-SG-75-13.