Appendix B

Quality Assurance Verification and Validation Tests for the Exposure Analysis Modeling System – Exams

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**United States
Environmental Protection
Agency**

Research and Development

Quality Assurance Verification and Validation Tests for the Exposure Analysis Modeling System – EXAMS

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Table of Contents

B.1 Introduction to the Exposure Analysis Modeling System (EXAMS) B-1
B.1.1 Background B-1
B.1.2 Exposure Analysis in Aquatic Systems B-3
B.1.3 The EXAMS Program B-3
B.1.4 EXAMS Process Models B-4
B.1.4.1 Ionization and Sorption B-4
B.1.4.2 Transformation Processes B-5
B.1.4.3 Transport Processes B-6
B.1.4.4 Chemical Loadings B-6
B.1.5 Ecosystems Analysis and Mathematical Systems Models B-6
B.1.5.1 EXAMS Design Strategy B-7
B.1.5.2 Temporal and Spatial Resolution B-8
B.1.5.3 Assumptions B-10

B.2 Verification of EXAMS B-11
B.2.1 Background B-11
B.2.2 Water Body Network B-13
B.2.3 Dispersion Parameters B-13
B.2.4 Water Balance B-14
B.2.4.1 Water Body Network 1 . . . . . B-14
B.2.4.2 Water Body Network 2 . . . . . B-15
B.2.4.3 Water Body Network 3 . . . . . B-16
B.2.5 Solids Balance B-16
B.2.5.1 Water Body Network 1 . . . . . B-17
B.2.5.2 Water Body Network 2 . . . . . B-17
B.2.5.3 Water Body Network 3 . . . . . B-18
B.2.6 Chemical Loadings and Conservative Transport B-19
B.2.6.1 Water Body Network 1 . . . . . B-19
B.2.6.2 Water Body Network 2 . . . . . B-19
B.2.6.3 Water Body Network 3 . . . . . B-20
B.2.7 Ionization B-20
B.2.7.1 Organic Acids B-21
B.2.7.2 Organic Bases B-22
B.2.8 Sorption B-22
B.2.8.1 Organic Chemicals B-23
B.2.8.2 Metals B-24
B.2.9 Volatilization B-24
B.2.9.1 Volatilization in Stream Reaches B-25
B.2.9.2 Volatilization in Ponds, Wetlands, and Lakes B-25
B.2.9.3 Effect of Ionization on Volatilization B-27
B.2.10 Transformation Processes B-28
B.2.10.1 Organic Chemical Transformations B-28
B.2.10.2 Mercury Transformations B-30
B.2.11 Test Robustness B-32
B.2.11.1 Screening across Sites B-32
B.2.11.2 Screening across Chemicals B-33

Table of Contents (continued)

B.2.11.3 Monte-Carlo Screening with Random Parameter Values B-34

B.3 EXAMS System Validation Case Studies B-40
B.3.1 Overview B-40
B.3.2 Linear Alkylbenzene Sulfonate in a Small Stream B-40
B.3.3 Phenol in the Monongahela River B-41
B.3.4 Disperse Yellow 42 Dye in a Pond B-41
B.3.5 Chlorophenol, Chloroquaiacol, and Chlorocatechol in Norrsundet Bay (Sweden) B-42
B.3.6 Three Herbicides and an Insecticide in Rice Paddies B-43
B.3.7 Xylenes, Dichlorobenzenes, Styrene, and 4-phenyldodecane in a small lowland river in U.K. B-44
B.3.8 Aniline and Lindane in River Calder B-45
B.3.9 Bensulfuron Methyl and Azimsulfuron in Rice Paddies B-45
B.3.10 Discussion of Case Studies B-46

References B-47

B.1 Introduction to the Exposure Analysis Modeling System (EXAMS)

B.1.1 Background

The HWIR Surface Water Module is one component of the 3MRA software system that is designed to evaluate the nationwide probability of human and ecological risk from chemicals placed in various waste management units (WMUs). The HWIR Surface Water Module takes the loadings calculated by the source, atmospheric, watershed, and groundwater modules, along with data on meteorology, hydrology, environmental conditions, and chemical reactivity, and calculates the chemical concentrations throughout the water body network over time. As illustrated in Figure B-1, the HWIR Surface Water Module consists of the core model EXAMS II and the interface module EXAMSIO (Ambrose and Burns, 2000; U.S. EPA 1999), which was developed specifically for the HWIR project. It reads data from other HWIR modules and databases, and builds EXAMS input files describing the water body environment and chemical properties, along with the command file that specifies the chemical loading history and controls the EXAMS simulation. EXAMSIO passes control to EXAMS, which conducts the simulation and produces intermediate results files. EXAMSIO then processes the intermediate files and passes the output data back to the proper HWIR database.

While the EXAMS component of the HWIR Surface Water Module is a fully functional model independent of this project, it is driven and constrained in various ways by EXAMSIO and the HWIR databases. For convenience, the HWIR Surface Water Module will be referred to here as H-EXAMS. This composite module is documented in an unpublished report (Ambrose and Burns, 2000), and in the HWIR99 Background document for surface water modules (U.S. EPA 1999), part of EPA Office of Solid Waste's web site of HWIR documents. While EXAMS can be run interactively or as a batch program, H-EXAMS is implemented solely as a batch process. H-EXAMS does not consider transformations due to photolysis or oxidation. Transformation rate constants for hydrolysis, biodegradation, and reduction are calculated by the HWIR chemical processor and passed through the batch chemical database to EXAMS. Internal EXAMS algorithms for calculating rate constants are bypassed.

EXAMSIO provides the link between other HWIR modules and databases and the EXAMS model. For each site simulation, HWIR software generates site simulation files (SSFs) detailing the chemical properties and the site characteristics. The source and natural media modules are then executed, followed by the exposure and risk modules. Modules produce time series calculations and store results in their global results files (GRFs). EXAMSIO reads results generated by the source module, the atmospheric module, the watershed module, and the aquifer module. Three batch EXAMS files are generated by EXAMSIO – the run file "hwirexp.exa," the chemical file "hwirexp1.chm," and the environment file "hwirexp.env." If two or more chemicals are included in one simulation, then separate files are created for each chemical (hwirexp2.chm, hwirexp3.chm, etc.). Next, EXAMS is executed, generating the temporary results files hwirexp.xms and (if storage level is set to maximum) report.xms. Finally, EXAMSIO reads hwirexp.xms and produces the properly named and formatted surface water GRF, which is used as input by the HWIR exposure modules.

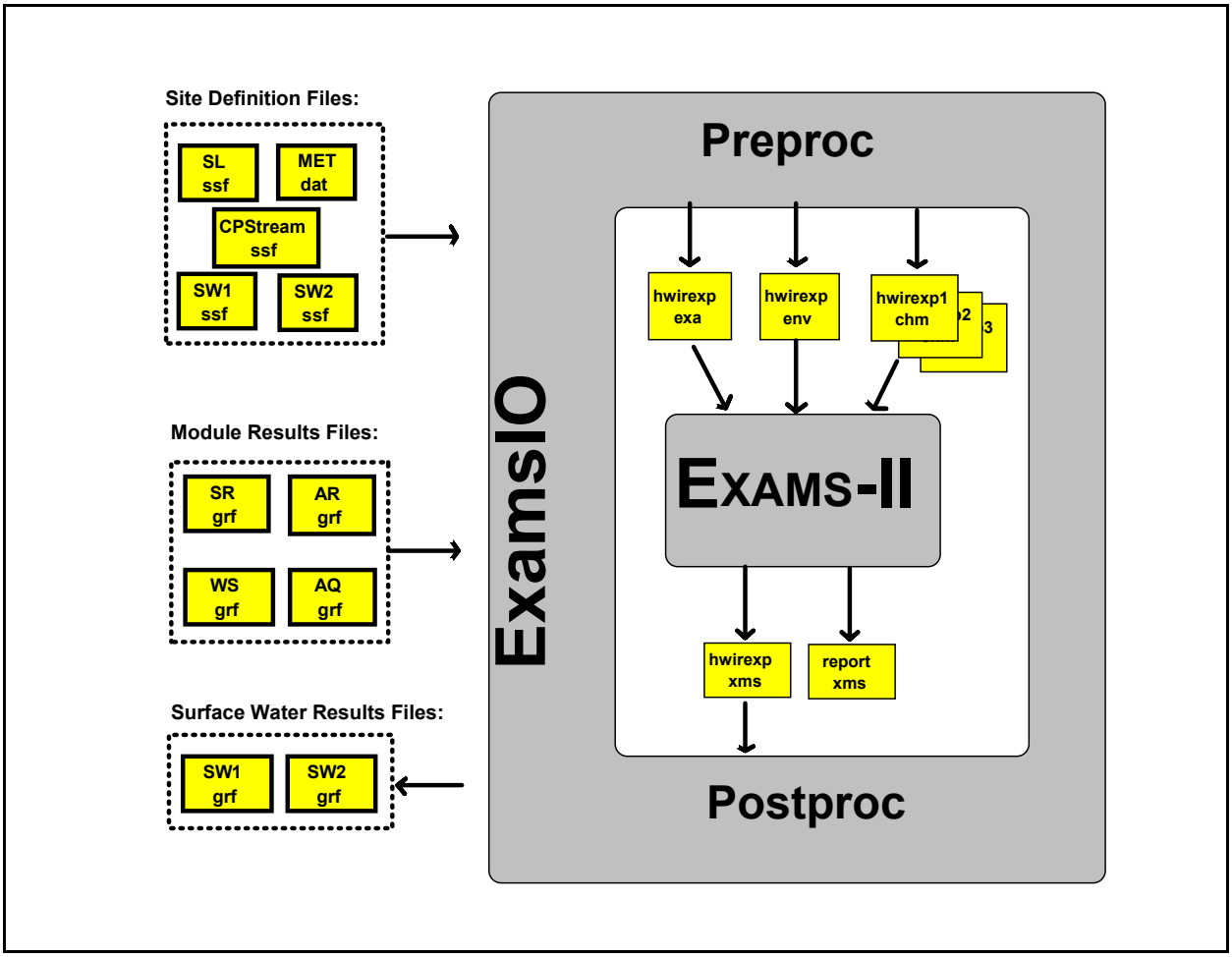

Figure B-1. Surface water module components.

The chemical file specifies the relevant chemical properties, including molecular weight, melting point, Henry's Law constant, vapor pressure, ionization constants, partition coefficients, solubilities, various rate constants, and reaction yield coefficients when appropriate. The environment file specifies all relevant aspects of the physical environment to be simulated. These properties include compartment geometry, advective flow paths, mixing characteristics, and environmental characteristics that influence chemical reactions, such as pH, DOC, microbial activity, and reductant concentration. The run file controls the EXAMS simulation. It sets simulation control variables at the beginning, then specifies yearly inflows and loadings for each modeled compartment. Yearly changes in various environmental properties are also specified, including TSS and water temperature.

The major model simplifications made in response to the project constraints include the use of average-yearly hydrological and loading inputs, the use of national distributions to specify some site-specific environmental conditions, and the use of a simple solids balance with no settling and burial. For sites that experience periodic drying, a small positive flow equivalent to 5 mm/year of direct precipitation onto the water body surface is maintained in order to keep the model functioning.

B.1.2 Exposure Analysis in Aquatic Systems

EXAMS was conceived as an aid to those who must execute hazard evaluations solely from laboratory descriptions of the chemistry of a newly synthesized toxic compound. EXAMS estimates exposure, fate, and persistence following release of an organic chemical into an aquatic ecosystem.

When a pollutant is released into an aquatic ecosystem, it is entrained in the transport field of the system and begins to spread to locations beyond the original point of release. During the course of these movements, chemical and biological processes transform the parent compound into daughter products. Residual concentrations can be compared to those posing a danger to living organisms. These "expected environmental concentrations" (EECs), or exposure levels, in receiving water bodies are one component of a hazard evaluation.

The toxicologist also needs to know which populations in the system are "at risk." Populations at risk can be deduced to some extent from the distribution or "fate" of the compound, that is, by an estimate of EECs in different habitats of single ecosystems. EXAMS reports a separate EEC for each compartment, and thus each local population, used to define the system.

B.1.3 The EXAMS Program

The need to predict chemical exposures from limited data has stimulated a variety of recent advances in environmental modeling. These advances fall into three general categories:

- Process models giving a quantitative, often theoretical, basis for predicting the rate of transport and transformation processes as a function of environmental variables.

- Procedures for estimating the chemical parameters required by process models. Examples include linear free energy relationships, and correlations summarizing large bodies of experimental chemical data.

- Systems models that combine unit process models with descriptions of the environmental forces determining the strength and speed of these processes in real ecosystems.

The EXAMS program is a deterministic, predictive systems model, based on a core of mechanistic process equations derived from fundamental theoretical concepts. The EXAMS computer code also includes descriptive empirical correlations that ease the user's burden of parameter calculations, and an interactive command language that facilitates the application of the system to specific problems.

EXAMS "predicts" in a somewhat limited sense of the term. Many of the predictive water-quality models currently in use include site-specific parameters that can only be found via field calibrations. After "validation" of the model by comparison of its calibrated outputs with additional field measurements, these models are often used to explore the merits of alternative management plans. EXAMS, however, deals with an entirely different class of problem. Because

newly synthesized chemicals must be evaluated, little or no field data may exist. Furthermore, EECs at any particular site are of little direct interest. In this case, the goal, at least in principle, is to predict EECs for a wide range of ecosystems under a variety of geographic, morphometric, and ecological conditions. EXAMS includes no direct calibration parameters, and its input environmental data can be developed from a variety of sources. The EECs generated by EXAMS are thus "evaluative" (Lassiter et al. 1979) predictions designed to reflect typical or average conditions. EXAMS' environmental database can be used to describe specific locales, or as a generalized description of the properties of aquatic systems in broad geographic regions.

EXAMS relies on mechanistic, rather than empirical, constructs for its core process equations wherever possible. Mechanistic (physically determinate) models are more robust predictors than are purely empirical models, which cannot safely be extended beyond the range of prior observations. EXAMS contains a few empirical correlations among chemical parameters, but these are not invoked unless the user approves.

B.1.4 EXAMS Process Models

In EXAMS, the loadings, transport, and transformations of a compound are combined into differential equations by using the mass conservation law as an accounting principle. This law accounts for all the compound entering and leaving a system as the algebraic sum of (1) external loadings, (2) transport processes exporting the compound out of the system, and (3) transformation processes within the system that degrade the compound to its daughter products. The fundamental equations of the model describe the rate of change in chemical concentrations as a balance between increases due to loadings, and decreases due to the transport and transformation processes removing the chemical from the system.

The set of unit process models used to compute the kinetics of a compound is the central core of EXAMS. These unit models are all "second-order" or "system-independent"models: each process equation includes a direct statement of the interactions between the chemistry of a compound and the environmental forces that shape its behavior in aquatic systems. Thus, each realization of the process equations implemented by the user in a specific EXAMS simulation is tailored to the unique characteristics of that ecosystem. Most of the process equations are based on standard theoretical constructs or accepted empirical relationships. For example, light intensity in the water column of the system is computed using the Beer-Lambert law, and temperature corrections for rate constants are computed using Arrhenius functions.

B.1.4.1 Ionization and Sorption

Ionization of organic acids and bases, complexation with dissolved organic carbon (DOC), and sorption of the compound with sediments and biota, are treated as thermodynamic properties or (local) equilibria that alter the operation of kinetic processes. For example, an organic base in the water column may occur in a number of molecular species (as dissolved ions, sorbed with sediments, etc.), but only the uncharged, dissolved species can be volatilized across the air-water interface. EXAMS allows for the simultaneous treatment of up to 28 molecular species of a chemical. These include the parent uncharged molecule, and singly, doubly, or triply charged cations and anions, each of which can occur in a dissolved, sediment-sorbed, DOC-complexed, or biosorbed form. The program computes the fraction of the total concentration of compound that is present in each of the 28 molecular structures.

B.1.4.2 Transformation Processes

EXAMS computes the kinetics of transformations attributable to direct photolysis, hydrolysis, biolysis, and oxidation reactions.

EXAMS includes two algorithms for computing the rate of photolytic transformation of a synthetic organic chemical. These algorithms accommodate the two more common kinds of laboratory data and chemical parameters used to describe photolysis reactions. The simpler algorithm requires only an average pseudo-first-order rate constant applicable to near-surface waters under cloudless conditions at a specified reference latitude. To control reactivity assumptions, the rate constant is coupled to nominal (normally unit-valued) reaction quantum yields for each molecular species of the compound. This approach makes possible a first approximation of photochemical reactivity, but neglects the very important effects of changes in the spectral quality of sunlight with increasing depth in a body of water. The more complex photochemical algorithm computes photolysis rates directly from the absorption spectra (molar extinction coefficients) of the compound and its ions, measured values of the reaction quantum yields, and the environmental concentrations of competing light absorbers (chlorophylls, suspended sediments, DOC, and water itself).

The total rate of hydrolytic transformation of a chemical is computed by EXAMS as the sum of three contributing processes. Each of these processes can be entered via simple rate constants, or as Arrhenius functions of temperature. The rate of specific-acid-catalyzed reactions is computed from the pH of each sector of the ecosystem, and specific-base catalysis is computed from the environmental pOH data. The rate data for neutral hydrolysis of the compound are entered as a set of pseudo-first-order rate coefficients (or Arrhenius functions) for reaction of the 28 (potential) molecular species with the water molecule.

EXAMS computes biotransformation of the chemical in the water column and in the bottom sediments of the system as entirely separate functions. Both functions are second-order equations that relate the rate of biotransformation to the size of the bacterial population actively degrading the compound (Paris et al.1982). This approach is of demonstrated validity for at least some biolysis processes, and provides the user with a minimal semi-empirical means of distinguishing between eutrophic and oligotrophic ecosystems. The second-order rate constants can be entered either as single-valued constants or as functions of temperature.

Oxidation reactions are computed from the chemical input data and the total environmental concentrations of reactive oxidizing species (alkylperoxy and alkoxyl radicals, etc.), corrected for ultra-violet light extinction in the water column. The chemical data can again be entered either as simple second-order rate constants or as Arrhenius functions. Oxidations due to singlet oxygen are computed from chemical reactivity data and singlet oxygen concentrations; singlet oxygen is estimated as a function of the concentration of DOC, oxygen tension, and light intensity. Reduction is included in the program as a simple second-order reaction process driven by the user entries for concentrations of reductants in the system. As with biolysis, this provides the user with a minimal empirical means of assembling a simulation model that includes specific knowledge of the reductants important to a particular chemical safety evaluation.

B.1.4.3 Transport Processes

Internal transport and export of a chemical occur in EXAMS via advective and dispersive movement of dissolved, sediment-sorbed, and biosorbed materials and by volatilization losses at the air-water interface. EXAMS provides a set of vectors that specify the location and strength of both advective and dispersive transport pathways. Advection of water through the system is then computed from the water balance, using hydrologic data (rainfall, evaporation rates, stream flows, groundwater seepages, etc.) supplied to EXAMS as part of the definition of each environment.

Dispersive interchanges within the system, and across system boundaries, are computed from the usual geochemical specification of the characteristic length, cross-sectional area, and dispersion coefficient for each active exchange pathway. EXAMS can compute transport of synthetic chemicals via whole-sediment bed loads, suspended sediment wash-loads, exchanges with fixed-volume sediment beds, ground-water infiltration, transport through the thermocline of a lake, losses in effluent streams, etc. Volatilization losses are computed using a two-resistance model. This computation treats the total resistance to transport across the air-water interface as the sum of resistances in the liquid and vapor phases immediately adjacent to the interface.

B.1.4.4 Chemical Loadings

External loadings of a toxicant can enter the ecosystem via point sources, non-point sources, dry fallout or aerial drift, atmospheric wash-out, and ground-water seepage entering the system. Any type of load can be entered for any system compartment, but the program will not implement a loading that is inconsistent with the system definition. For example, the program will automatically cancel a rainfall loading entered for the hypolimnion or benthic sediments of a lake ecosystem. When this type of corrective action is executed, the change is reported to the user via an error message.

B.1.5 Ecosystems Analysis and Mathematical Systems Models

The EXAMS program was constructed from a systems analysis perspective. The system environment comprises those factors (or "forcing functions") affecting system outputs over which the system has little or no control. Examples for an aquatic ecosystem include runoff and sediment erosion from its watershed, insolation, and rainfall. System resources are defined as those factors affecting performance over which the system exercises some control. Resources of an aquatic ecosystem include, for example, the pH throughout the system, light intensity in the water column, and dissolved oxygen concentrations. Each of the components or "state variables" of a system can be described in terms of its local input/output behaviors and its causal connections with other elements of the system. The systems approach lends itself to the formulation of mathematical systems models, which are simply tools for encoding knowledge of transport and transformation processes and deriving the implications of this knowledge in a logical and repeatable way.

A systems model, when built around relevant state variables (measurable properties of system components) and causal process models, provides a method for extrapolating future states of systems from knowledge gained in the past. In order for such a model to be generally useful, however, most of its parameters must possess an intrinsic interest transcending their role in any

particular computer program. For this reason, EXAMS was designed to use chemical descriptors (Arrhenius functions, pKa, vapor pressure, etc.) and water quality variables (pH, chlorophyll, biomass, etc.) that are independently measured for many chemicals and ecosystems.

B.1.5.1 EXAMS Design Strategy

The conceptual view adopted for EXAMS begins by defining aquatic ecosystems as a series of distinct subsystems, interconnected by physical transport processes that move synthetic chemicals into, through, and out of the system. These subsystems include the epilimnion and hypolimnion of lakes, littoral zones, benthic sediments, etc. The basic architecture of a computer model also depends, however, on its intended uses. EXAMS was designed for use by toxicologists and decision-makers who must evaluate the risk posed by use of a new chemical, based on a forecast from the model. The EXAMS program is itself part of a "hazard evaluation system," and the structure of the program was necessarily strongly influenced by the niche perceived for it in this "system."

Many intermediate technical issues arise during the development of a systems model. Usually these issues can be resolved in several ways; the modeling "style" or design strategy used to build the model guides the choices taken among the available alternatives. The strategy used to formulate EXAMS begins from a primary focus on the needs of the intended user and, other things being equal, resolves most technical issues in favor of the more efficient computation. For example, all transport and transformation processes are driven by internal resource factors (pH, temperature, water movements, sediment deposition and scour, etc.) in the system, and each deserves separate treatment in the model as an individual state variable or function of several state variables. The strategy of model development used for EXAMS suggests, however, that the only state variable of any transcendent interest to the user is the concentration of the chemical itself in the system compartments. EXAMS thus treats all environmental state variables as coefficients describing the state of the ecosystem, and only computes the implications of that state, as residual concentrations of chemicals in the system.

Although this approach vastly simplifies the mathematical model, with corresponding gains in efficiency and speed, the system definition is now somewhat improper. System resources (factors affecting performance that are subject to feedback control) have been redefined as part of the system environment. In fact, the "system" represented by the model is no longer an aquatic ecosystem, but merely a chemical pollutant. Possible failure modes of the model are immediately apparent. For example, introduction of a chemical subject to alkaline hydrolysis and toxic to plant life into a productive lake would retard primary productivity. The decrease in primary productivity would lead to a decrease in the pH of the system and, consequently, a decrease in the rate of hydrolysis and an increase in the residual concentration of the toxicant. This sequence of events would repeat itself indefinitely, and constitutes a positive feedback loop that could in reality badly damage an ecosystem. Given the chemical buffering and functional redundancy present in most real ecosystems, this example is inherently improbable, or at least self-limiting. More importantly, given the initial EEC, the environmental toxicologist could anticipate the potential hazard.

There is a more telling advantage, moreover, to the use of environmental descriptors in preference to dynamic environmental state variables. Predictive ecosystem models that include all the factors of potential importance to the kinetics of toxic pollutants are only now being

developed, and will require validation before any extensive use. Furthermore, although extremely fine-resolution (temporal and spatial) models are often considered an ultimate ideal, their utility as components of a fate model for synthetic chemicals remains suspect. Ecosystems are driven by meteorological events, and are themselves subject to internal stochastic processes. Detailed weather forecasts are limited to about nine days, because at the end of this period all possible states of the system are equally probable. Detailed ecosystem forecasts are subject to similar constraints (Platt et al. 1977). For these reasons, EXAMS was designed primarily to forecast the prevailing climate of chemical exposures, rather than to give detailed local forecasts of EECs in specific locations.

B.1.5.2 Temporal and Spatial Resolution

When a synthetic organic chemical is released into an aquatic ecosystem, the entire array of transport and transformation processes begins at once to act on the chemical. The most efficient way to accommodate this parallel action of the processes is to combine them into a mathematical description of their total effect on the rate of change of chemical concentration in the system. Systems that include transport processes lead to partial differential equations, which usually must be solved by numerical integration. The numerical techniques in one way or another break up the system, which is continuously varying in space and time, into a set of discrete elements. Spatial discrete elements are often referred to as "grid points" or "nodes", or, as in EXAMS, as "compartments." Continuous time is often represented by fixing the system driving functions for a short interval, integrating over the interval, and then "updating" the forcing functions before evaluating the next time-step. At any given moment, the behavior of the chemical is a complicated function of both present and past inputs of the compound and states of the system.

EXAMS is oriented toward efficient screening of a multitude of newly invented industrial chemicals and pesticides. Ideally, a full evaluation of the possible risks posed by manufacture and use of a new chemical would begin from a detailed time-series describing the expected releases of the compound into aquatic systems over the entire projected history of its manufacture. Given an equivalently detailed time-series for environmental variables, machine integration would yield a detailed picture of EECs in the receiving water body over the entire period of concern. The great cost of this approach, however, militates against its use as a screening tool. Fine resolution evaluation of synthetic chemicals can probably be used only for compounds that are singularly deleterious and of exceptional economic significance.

The simplest situation is that in which the chemical loadings to systems are known only as single estimates pertaining over indefinite periods. This situation is the more likely for the vast majority of new chemicals, and was chosen for development of EXAMS. It has an additional advantage. The ultimate fate and exposure of chemicals often encompasses many decades, making detailed time traces of EECs feasible only for short-term evaluations. In EXAMS, the environment is represented via long-term average values of the forcing functions that control the behavior of chemicals. By combining the chemistry of the compound with average properties of the ecosystem, EXAMS reduces the screening problem to manageable proportions. These simplified "first-order" equations are solved algebraically in EXAMS's steady-state Mode 1 to give the ultimate (i.e., steady-state) EECs that will eventually result from the input loadings. In addition, EXAMS provides a capability to study initial value problems ("pulse loads" in Mode 2), and seasonal dynamics in which environmental driving forces are updated on a monthly basis

(Mode 3). Mode 3 is particularly valuable for coupling to the output of the PRZM model, which can provide a lengthy time-series of contamination events due to runoff and erosion of sediments from agricultural lands.

Daily pesticide export values from PRZM are transferred to EXAMS as "pulse loading" events at the beginning of the day. The peak concentration on that day is then reported by EXAMS as the average of the start-of-day and end-of-day values. This approximation of PRZM runoff events does not introduce a gross distortion of the facts: For a 1-ha 2-m deep pond with an initial concentration of 1 mg/L of a pesticide with a 2-day half-life, EXAMS reports a first-day peak of 0.854 mg/L. If the same amount of pesticide is permitted to enter the pond as a steady load over 24 hours, the peak value is 0.849 mg/L, occurring at the end of the 24 hour period. If the load were to enter over a run-off duration of 4 hours, the pond would achieve a peak concentration of 0.989 mg/L.

Transport of a chemical from a loading point into the bulk of the system takes place by advected flows and by turbulent dispersion. The simultaneous transformations presently result in a continuously varying distribution of the compound over the physical space of the system. This continuous distribution of the compound can be described via partial differential equations. In solving the equations, the physical space of the system must be broken down into discrete elements. EXAMS is a compartmental or "box" model. The physical space of the system is broken down into a series of physically homogeneous elements (compartments) connected by advective and dispersive fluxes. Each compartment is a particular volume element of the system, containing water, sediments, biota, dissolved and sorbed chemicals, etc. Loadings and exports are represented as mass fluxes across the boundaries of the volume elements; reactive properties are treated as point processes within each compartment.

In characterizing aquatic systems for use with EXAMS, particular attention must be given the grid-size of the spatial net used to represent the system. In effect, the compartments must not be so large that internal gradients have a major effect on the estimated transformation rate of the compound. In other words, the compartments are assumed to be "well-mixed," that is, the reaction processes are not slowed by delays in transporting the compound from less reactive to more reactive zones in the volume element. Physical boundaries that can be used to delimit system compartments include the air-water interface, the thermocline, the benthic interface, and perhaps the depth of bioturbation of sediments. Some processes, however, are driven by environmental factors that occur as gradients in the system, or are most active at interfaces. For example, irradiance is distributed exponentially throughout the water column, and volatilization occurs only at the air-water interface. The rate of these transformations may be overestimated in, for example, quiescent lakes in which the rate of supply of chemical to a reactive zone via vertical turbulence controls the overall rate of transformation, unless a relatively fine-scale segmentation is used to describe the system. Because compartment models of strongly advected water masses (rivers) introduce some numerical dispersion into the calculations, a relatively fine-scale segmentation is often advisable for highly resolved evaluations of fluvial systems. In many cases the error induced by highly reactive compounds will be of little moment to the probable fate of the chemical in that system, however. For example, it makes little difference whether the photolytic half-life of a chemical is 4 or 40 minutes; in either case it will not long survive exposure to sunlight.

B.1.5.3 Assumptions

EXAMS has been designed to evaluate the consequences of longer-term, primarily time-averaged chemical loadings that ultimately result in trace-level contamination of aquatic systems. EXAMS generates a steady-state, average flow field (long-term or monthly) for the ecosystem. The program thus cannot fully evaluate the transient, concentrated EECs that arise, for example, from chemical spills. This limitation derives from two factors. First, a steady flow field is not always appropriate for evaluating the spread and decay of a major pulse (spill) input. Second, an assumption of trace-level EECs, which can be violated by spills, has been used to design the process equations used in EXAMS. The following assumptions were used to build the program.

- A useful evaluation can be executed independently of the chemical's actual effects on the system. In other words, the chemical is assumed not to itself radically change the environmental variables that drive its transformations. Thus, for example, an organic acid or base is assumed not to change the pH of the system; the compound is assumed not to itself absorb a significant fraction of the light entering the system; bacterial populations do not significantly increase (or decline) in response to the presence of the chemical.

- EXAMS uses linear sorption isotherms, and second-order (rather than Michaelis-Menten-Monod) expressions for biotransformation kinetics. This approach is known to be valid for the low concentrations of typical of environmental contaminants; its validity at high concentrations is less certain. EXAMS controls its computational range to ensure that the assumption of trace-level concentrations is not grossly violated. This control is keyed to aqueous-phase (dissolved) residual concentrations of the compound: EXAMS aborts any analysis generating EECs in which any dissolved species exceeds 50% of its aqueous solubility (see Section 2.2.2 for additional detail). This restraint incidentally allows the program to ignore precipitation of the compound from solution and precludes inputs of solid particles of the chemical. Although solid precipitates have occasionally been treated as a separate, non-reactive phase in continuous equilibrium with dissolved forms, the efficacy of this formulation has never been adequately evaluated, and the effect of saturated concentrations on the linearity of sorption isotherms would introduce several problematic complexities to the simulations.

- Sorption is treated as a thermodynamic or constitutive property of each segment of the system, that is, sorption/desorption kinetics are assumed to be rapid compared to other processes. The adequacy of this assumption is partially controlled by properties of the chemical and system being evaluated. Extensively sorbed chemicals tend to be sorbed and desorbed more slowly than weakly sorbed compounds; desorption half-lives may approach 40 days for the most extensively bound compounds. Experience with the program has indicated, however, that strongly sorbed chemicals tend to be captured by benthic sediments, where their release to the water column is controlled by their availability to benthic exchange processes. This phenomenon overwhelms any accentuation of the speed of processes in the water column that may be caused by the assumption of local equilibrium.

B.2 Verification of EXAMS

B.2.1 Background

H-EXAMS was subjected to a series of tests to verify that the software accurately performs its prescribed computations. Model output was compared with different analytical solutions for a set of simplified test cases. These verification tests should be distinguished from model validation, in which model predictions are compared against observed data. The tests documented here were intended to verify that EXAMSIO correctly implements EXAMS within the HWIR system. In addition, the tests verify that EXAMS accurately reproduces the expected analytical solutions.

H-EXAMS must automatically construct and execute a simulation for each water body system at a site using the HWIR databases that are generated by each Monte-Carlo iteration in a FRAMES-HWIR implementation. The general steps in a simulation are to construct a proper water body network, conduct a water balance, conduct a solids balance, and calculate chemical transport and fate. These general steps form the structure of the module testing program. The general requirements of the surface water module are presented in Table B-1, along with specific test identification numbers.

Each of these general steps requires that the module read data from one or more of the HWIR databases, make intermediate calculations, write data to one or more intermediate EXAMS batch files, and transfer the intermediate data into a spawned EXAMS application. Steps 5 through 9 further require EXAMS to make intermediate calculations, conduct a simulation for a specified period, and transfer simulation results to an intermediate EXAMS output file. Steps 4, 5, 7, and 9 require the module to read the data in the EXAMS output file and produce a properly-averaged and formatted HWIR output file. Finally, Step 10 requires the module to perform all calculations without fatal error across a variety of sites, waste management units, and chemicals.

Table B-1. General Requirements for Testing the Surface Water Module

Step	Description	Test Number
1	Construct the water body network (section 3)	1.0, 2.0, 3.0
2	Construct dispersive exchanges (section 4)	1.0, 2.0, 3.0
3	Conduct the water balance (section 5)	1.0, 2.0, 3.0
4	Calculate solids transport (section 6)	1.0, 2.0, 3.0
5	Calculate conservative chemical transport (Section 7)	1.0, 2.0, 3.0
6	Calculate ionic speciation for ionizing organic chemicals (Section 8)	1.1, 1.2
7	Calculate partitioning to solids and DOC (Section 9)	3.1, 3.2
8	Calculate volatilization loss (Section 10)	3.3(a,b,c), 3.4(a-h), 3.5(a,b)
9	Calculate chemical transformation (Section 11)	1.3(a-d), 1.4
10	Test for robustness (Section 12)	4.1 - 4.6, 5.1 - 5.5, 6.1 - 6.5

All tests in Steps 1 through 9 were done using one of three simplified water body networks present at a hypothetical site (Figure B-2). The compartment structures for the three test water body networks are illustrated in Figure B-3. The first two networks are simple one-reach water bodies. Network 1 is a pond with outflow, and network 2 is a lake with no surface

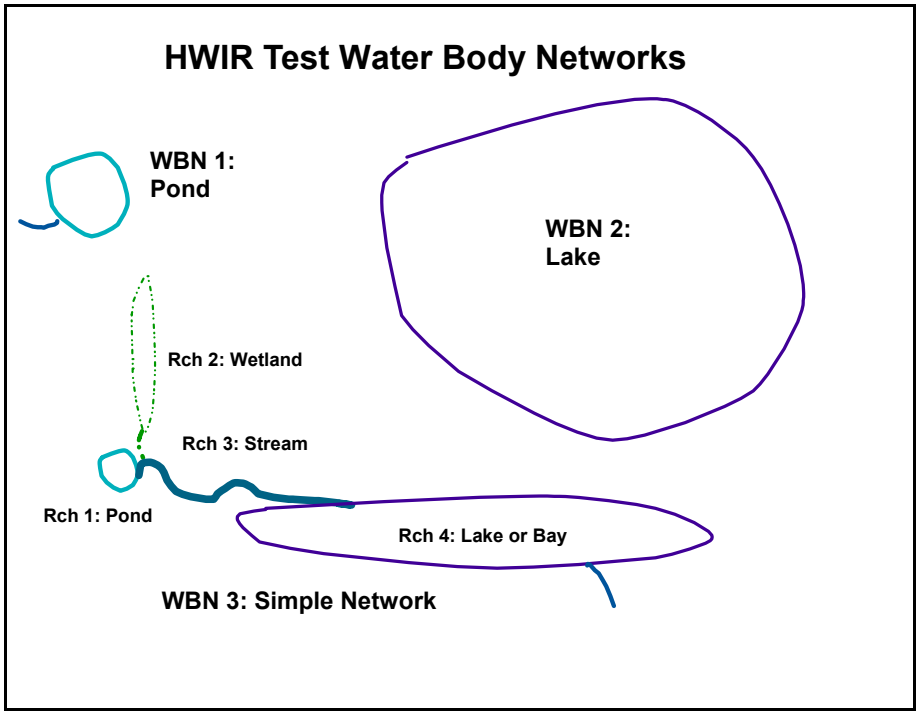

Figure B-2. HWIR test water body networks.

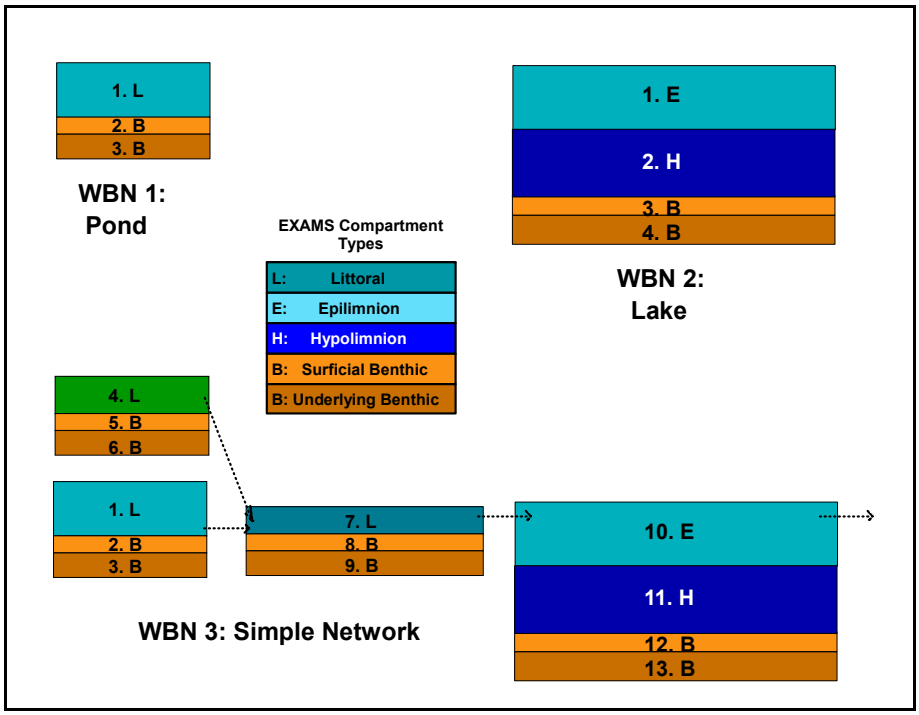

Figure B-3. EXAMS water body compartment networks.

outflow. Network 3 is composed of four reaches. Two headwaters reaches (1 and 2) are connected to reach 3, which is connected to exiting reach 4. The reaches are designated pond, wetland, stream, and lake, respectively. All tests on WBN3 were repeated with reach 4 designated "Bay". Results in both cases should be identical. Analytical solutions based on the mass balance principal were used for loading, transport, and transformation tests. Basic chemical principals and formulas were used to test speciation and partitioning. The robustness tests in Step 10 required operation of the surface water module within the HWIR production system. These tests confirm that EXAMSIO converts HWIR site and reach information into the proper EXAMS compartment structures with valid geometry.

B.2.2 Water Body Network

These tests confirm that EXAMSIO converts HWIR site and reach information into the proper EXAMS compartment structures with valid geometry. The compartment structures for the three test water body networks are illustrated in Figure B-3. The EXAMS variables being verified in Step 1 include the following:

- Type Segment, the compartment type
- AREA, the compartment surface area
- DEPTH, the compartment mean depth
- LENGth, the compartment length
- WIDTH, the compartment width

The first water body network is a simple pond. The purpose of this test was to verify that the module constructs the proper water column and benthic compartment structure with valid geometry. The second water body network is a simple lake with no exiting surface water flow. The purpose of this test is to verify that the module constructs the proper epilimnion, hypolimnion, and benthic compartment structure with valid geometry. The third water body network contains four reaches. A headwaters pond and a headwaters wetland drain into a common stream reach, which empties into a downstream lake. The purpose of this test is to verify that the module constructs this reach network containing the proper water column and benthic compartment structure with valid geometry. Examination of the EXAMS output files confirmed that the structure and geometry were transferred properly in all three cases.

B.2.3 Dispersion Parameters

The next series of tests is for proper dispersion pathways and coefficients. These tests confirm that EXAMSIO converts HWIR reach connectivity information into the proper EXAMS dispersive transport fields with proper dispersion coefficients. For the simple HWIR networks, longitudinal dispersion between reaches is not simulated. Within all reaches, pore water diffusion is modeled between the two benthic compartments and bulk exchange is modeled between the surficial benthic compartment and the water column compartment (the lower hypolimnetic compartment for lakes and bays). For lakes and bays, dispersion across the thermocline separating the epilimnion from the hypolimnion is also modeled. Surface area is specified in the site layout file "SL.ssf" for ponds, wetlands, lakes, and bays, and calculated for stream reaches. Dispersion coefficients are specified in the surface water input files for each network. The EXAMS variables being verified in Step 2 include the following:

- JTURB, the first exchange compartment number
- ITURB, the second exchange compartment number
- XSTUR, the exchange cross-sectional area
- CHARL, the characteristic mixing length
- DSP, the dispersion coefficient

The purpose of this test was to verify that the module constructs the proper dispersion pathways between the water column and benthic compartments, and that the proper dispersion coefficients were assigned. The first water body network is a simple pond. The two dispersion pathways—water column to surface benthic layer and surface benthic layer to underlying benthic layer—were set up and coefficients were transferred from the HWIR databases appropriately. The second water body network is a simple lake. The three dispersion pathways—epilimnion to hypolimnion, hypolimnion to surface benthic layer, and surface benthic layer to underlying benthic layer—were set up and coefficients were transferred from the HWIR databases appropriately. The third water body network contains stream, wetland, pond, and lake reaches. Proper vertical dispersion pathways were set up for each reach, and coefficients were transferred from the HWIR databases appropriately.

B.2.4 Water Balance

The next set of tests is for proper water balances. These tests confirm that EXAMSIO converts HWIR reach connectivity and inflow information into the proper EXAMS advective transport fields with proper compartment inflows. For all water body networks at a site, various HWIR data files specify reach-reach and watershed subbasin-reach connectivity, baseflow and runoff flow to each reach, annual average precipitation and evaporation, and upstream inflows.

The EXAMS variables being verified in Step 3 include the following:

- RAIN, the total yearly rainfall rate
- EVAP, the total yearly evaporation rate
- NPSFL, the total yearly watershed runoff flow
- SEEPS, the total yearly groundwater seepage inflow
- JFRAD, the upstream compartment number for flow path
- ITOAD, the downstream compartment number for flow path
- ADVPR, the advection parameter for flow path

B.2.4.1 Water Body Network 1

The first water body network is a simple pond with exiting surface water flow. The purpose of this test is to verify that the module constructs the proper advection pathways through the water column and benthic compartments, and that the proper inflows are assigned. Rainfall and evaporation data read from the meteorological file were verified in the EXAMS output tables. Watershed runoff and baseflow were mapped from the proper watershed subbasin, and runoff volumes were passed to EXAMS with appropriate units conversion. Converting watershed baseflow into EXAMS seepage inflow takes extra calculational steps to account for evaporation losses. These calculations were checked to confirm that seepage flow was determined as intended.

The advection pathways are set up using reach type and connectivity information in the site layout file. In this case, the single reach is designated "exiting," so the first pathway was set up from water column compartment 1 to 0, with an advection parameter of 1.0 (indicating that all excess flow in compartment 1 leaves by this pathway). In addition, vertical pathways were set up to route seepage water from lower benthic segment to upper benthic segment, and from there to the water column. The advection parameters for seepage were also set to 1, indicating that all excess flow is directed upward. This advective flow connectivity was confirmed by inspection of the EXAMS output files. These tests confirm the inflows and advection pathways set up and transferred by EXAMSIO for this water body. For this simple pond, annual reach flow is the sum of seepage and watershed inflow along with precipitation and evaporation flows. EXAMS does not provide tables to allow direct confirmation of calculated internal flows. These were confirmed indirectly by checking conservative mass balances.

B.2.4.2 Water Body Network 2

The second water body network is a simple lake with no exiting surface water flow. The purpose of this test is to verify that the module constructs the proper advection pathways through the water column and benthic compartments, and that the proper inflows are assigned. Rainfall and evaporation data read from the meteorological file were verified in the EXAMS output tables. Watershed runoff and baseflow were mapped from the proper watershed subbasin, and runoff volumes were passed to EXAMS with appropriate units conversion. Conversion of watershed baseflow into EXAMS seepage inflow was checked to confirm that seepage flow was determined as intended.

The advection pathways are set up using reach type and connectivity information in the site layout file. In this case, the single reach is designated "other," indicating no surface exiting pathway. Excess flow, then, is routed as seepage loss. The first pathway is set up from epilimnion to hypolimnion, with an advection parameter of 1.0 (indicating that all excess flow in compartment 1 leaves by this pathway). Additional downward pathways are set up to route seepage outflow from hypolimnion to upper benthic compartment , from there to lower benthic compartment , and thence of the system. In addition, upward seepage inflow pathways are set up from lower benthic compartment to upper benthic compartment, from there to the hypolimnion compartment, and finally to the epilimnion. The total seepage outflow is the sum of the net surface inflow (runoff plus precipitation minus evaporation) and the subsurface seepage inflow. The total recirculating flow crossing the lower benthic interface is the sum of the subsurface seepage inflow and the total seepage outflow. The advection parameters for downward seepage are set to the total seepage outflow divided by the total recirculating flow; the complimentary advection parameters for upward seepage are set to the subsurface seepage inflow divided by the total recirculating flow. This advective flow connectivity was confirmed by inspection of the EXAMS output files. These tests confirm the inflows and advection pathways set up and transferred by EXAMSIO for this water body. For this simple pond, annual reach flow is the sum of seepage and watershed inflow along with precipitation and evaporation flows. EXAMS does not provide tables to allow direct confirmation of calculated internal flows. These were confirmed indirectly by checking conservative mass balances.

B.2.4.3 Water Body Network 3

The third water body network contains four reaches. A headwaters pond and a headwaters wetland drain into a common stream reach, which empties into a downstream lake. The purpose of this test is to verify that the module constructs the proper advection pathways through the water column and benthic compartments, and that the proper inflows are assigned. Rainfall and evaporation data read from the meteorological file were verified in the EXAMS output tables. Watershed runoff and baseflow were mapped from the proper watershed subbasin, including fractional flow pathways from a watershed to different reaches. Runoff volumes were passed to EXAMS with appropriate units conversion. Conversion of watershed baseflow into EXAMS seepage inflow was checked to confirm that seepage flow was determined as intended.

The advection pathways are set up using reach type and connectivity information in the site layout file. First, pathways are determined for surface water flow among compartments 1, 4, 7, and 10. In this case, reach 4 is an exiting reach, and all excess water in its surface water compartment (10) is routed outside the network (i.e., to 0). Thus a flow pathway from 10 to 0 with an advective fraction 1.0 is set up (see Table B.10 below). WBNRchNumRch indicates that one upstream reach is connected to reach 4. WBNRchRchIndex specifies that the upstream reach index is 3, and WBNRchRchFrac specifies that 100% of the excess flow in reach 3 is routed to 4. Thus a flow pathway from EXAMS compartment 7 to 10 is set up with an advection fraction of 1.0. Finally, WBNRchNumRch indicates that two upstream reaches are connected to reach 3. WBNRchRchIndex specifies that the upstream reach indexes are 1 and 2; WBNRchRchFrac specifies that 100% of the excess flow in reaches 1 and 2 are routed to 3. Thus flow pathways from EXAMS compartment 1 to 7 and from 4 to 7 are set up with advection fractions of 1.0. The four surface water pathways are confirmed by inspection of EXAMS output tables.

Next, upward seepage pathways are set up from the lower benthic compartments in each reach. These pathways route seepage water from the lower benthic compartment to the upper benthic compartment, and from the upper benthic compartment to the surface water. For lakes, seepage water entering the hypolimnion is further routed to the epilimnion. Because in this network all surface water is routed downstream with no seepage loss, the upward advection fractions are set to 1.0. The nine seepage flow pathways are confirmed by inspection of EXAMS output tables.

B.2.5 Solids Balance

The next set of tests is for proper solids transport. These tests confirm that EXAMSIO converts HWIR solids loading information into the proper EXAMS solids concentrations. These tests also confirm that EXAMSIO properly translates HWIR solids properties into EXAMS compartment solids properties. For all water body networks at a site, the HWIR data files provide watershed subbasin-reach connectivity, solids organic carbon fractions, solids erosion loadings to each reach, upstream inflows, and sediment properties.

The EXAMS variables being verified in Step 4 include the following:

- SUSED, the water column compartment suspended solids concentration
- BULKD, the benthic compartment bulk density

- PCTWA, the benthic compartment percent water
- FROC, the fraction organic solids

In addition, the HWIR output variable WBNTSSWater is being verified in step 4. These calculations not only verify the solids computations in the surface water module, but also the internal flow computations.

B.2.5.1 Water Body Network 1

The first water body network is a simple pond with exiting surface water flow. The purpose of this test is to verify that the module reads the proper pond sediment properties and solids loadings, and correctly executes a conservative solids mass transport in a single pond reach. First, basic pond sediment properties were verified, including sediment organic carbon content along with bulk density and "percent water," which are calculated from porosity and dry density.

Next, the water column suspended solids concentrations were checked. EXAMSIO calculates the total suspended solids concentration as the sum of in-stream background contributions from bank erosion and primary productivity, and external contributions from watershed erosion. The bank erosion contribution and productivity contributions were correctly set to 1.0 and 0.60 mg/L, respectively. Thus, background solids concentration is 1.6 mg/L.

The annual watershed contribution to solids is calculated by dividing the annual watershed erosion loading by the annual reach flow. In this test, erosion loadings from watershed subbasin 5 for the first three years are 100000,10000, and 1000000 g/day. Reach flows for the first three years are 150, 139, and 160 m^3/day, yielding solids concentrations of 667, 71.9, and 6250 mg/L, respectively. Adding background values, the total suspended solids concentrations for the first three years should be 669, 73.5, and 6252 mg/L. These values are confirmed by comparison with EXAMS output tables.

The final check of this section is for the fraction organic carbon of suspended solids. This is calculated as the weighted average of the organic carbon content of biotic solids and the organic carbon content of abiotic solids. These calculations give a long-term average abiotic solids concentration of 2144 mg/L and an average organic carbon fraction of (2144 * 0.05 + 0.6 * 0.25) / 2145, or 0.0501. This organic carbon fraction is confirmed in EXAMS output tables.

B.2.5.2 Water Body Network 2

The second water body network is a simple lake with no exiting surface water flow. The purpose of this test is to verify that the module reads the proper lake sediment properties and solids loadings, and correctly executes a conservative solids mass transport in a single lake reach. First, basic lake sediment properties were verified, including sediment organic carbon content along with bulk density and "percent water," which are calculated from porosity and dry density.

Next, the water column suspended solids concentrations were checked. The bank erosion contribution and productivity contributions were correctly set to 1.0 and 0.60 mg/L, respectively, giving a total background solids concentration of 1.6 mg/L. The annual watershed contribution

to solids is calculated by dividing the annual watershed erosion loading in WS.grf by the annual reach flow. In this test, erosion loadings from watershed subbasin 6 are 100000 g/day every year. Reach flows for the first 3 years are 525, 945, and 2002, yielding solids concentrations of 190, 106, and 50.0 mg/L, respectively. Adding background values, the total suspended solids concentrations for the first three years should be 192, 107, and 51.6 mg/L. These values are confirmed by comparison with EXAMS output tables.

The final check of this section is for the fraction organic carbon of suspended solids. This is calculated as the weighted average of the organic carbon content of biotic solids and the organic carbon content of abiotic solids. These calculations give a long-term average abiotic solids concentration of 100 mg/L and an average organic carbon fraction of (100 * 0.05 + 0.6 * 0.25) / 101, or 0.0512. This organic carbon fraction is confirmed in EXAMS output tables.

B.2.5.3 Water Body Network 3

The third water body network contains four reaches. A headwaters pond and a headwaters wetland drain into a common stream reach, which empties into a downstream lake. The purpose of this test is to verify that the module reads the proper lake, river, pond, and wetland sediment properties and solids loadings, and correctly executes a conservative solids mass transport in a multiple reach system. First, basic sediment properties were verified, including sediment organic carbon content along with bulk density and "percent water," which are calculated from porosity and dry density.

Next, the water column suspended solids concentrations were checked. The bank erosion contribution is simply set to a minimum background value of 5 mg/L in stream reaches and 1 mg/L in non-stream reaches. The incremental reach bank loadings are equal to the product of reach flows and these background concentrations. Given the reach flows of 1000, 1000, 3500, and 3996 m^3/day, the corresponding bank erosion loadings are 1000, 1000, 17500, and 3996 g/day. The annual watershed contribution to solids is calculated by dividing the annual watershed erosion loading by the annual reach flow. In this test, erosion loadings from watershed subbasins1 through 4 are a constant 100,000 g/day. Loadings from subbasins 1, 2, and 3 are mapped 100% to reaches 1, 2, and 3, respectively. Subbasin 4 loadings are split, 50% going to reach 3 and 50% going to reach 4. The resulting total watershed loadings are 100000, 100000, 150000, and 50000 g/day to reaches 1 through 4, respectively.

Total cumulative abiotic solids loadings to reaches 1 through 4 are 101000, 101000, 369500, and 423496 g/day. Dividing by corresponding reach flows yields abiotic solids concentrations of 101, 101, 105.6, and 106.0 mg/L in reaches 1 through 4. Adding biotic solids concentrations gives total solids concentrations of 101.6, 103, 106.6, and 107.5 mg/L. These values are confirmed in EXAMS output tables.

The final check of this section is for the fraction organic carbon of suspended solids. This is calculated as the weighted average of the organic carbon content of biotic and abiotic solids. The weighted average organic carbon fractions are 0.0512, 0.0539, 0.0518, and 0.0527, and are confirmed in EXAMS output tables.

B.2.6 Chemical Loadings and Conservative Transport

External loadings of a toxicant can enter the ecosystem via point sources, non-point sources, dry fallout or aerial drift, atmospheric wash-out, and ground-water seepage entering the system. This Step 5 test verifies that chemical loadings are passed to EXAMS and transported through the EXAMS water body compartments properly. Four chemical loading pathways are employed – watershed runoff, direct source runoff, seepage inflow, and atmospheric deposition. These tests confirm that EXAMSIO converts HWIR chemical loading information into the proper EXAMS chemical loadings. These tests also confirm that EXAMS properly transports conservative (non-reactive) chemicals through the water body networks, yielding correct concentrations.

The EXAMS variables verified in Step 5 include the following:

- Rainfall, the total atmospheric deposition loading
- Drift, the source runoff loading
- NPS Loads, the watershed runoff and erosion loading
- Seeps, the groundwater seepage loading

In addition, the HWIR output water column concentration were also verified in step 5.

B.2.6.1 Water Body Network 1

The first water body network is a simple pond with exiting surface water flow. The purpose of this test is to verify that the module reads the proper source, atmospheric, and seepage loadings, and correctly executes conservative chemical mass transport in a single reach.

Three types of chemical loadings to the first water body network were tested – source runoff, atmospheric deposition, and groundwater seepage Loading pathways and time variable loading values were specified, including a constant source runoff for the first 10 years, variable wet deposition flux for the first 5 years, and variable groundwater seepage loading for years 20 through 60. All loadings were transferred properly as verified in EXAMS output tables.

Given these loadings and the reach flows, water column concentrations for this non-reactive chemical can be calculated and compared with model output in the surface water output file. Calculated concentrations for each year should equal the total annual load divided by the annual flow. These were confirmed by the time history from the surface water output file. These tests confirmed not only that the loadings are applied correctly within EXAMS, but also that the mass balance was conducted correctly, and that results were correctly averaged and transferred by the EXAMSIO postprocessor to the HWIR output file for use by exposure and risk modules.

B.2.6.2 Water Body Network 2

The second water body network is a simple lake with no exiting surface water flow. The purpose of this test was to verify that the module reads the proper atmospheric, watershed, and groundwater loadings, and applies them correctly within EXAMS.

Three types of chemical loadings to the second water body network were tested – watershed runoff, atmospheric deposition, and groundwater seepage. Loading pathways and time variable loading values were specified, including variable watershed runoff for the first 20 years, constant particle dry and wet deposition fluxes for years 1 through 15, and variable groundwater seepage loading for years 20 through 60. All loadings were transferred properly as verified in EXAMS output tables. Predicted concentrations cannot be easily confirmed because of the complications due to the two-layer water column.

B.2.6.3 Water Body Network 3

The third water body network contains four reaches. A headwaters pond and a headwaters wetland drain into a common stream reach, which empties into a downstream lake. The purpose of this test was to verify that the module reads the proper source, atmospheric, watershed, and groundwater loadings, and correctly executes a conservative chemical mass transport in a simple network.

Four types of chemical loadings to the third water body network were tested – source runoff, atmospheric deposition, watershed runoff, and groundwater seepage. Split and multiple loading pathways were specified for this test. Two source runoff pathways were specified, with constant loadings over the first 10 years. Four constant vapor wet, particle dry, and particle wet deposition fluxes were specified to reach 4 for years 1 through 10. Constant watershed runoff loadings over 15 and 20 years were specified from sub-basins 1 through 4, with runoff from sub-basin 4 directed to two separate reaches. Finally, two groundwater plumes were specified for years 20–60, with 50% of the loading from plume 2 directed to one reach. All loadings were transferred properly as verified in EXAMS output tables.

Calculated concentrations for each year should equal the total annual load to a reach divided by the total annual flow. These are confirmed (with minor deviations in the third significant figure) in the time history from the surface water output file for reaches 1 through 3, which have a single water column layer. For reach 4, EXAMS calculates separate concentrations in the epilimnion and the hypolimnion, and reports volume-weighted average concentrations in the output file. These average concentrations should generally be a bit lower than the total load divided by the total flow, depending on the relative rates of mixing across the thermocline versus outflow. This is confirmed in the output file.

These tests confirm not only that the loadings were applied correctly within EXAMS, but also that the mass balance was conducted correctly, and that results were correctly averaged and transferred by the EXAMSIO postprocessor to the HWIR output file for use by exposure and risk modules.

B.2.7 Ionization

Ionization of organic acids and bases are treated by EXAMS as thermodynamic properties or (local) equilibria that alter the operation of kinetic processes. For example, an organic base in the water column may occur in a number of molecular species (as dissolved ions, sorbed with sediments, etc.), but only the uncharged, dissolved species can be volatilized across the air-water interface. EXAMS allows for the simultaneous treatment of up to 28 molecular species of a chemical. These include the parent uncharged molecule, and singly, doubly, or triply charged

cations and anions, each of which can occur in a dissolved, sediment-sorbed, DOC-complexed, or biosorbed form. The program computes the fraction of the total concentration of compound that is present in each of the 28 molecular structures (the "distribution coefficients," α).

A series of simulations was run with the simple pond (water body network 1) to confirm that water body pH and chemical dissociation constant values are passed properly to EXAMS, and that EXAMS calculates ionic speciation correctly. Simulation output was compared with theoretical calculations based on equations presented in section B.2.4.1 of the documentation report (Ambrose and Burns, 2000; U.S. EPA, 1999).

The EXAMS variables being verified in Step 6 include the following:

- Chemical Species (0) and (-1), the ratio of the first ionization for an organic acid
- Chemical Species (-1) and (-2), the ratio of the second ionization for an organic acid
- Chemical Species (0) and (+1), the ratio of the first ionization for an organic base
- Chemical Species (+1) and (+2), the ratio of the second ionization for an organic base

B.2.7.1 Organic Acids

Test 1.1 is a series of simulations run for organic acids, as outlined below. The purpose of this series of tests is to verify that the module reads the proper pH and pKa data and correctly executes the indicated dissociation reactions, giving the proper proportions of the neutral molecule RH_3, the singly charged anion RH_2^-, and the doubly charged anion RH^{2-}. The (negative log) dissociation constants pK_{a1} and pK_{a2} were set to 6 and 8, respectively, and a series of simulations were run with water body pH varying from 9 to 5. For each simulation, results are verified by inspection of the EXAMS summary output file report.xms,

Ratios of chemical species by valency in any segment can be compared directly to theoretical species ratios. For the series of simulations in this test, EXAMS chemical species concentrations are converted to percentages of the total concentration, and presented along with theoretical species ratios in the following table (Table B-2). These tests confirmed that EXAMS is receiving and processing the organic acid ionization data properly.

Table B-2. Speciation Calculations for Organic Acids

pH	Theoretical Species Ratios for pK_{a1}=6, pK_{a2}=8		EXAMS Speciation Calculations, percent		
	RH_3/RH_2^-	RH_2^-/RH^{2-}	RH_3	RH_2^-	RH^{2-}
9	10^{-3}	10^{-1}	0.0091	9.1	91.
8	10^{-2}	10^{0}	0.50	50.	50.
7	10^{-1}	10^{1}	8.3	83.	8.3
6	10^{0}	10^{2}	50.	50.	0.50
5	10^{1}	10^{3}	91.	9.1	0.0091

B.2.7.2 Organic Bases

Test 1.2 is a series of simulations run for organic bases, as outlined below. The purpose of this series of tests is to verify that the module reads the proper pH and pKa data and correctly executes the indicated base dissociation reactions, giving the proper proportions of the neutral molecule RH_3, the singly charged cation RH_4^+, and the doubly charged cation RH_5^{2+}. The (negative log) dissociation constants pK_{a1} and pK_{a2} were set to 8 and 6, respectively, and a series of simulations were run with water body pH varying from 9 to 5. For each simulation, results are verified by inspection of the EXAMS summary output file report.xms.

Ratios of chemical species by valency in any segment can be compared directly to theoretical species ratios. For the series of simulations in this test, EXAMS chemical species concentrations are converted to percentages of the total concentration, and presented along with theoretical species ratios in the following table (Table B-3). These tests confirm that EXAMS is receiving and processing the organic base ionization data properly.

B.2.8 Sorption

Test 3.1 is a series of simulations run for hydrophobic organic chemicals, as outlined below. Two simulations were run with water body network 3 to confirm that chemical partition coefficients and related environmental properties are passed properly to EXAMS, and that EXAMS calculates phase distribution correctly. Simulation output was compared with theoretical concentration ratios based on equations presented in the documentation report. H-EXAMS uses partition coefficients to compute the sorption of a chemical to abiotic solids, biotic solids, and DOC. Coefficients for organic chemicals are processed in a different manner than those for metals, and are tested separately.

Table B-3. Speciation Calculations for Organic Bases

pH	Theoretical Species Ratios for pK_{b1}=8, pK_{b2}=6		EXAMS Speciation Calculations, percent		
	RH_3/RH_4^+	RH_4^+/RH_5^{2+}	RH_3	RH_4^+	RH_5^{2+}
9	10^3	10^1	100.	0.10	0.010
8	10^2	10^0	98.	0.98	0.98
7	10^1	10^{-1}	48.	4.8	48.
6	10^0	10^{-2}	0.98	0.98	98.
5	10^{-1}	10^{-3}	0.010	0.10	100.

The EXAMS variables being verified in Step 7 include the following:

- Chemical Concentrations for Sediments and Dissolved, the ratio by compartment
- Chemical Concentrations for Biota and Dissolved, the ratio by compartment
- Chemical Concentrations for DOC Complexed ($\times 10^{-3}$) and Dissolved, the ratio by compartment

B.2.8.1 Organic Chemicals

The purpose of this test is to verify that the module reads the proper solids organic carbon fractions and DOC concentrations, as well as Koc and Kow values, and correctly executes the phase partitioning reactions giving the proper proportions of the dissolved, sediment-sorbed, DOC-bound, and benthos concentrations. The octanol-water partition coefficient and the organic carbon partition coefficient were set to 400 and 200, respectively.

For organic chemicals, the organic carbon partition coefficient, K_{OC}, is used along with the organic carbon fraction of solids, f_{OC}, to calculate the effective partition coefficient to solids K_{PS}. Given f_{OC} values of 0.05, 0.5, 0.005, and 0.05 for reaches 1 through 4, K_{PS} should be equal to 10, 100, 1 and 10. These values are confirmed in the table (Table B-4) below. EXAMS internally calculates partition coefficients for biotic solids and for DOC based on empirical equations. From these equations, K_{PB} should be 100, and K_{DOC} should be 8 L_W /kg. The unitless partition coefficient K'_{DOC} relating DOC-bound concentrations in mg/L_W to the dissolved DOC concentrations is the product of K_{DOC} and the reach variable DOC concentration (with a units adjustment). DOC concentrations for streams, ponds and lakes, and wetlands were set to 1.25, 12.5, and 125, respectively, giving values of K'_{DOC} of 10^{-5}, 10^{-4}, and 10^{-3}, respectively.

These partition coefficients are summarized in the table below (Table B-4), along with the calculated concentrations at the end of the first year from EXAMS. The relationships between

Table B-4. Organic Chemical Partitioning in WBN 3

Reach, Compartment	Partition Coefficients			EXAMS Concentrations			
	K'_{DOC} L/L	K_{PS} L/kg	K_{PB} L/kg	C_D mg/L	C_{DOC} mg/L	C_S mg/kg	C_B mg/kg
1: Pond	focsed = 0.05, DOC = 12.5 mg/L						
water	10^{-4}	10		6.00e-2	6.00e-6	6.00e-1	-
upper sed	10^{-4}	10	10^2	5.49e-3	5.49e-7	5.49e-2	5.48e-1
lower sed	10^{-4}	10		6.90e-7	6.90e-11	6.90e-6	-
2: Wetland	focsed = 0.50, DOC = 125 mg/L						
water	10^{-3}	10		5.00e-2	5.00e-5	5.00e0	
upper sed	10^{-3}	10^2	10^2	9.49e-3	9.49e-6	9.49e-1	9.49e-1
lower sed	10^{-3}	10^2		2.34e-6	2.34e-9	2.34e-4	
3: Stream	focsed = 0.005, DOC = 1.25 mg/L						
water	10^{-5}	10		5.54e-2	5.54e-7	5.54e-2	
upper sed	10^{-5}	1	10^2	2.03e-2	2.03e-7	2.03e-2	2.03e0
lower sed	10^{-5}	1		4.30e-5	4.30e-10	4.30e-5	
4: Lake	focsed = 0.05, DOC = 12.5 mg/L						
epilimnion	10^{-4}	10		5.53e-1	5.53e-5	5.53e0	
hypolimnion	10^{-4}	10		5.48e-1	5.48e-5	5.48e0	
upper sed	10^{-4}	10	10^2	3.65e-1	3.65e-5	3.65e0	3.65e+1
lower sed	10^{-4}	10		8.94e-4	8.94e-8	8.94e-3	

B.2.8.2 Metals

Test 3.2 is a series of simulations run for metals, as outlined below. The purpose of this test was to verify that the module reads the proper DOC concentrations and chemical partition coefficients, and correctly executes the phase partitioning reactions giving the proper proportions of the dissolved, sediment-sorbed, DOC-bound, and benthos concentrations. In this metals partitioning test, K_{PW} was set to 1000, K_{PSed} was set to 100, K_{PB} was set to 10, and K_{DOC} was set to 80 L/kg. Given DOC concentrations of 1.25, 12.5, and 125 for streams, ponds/lakes, and wetlands, the calculated values of K'_{DOC} are10^{-4}, 10^{-3}, and 10^{-2}, respectively. These partition coefficients are summarized in the table (Table B-5) below, along with the calculated concentrations from EXAMS. The relationships between the dissolved concentration and the chemical concentrations associated with DOC, solids, and biota exactly match the computed partition coefficients, verifying the treatment of sorption for metals.

Table B-5. Metals Partitioning in WBN 3

Reach, Compartment	Partition Coefficients			EXAMS Concentrations			
	K'_{DOC} L/L	K_{PS} L/kg	K_{PB} L/kg	C_D mg/L	C_{DOC} mg/L	C_S mg/kg	C_B mg/kg
1: Pond	DOC = 10 mg/L						
water	10^{-3}	10^{3}		5.44e-2	5.44e-5	5.44e+1	-
upper sed	10^{-3}	10^{2}	10	2.69e-2	2.69e-5	2.69e0	2.69e-1
lower sed	10^{-3}	10^{2}		3.37e-6	3.37e-9	3.37e-4	-
2: Wetland	DOC = 100 mg/L						
water	10^{-2}	10^{3}		4.47e-2	4.47e-4	4.447+1	
upper sed	10^{-2}	10^{2}	10	8.43e-3	8.43e-5	8.43e-1	8.43e-2
lower sed	10^{-2}	10^{2}		2.08e-6	2.08e-8	2.08e-4	
3: Stream	DOC = 1 mg/L						
water	10^{-4}	10^{3}		5.00e-2	5.00e-6	5.00e+1	
upper sed	10^{-4}	10^{2}	10	4.89e-2	4.89e-6	4.89e0	4.89e-1
lower sed	10^{-4}	10^{2}		6.18e-5	6.18e-9	6.18e-3	
4: Lake	DOC = 10 mg/L						
epilimnion	10^{-3}	10^{3}		4.97e-1	4.97e-4	4.97e+2	
hypolimnion	10^{-3}	10^{3}		4.93e-1	4.93e-4	4.93e+2	
upper sed	10^{-3}	10^{2}	10	4.68e-1	4.68e-4	4.68e+1	4.68e0
lower sed	10^{-3}	10^{2}		4.02e-4	4.02e-7	4.02e-2	

B.2.9 Volatilization

A series of simulations was run with water body network 3 to confirm that Henry's Law constant and related environmental properties are passed properly to EXAMS, and that EXAMS calculates volatilization loss rates correctly. Simulation output was compared with calculations based on equations presented in the documentation report (Ambrose and Burns, 2000; U.S. EPA,

1999). H-EXAMS uses the Whitman two-resistance model to calculate volatilization loss rate constants. EXAMS bases the gas transfer term on the wind-driven water vapor exchange velocity, which is calculated in the same way for all water body types. The liquid phase transfer term is based on the oxygen exchange (reaeration) velocity. Different sets of equations are used to calculate the reaeration velocity for flowing and stagnant water bodies. The volatilization equations are tested by manipulating input data for test water body network 3 and examining intermediate calculations for stream reach 3 and pond reach 1.

The EXAMS variables being verified in Step 8 include the following:

- KO2, the reaeration velocity
- WIND, the wind speed at 10 cm height
- Local pseudo-first-order process half-lives for Volatil(ization)

B.2.9.1 Volatilization in Stream Reaches

Test 3.3 is a simulation run for volatile organic chemicals, as outlined below. The purpose of this test was to verify that the module reads the proper volatilization parameter values and correctly executes the volatile loss algorithms in stream reaches.

To fully test the range of computations in the volatilization equations, the Henry's Law constant was varied between 10^{-2}, 10^{-4} and 10^{-6}atm-m^3/mole, and flow between 3500, 10^6, and 10^7 m^3/day. Wind speed averaged 5 m/sec and water temperature was held constant at 20°C. Hydraulic width coefficients $ahyd_W$ and $bhyd_W$ were set to 10 and 0.25, respectively; and hydraulic depth coefficients $ahyd_d$ and $bhyd_d$ were set to 0.5 and 0.4. Molecular weight was set to 278. For each simulation test, several volatilization properties were hand-calculated from the original equations and verified by inspection of the EXAMS summary file. For H of 10^{-6}, the gas phase resistance should control the overall volatilization rate, while for H of 10^{-2}, the liquid phase resistance should control; at 10^{-4}, the gas and liquid phase resistances should contribute almost equally to the overall rate. The results of these tests, summarized in Table B-6 below, verify that the H-EXAMS stream volatilization routines are performing as expected.

Table B-6. Calculated and Simulated Stream Volatilization Half-lives

Flow, m^3/day	Depth, meters	H = 10^{-2} atm-m^3/mole		H = 10^{-4} atm-m^3/mole		H = 10^{-6} atm-m^3/mole	
		Calculated $t_{1/2}$, hr	EXAMS $t_{1/2}$, hr	Calculated $t_{1/2}$, hr	EXAMS $t_{1/2}$, hr	Calculated $t_{1/2}$, hr	EXAMS $t_{1/2}$, hr
3.5×10^3	0.084	1.5	1.5	4.7	4.7	320	320
10^6	1.33	28	28	58	58	3080	3080
10^7	3.35	70	70	147	146	7747	7740

B.2.9.2 Volatilization in Ponds, Wetlands, and Lakes

Volatilization in stagnant water bodies is driven by wind speed. EXAMS proportions the liquid-phase transfer velocity to the reaeration velocity K_{O2}. To calculate reaeration in stagnant water bodies, the theoretically-based equations from O'Connor (1983), summarized in Ambrose and Burns (2000), were used in H-EXAMS. Ponds and wetlands were assumed to be in the

intermediate size class, while lakes and bays were assumed to be in the large size class. Test 3.4 is a series of simulations run for volatile organics, as outlined below. The purpose of these tests is to verify that the module reads the proper values, and correctly executes the non-stream volatile loss algorithms.

The Henry's Law constant (ChemHLC) was set to 0.01 atm-m^3/mole. Several simulations were run with different average wind speeds. For each simulation test, calculated reaeration velocities in reach 1 (pond), reach 2 (wetland) and reach 3 (lake) were extracted from the EXAMS summary output file. The complex calculations are checked against two simpler empirical formulas—Banks (1975) and Baca and Arnett (1976). For purposes of this comparison, the reaeration velocity KO2 was derived from this formula assuming that the mixed surface layer is 1 meter in depth. KO2 values computed from these independent formulas for a range of wind speeds are summarized in the adjacent chart, along with the values calculated for ponds and lakes using the O'Connor equations implemented in H-EXAMS (with units converted from cm/hr to m/day for this comparison). Inspection of the chart (Figure B-4) shows that H-EXAMS reaeration values are within the range of the simpler formulas, providing a general verification of this model component. Most HWIR sites have average annual wind speeds between 3 and 6 m/second. In this range, the O'Connor equations track the Banks equations closely, as summarized in the table (Table B-7) below.

Figure B-4. Comparison of wind-driven reaeration formulas

Table B-7. Wind Speed Effect on Reaeration

Wind Speed, m/sec	Calculated Reaeration Velocity, m/day				
	H-EXAMS Pond	H-EXAMS Lake	Banks	Baca and Arnett, low	Baca and Arnett, high
1	0.19	0.24	0.36	0.091	0.87
2	0.37	0.48	0.51	0.18	1.7
3	0.55	0.71	0.63	0.26	2.6
4	0.74	0.97	0.72	0.35	3.5
5	0.93	1.2	0.81	0.43	4.3
6	1.5	1.9	1.0	0.52	5.2
7	2.2	2.8	1.4	0.61	6.1

B.2.9.3 Effect of Ionization on Volatilization

Test 3.5 is a series of simulations run for volatile organic acids, as outlined below. The purpose of this test was to verify that speciaton parameters from the HWIR chemical and site databases were affecting the volatilization rate properly. In this test, Henry's Law constant was set to 0.01 atm-m^3/mole, and average wind speed was set to 5 m/sec. When no ionization is specified, the volatilization half-lives for the neutral species in reaches 1 through 4 are calculated to be 60, 24, 1.5, and 46 hr, respectively.

For organic acids, Test 3.5a sets up one dissociation with pK_{a1} equal to 9. In subsequent runs, the value is set to 8, 7, 6, and 5. pH is held constant at 7. For each simulation, the internal speciation and volatilization results were examined from EXAMS. First, by inspection, the ratio of the charged species (valency of -1) to the neutral species (valency of 0) compares exactly with theoretical expectations. Next, the fraction neutral (RH_3) was calculated from the individual species concentrations. This fraction neutral at different pKa values should also equal the ratio of the volatilization rate constants under neutral and ionizing conditions. This ratio can be checked by taking the reciprocal of the half-lives under neutral and ionizing conditions in EXAMS. Because half lives are reported to only two significant figures, this comparison does not always match precisely. Nevertheless, to the available accuracy, these results verify that EXAMS is receiving the speciation parameters and producing correct speciation and volatilization results for organic acids (see summary Table B-8 below).

For organic bases, Test 3.5b sets up one dissociation with pK_{b1} equal to 9. In subsequent runs, the value is set to 8, 7, 6, and 5. pH is held constant at 7. The results verify that EXAMS is receiving organic base speciation parameters and producing correct speciation and volatilization results (see summary Table B-9 below).

Table B-8. Speciation and Volatilization of Volatile Organic Acids

pK_{a1}	Theoretical Species Calculations for pH = 7		EXAMS Speciation and Volatilization Calculations				
	RH_3/RH_2^-	fraction RH_3	fraction RH_3	fraction of neutral k_V by reach			
9	10^2	0.990	0.990	1.0	1.0	1.0	.98
8	10^1	0.909	0.909	.91	.92	.88	.90
7	10^0	0.500	0.500	.50	.51	.50	.50
6	10^{-1}	0.0909	0.0909	.091	.092	.088	.091
5	10^{-2}	0.0099	0.0099	.0099	.0100	.0098	.0099

Table B-9. Speciation and Volatilization of Volatile Organic Bases

pK_{b1}	Theoretical Species Calculations for pH = 7		EXAMS Speciation and Volatilization Calculations				
	RH_3/RH_4^+	fraction RH_3	fraction RH_3	fraction of neutral k_V by reach			
9	10^2	0.99	0.990	1.0	1.0	1.0	.98
8	10^1	0.91	0.909	.91	.92	.88	.90
7	10^0	0.50	0.500	.50	.51	.50	.50
6	10^{-1}	0.0909	0.0909	.091	.092	.088	.091
5	10^{-2}	0.0099	0.0099	.0099	.0100	.0098	.0099

B.2.10 Transformation Processes

A series of simulations was run with the simple pond (water body network 1) to confirm that chemical transformation constants along with ancillary environmental information are passed properly to EXAMS, and that EXAMS calculates transformation losses correctly. All transformation tests were run on the simple pond, water body network 1. Simulation output was compared with theoretical calculations based on equations presented in the documentation report (Ambrose and Burns, 2000; U.S. EPA, 1999).

The EXAMS variables being verified in Step 9 include the following:

- Local pseudo-first-order process half-lives for Hydrol(ysis)
- Local pseudo-first-order process half-lives for Biolysis (here, aerobic biodegradation for water column compartments and anaerobic biodegradation for benthic compartments)
- Local pseudo-first-order process half-lives for Reduct(ion)
- Total Chemical Concentrations in the Water Column
- Dissolved Chemical Concentrations in the Benthic Sediments

These are found in Tables 12, 13, and 15 in report.xms. In addition, chemical concentrations are confirmed in SW1.ssf.

B.2.10.1 Organic Chemical Transformations

Test 1.3 is a series of simulations run for organic chemicals. The purpose of this series of tests is to verify that H-EXAMS properly sets ancillary environmental properties to enable the first-order transformation reactions and transfers transformation rate constants from the HWIR chemical database to EXAMS. Further, this series tests whether EXAMS correctly executes the indicated transformation reactions, giving the proper chemical half-lives and water body concentrations.

In each test, one of the HWIR transformation reactions – hydrolysis, aerobic biodegradation, anaerobic biodegradation, and reduction – was enabled by specifying a value for the rate constant in the water body chemical database. As a result, chemical transformation half-lives calculated by EXAMS should be equal to (24 · 0.693/*k)* hours, where *k* is the transformation rate constant in day^{-1}. Steady-state chemical concentrations in any EXAMS compartment should be given by the following equation:

$$C_T = \frac{L_T}{Q + k \cdot f_D \cdot V} \tag{B-1}$$

where C_T is the total chemical concentration, in mg/L, L_T is the total chemical loading, in g/day, Q is the total flow, in m^3/day, *k* is the transformation rate constant, in day^{-1}, f_D is the chemical dissolved fraction, and V is the water column volume, in m^3.

Benthic-water column exchange is set to 0 for this test in order to better approximate the simple analytical solution. Three EXAMS transformation rates used here—water column biodegradation, sediment biodegradation, and reduction—use mixed, second-order kinetics. The net loss rate constant is the product of a second-order rate constant and an appropriate environmental property. In this HWIR implementation, the net loss rate constant for each transformation reaction is supplied in the chemical file. The surface water model interface EXAMSIO transfers the value of this first-order rate constant to the EXAMS second-order rate constant and sets the associated environmental property to unity.

In this example pond, the volume is 1000 m^3 (Section 3.1.2). For the first 3 years, the total chemical loading is a relatively constant 10 g/day (Section 7.1.2), and flows are 150, 139, and 160 m^3/day (Section 5.1.2). No partitioning information is specified, so the dissolved chemical fraction is 1.0. When rate constants for water column reactions (hydrolysis and aerobic biodegradation) are set to 0.693 day^{-1}, half-lives should be 24 hours. From Eq. B-1, water column total chemical concentrations should equal 0.01186 mg/L, 0.01202 mg/L, and 0.01172 mg/L in years 1, 2, and 3. These are confirmed in the EXAMS output tables and in the HWIR surface water results file.

Eq. B-1 can also be applied to dissolved pore water concentrations in benthic compartments. In the HWIR application, two sediment layers are simulated for each reach. Groundwater flow and loadings enter the underlying layer and are advected upward through the surficial layer and into the water column. H-EXAMS reports chemical concentrations in the upper sediment layer. To test those calculations, Eq. B-1 can be modified and set up in series:

$$C_{D,BL} = \frac{L_{Seep}}{Q_{Seep} + k \cdot f_D \cdot V_{BL} \cdot n_{BL}} \tag{B-2}$$

$$C_{D,BU} = \frac{Q_{Seep} \cdot C_{D,BL}}{Q_{Seep} + k \cdot f_D \cdot V_{BU} \cdot n_{BU}} \tag{B-3}$$

where $C_{D,BL}$ and $C_{D,BU}$ are the dissolved pore water concentrations in the lower and upper sediment layers, in mg/L, L_{Seep} is the seepage loading in g/day, Q_{Seep} is the seepage flow, in m^3/day, V_{BL} and V_{BU} are the total volumes of the lower and upper sediment layers, in m^3, and n_{BL} and n_{BU} are the porosities of the lower and upper sediment layers, in L_W/L. For the test pond, Q_{Seep} = 50.15, V_{BL} = 250, V_{BU} = 60, n_{BL} = 0.40, and n_{BU} = 0.50. L_{Seep} = 40.09 g/day in years 21 - 40, and 50.116 g/day in years 41 - 60. When f_D is 1 and k is 0.693, $C_{D,BL}$ should equal 0.3356 mg/L in years 21 - 40, and 0.4196 mg/L in years 41 - 60. $C_{D,BU}$ should equal 0.2372 mg/L in years 21 - 40, and 0.2966 in years 41 - 60. When the benthic-water column exchange coefficient E_sw is set to 0 (to eliminate interference from the surface water column), the surface water output file should report dissolved benthic concentrations equal to $C_{D,BU}$.

The reduction and anaerobic biodegradation half lives of 24 hours (corresponding to rate constants of 0.693 day^{-1}) are confirmed for the benthic compartments in the EXAMS output tables, and the dissolved benthic concentrations are confirmed in both in EXAMS tables and in the HWIR surface water output files.

These and similar tests with different rate constants verify that H-EXAMS processes organic chemical transformation reactions accurately.

B.2.10.2 Mercury Transformations

Test 1.4 is a simulation run for mercury. The purpose of this test was to verify that H-EXAMS properly sets up and executes the mercury transformation reactions, including the transfer of mass to reaction products. Mercury is simulated in H-EXAMS with three interacting chemical components representing inorganic divalent mercury (HgII), methyl mercury (MeHg), and elemental mercury (Hg0). Atmospheric and watershed loadings are predominantly in the form of HgII. In the water body, HgII can be reduced to Hg0 and methylated to MeHg. Hg0 can be oxidized back to HgII and volatilized to the atmosphere. MeHg can be demethylated back to HgII and to Hg0.

To implement these mercury reactions, H-EXAMS sets the number of chemicals to 3, assigning component HgII to chemical 1, MeHg to chemical 2, and Hg0 to chemical 3. As an organic chemical model, EXAMS handles volatilization but does not include process modules for the mercury transformation reactions. These are handled by passing appropriate mercury transformation rate constants and yield coefficients to the EXAMS biodegradation and reduction reactions for each mercury component.

These tests first confirmed that all chemical properties, rate constants, and reaction coefficients were transferred to EXAMS properly. Reaction processes include partitioning, volatilization, water column methylation, benthic methylation, water column reduction, water column demethylation, benthic demethylation, water column *Mer* demethylation, and water

column oxidation. All rate constants, reaction products, and yield coefficients were confirmed in EXAMS output tables.

Mercury test simulations were run using steady hydrologic and solids input. All environmental properties were checked for proper transfer to EXAMS. Loadings of divalent mercury from atmosphere deposition and watershed runoff were read and converted to yearly EXAMS loadings. In the atmospheric file, 25 years of steady vapor wet deposition at 5.48e-8 g/m^2-day (20 ug/m^2-year) and particulate dry deposition at 2.74e-8 g/m^2-day (10 ug/m^2-year) are specified. In the watershed output file, 20 years of steady runoff loading at 10^{-3} g/day is specified. These loadings imply a rainfall mercury concentration of 25 ng/L and a runoff mercury concentration of 10 ng/L. Given the soil erosion loading of 10^5 g/day (10^3 mg/L in runoff water), the runoff mercury concentration is consistent with a background level soil mercury concentration of about 5 to 10 ng/g and a soil mercury partition coefficient of 10^3 to 10^4 L/kg.

Transformation rate constants are supplied for the dissolved and solids-sorbed phases. The DOC-complexed phase is nonreactive. To calculate the reaction process half-lives, the fraction of chemical in the DOC-complexed phase must be calculated. From partitioning equations and the specified chemical and environmental data, the dissolved plus solids-sorbed fraction, $f_{reactive}$, of HgII is calculated to be 0.9855in the water column and 0.99999 in the upper benthic layer. For methyl mercury, the resulting $f_{reactive}$ is calculated to be 0.99206 in the water column and 0.99963 in the benthic layers.

For a transformation reaction with a first-order rate constant k, the half-life should be $0.69315/(k \times f_{reactive})$. Based on the rate constants and the reactive fractions calculated above, reaction half-lives should be 33,770 hours for water column methylation, 166,300 hours for benthic methylation, 1687 hours for divalent mercury reduction, 3359 hours for water column demethylation, 33,340 hours for benthic demethylation, 16,770 hours for *Mer* demethylation, and 16620 hours for oxidation. These transformation half-lives were confirmed in EXAMS output tables.

Output from EXAMS and in SW1.grf show that mercury concentrations are at steady state levels in year 20. The distribution of divalent and methyl mercury among competing phases in the water column and benthic sediments was confirmed against the equilibrium partition coefficients. While the simulated mercury concentrations cannot be verified exactly against analytical solutions, they can be checked approximately. The steady-state (year 20) total water column concentrations for divalent, methyl, and elemental mercury in the output file are 6.318 ng/L, 0.529 ng/L, and 0.131 ng/L, respectively. The total concentration of 6.98 ng/L is just below the 7.2 ng/L calculated for a conservative chemical as total load divided by total flow. This makes sense for a simulation where the only chemical losses come from advective export and volatilization of a small fraction of the total chemical (elemental mercury comprises just 1.88% of the total water column mercury).

To refine this comparison, Eq. B-1 can be used for total mercury. The total loadings come to 1.082×10^{-3} g/day, and the flow is 150 m^3/day. The elemental mercury volatilization loss rate of 0.326 day^{-1} can be calculated from the reported half-life of 51 hours in Table 12 in report.xms. The elemental mercury fraction is 1.88%. Applying the steady-state analytical equation with a total mercury loss rate constant of 0.326×0.0188 gives a total mercury

concentration of 6.93 ng/L, which is very close to the year 20 total here of 6.98 ng/L. This comparison provides a good bottom-line check on many of the mercury calculations in the surface water module.

B.2.11 Test Robustness

Steps 1 through 9 test individual processes or combinations of processes on three sites. While these sites represent a range of normal environmental and chemical conditions, they do not test extreme conditions that might be encountered in the operation of this software for national risk assessment. It is possible that some combinations of parameter values could cause unforseen errors in the surface water module. The robustness tests outlined in this section are designed to screen for module failures due to various combinations of parameter values across sites, chemicals, and waste management units.

Test series 4, 5, and 6, described in separate sections below, comprise the robustness testing program for the surface water module. These tests are conducted within the HWIR production system, as outlined in Section B.2.2. Two different computers were used for test series 4 and 5. Computer 1 is a Dell Optiplex GS1 with 128 MB RAM and a Windows 98™ operating system. Computer 2 is an IBM Personal Computer 300 PL with 128 MB RAM and a Windows 95™ operating system. The full HWIR atmospheric database was installed on computer 1, allowing Monte-Carlo iterations. Test series 6, which requires this feature, was run on computer 1 but not computer 2.

B.2.11.1 Screening Across Sites

This series of tests involves simulations of selected chemicals in various types of waste management units across all sites in the database. The purpose of this series of tests is to screen for fatal errors that might be generated in the surface water module due to extreme combinations of environmental parameters interacting with different classes of chemicals. The waste pile (WP) and land application unit (LAU) represent runoff, leaching, and volatile release pathways, while the landfill (LF) and surface impoundment (SI) are restricted to leaching and volatile release. The aerated tank (AT) is subject to volatile release only. Low and high waste levels are chosen for lead to test for problems that might be generated by very small as well as very large calculated concentrations. The suggested site screening tests are summarized in the table (Table B-10) below.

Table B-10. Suggested Site Screening Tests

Test	Chemical	Site	WMU	Waste Level
4.1	benzene	all	all	5
4.2	thiram	all	SI, LAU	5
4.3	benzo(a)pyrene	all	LAU, WP	5
4.4	2,4-D	all	SI, LF	5
4.5	lead	all	LAU	1,5
4.6	mercury	all	LAU, WP, LF	5

Benzene was selected to represent volatile organic chemicals, with a Henry's Law constant of about 0.003 m^3-atm/M. Thiram is one of the most reactive chemicals, with an alkaline hydrolysis loss rate constant that can reach 1 day^{-1} at high aquatic pH levels close to 9 (even higher rate constants are possible in the waste management units where pH can exceed 12). Benzo(a)pyrene is one of the most hydrophobic chemicals, with an organic carbon partition coefficient of around 8×10^5 L/kg. 2,4-D is an organic acid that ionizes with a pKa of about 3, so that most of the chemical is in the anionic form in water bodies. Lead is a cationic heavy metal with a high partition coefficient of about 10^5. Finally, mercury is a complex bioaccumulating metal with transformation reactions linking its three major components.

For more thorough site coverage, each of the tests here was run with all the WMUs selected. Two failures in the surface water module were found and corrected during this series of tests. In addition, some failures in other modules and processors were detected and reported to appropriate members of the HWIR team. Using the updated modules, no surface water failures occur during these tests.

B.2.11.2 Screening across Chemicals

This series of tests involves simulations of all chemicals in the database in two types of waste management units at selected sites. The purpose of this series of tests is to screen for fatal errors that might be generated in the surface water module due to extreme combinations of chemical parameters interacting with different classes of environments. Copper and cobalt had to be excluded from this test, because required data were not available in the current version of the HWIR system. Furthermore, of the three mercury components, only divalent mercury should be selected for simulation; methyl mercury and elemental mercury are generated in the water bodies from divalent mercury. Low and high waste levels are chosen to test for problems that might be generated by very small or very large calculated concentrations. The suggested chemical screening tests are summarized in the table (Table B-11) below.

Table B-11. Suggested Chemical Screening Tests

Test	Chemical	Site	WMU	Waste Level
5.1	all	0930205	SI	1,5
5.2	all	1333001	LAU	1,5
5.3	all	0724909	WP	1,5
5.4	all	1434022	AT	1,5
5.5	all	0730914	LF	1,5

Site 0930205 is located in rural North Carolina near Badin. This site contains two water body networks. The first has five reaches, including stream, lake, and wetland reaches; the second is a lake with no exiting surface flow. Site 1333001 is located in rural South Carolina near Florence. This site also contains two water body networks. The first is a simple first order stream, while the second is a 7th order river with two adjacent wetlands. One of the wetlands receives contaminated seepage over a long period of time from an adjacent LAU. Site 0724909 is located in rural North Dakota near Williston. A single water body network has 11 reaches, including 2nd and 3rd order streams, 3 lakes, and 2 wetlands. This area is somewhat arid, and

some reaches are subject to periodic drying. Site 1434022 is located in urban California near Torrance. Two small lakes are located near the facility. These water bodies have no outflow and are subject to high evaporation. Finally, site 0730914 is located in rural Texas near Elgin. A single water body network has 18 reaches, including 2nd through 4th order streams and 7 small lakes. These five sites are illustrated at the end of this section.

No new failures in the surface water module were generated by this series of tests. Some failures in other modules and processors were detected and reported to appropriate members of the HWIR team. Using the updated modules and processors from test series 4, this series of tests runs with no surface water module failures.

B.2.11.3 Monte-Carlo Screening with Random Parameter Values

The final series of tests involves multiple simulations of selected chemicals at selected sites. The purpose of this series of tests is to screen for fatal errors that might be generated in the surface water module due to extreme combinations of chemical and environmental parameters. Different combinations of values are generated by selecting a large number of realizations for each test. At least 100 are recommended (200 realizations were run here). High waste levels are chosen to test for problems that might be generated by very large calculated concentrations. The suggested Monte-Carlo screening tests are summarized in the table (Table B-12) below.

Table B-12. Suggested Monte-Carlo Screening Tests

Test	Chemical	Site	WMU	Waste Level
6.1	2,4-D	0930205	WP	5
6.2	lead	1333001	LAU	5
6.3	benzo(a)pyrene	0724909	WP	5
6.4	benzene	1434022	AT,SI	5
6.5	thiram	0730914	WP	5

No new failures in the surface water module were generated by this series of tests. Some failures in other modules and processors were detected and reported to appropriate members of the HWIR team. Using the updated modules and processors from test series 4, this series of tests runs with no surface water module failures.

This site (Figure B-5) contains three waste management unit (WMU) types, including aerated tank, surface impoundment, and waste pile. The underlying geology is metamorphic and igneous rock. Two water body networks are present. The first has five reaches, including streams, a 5.4 ha lake (reach 3), and a 10.1 ha wetland (reach 5). The second network is a 358 ha lake with no exiting surface flow. Potential runoff and leaching pathways connect the WMUs to this lake.

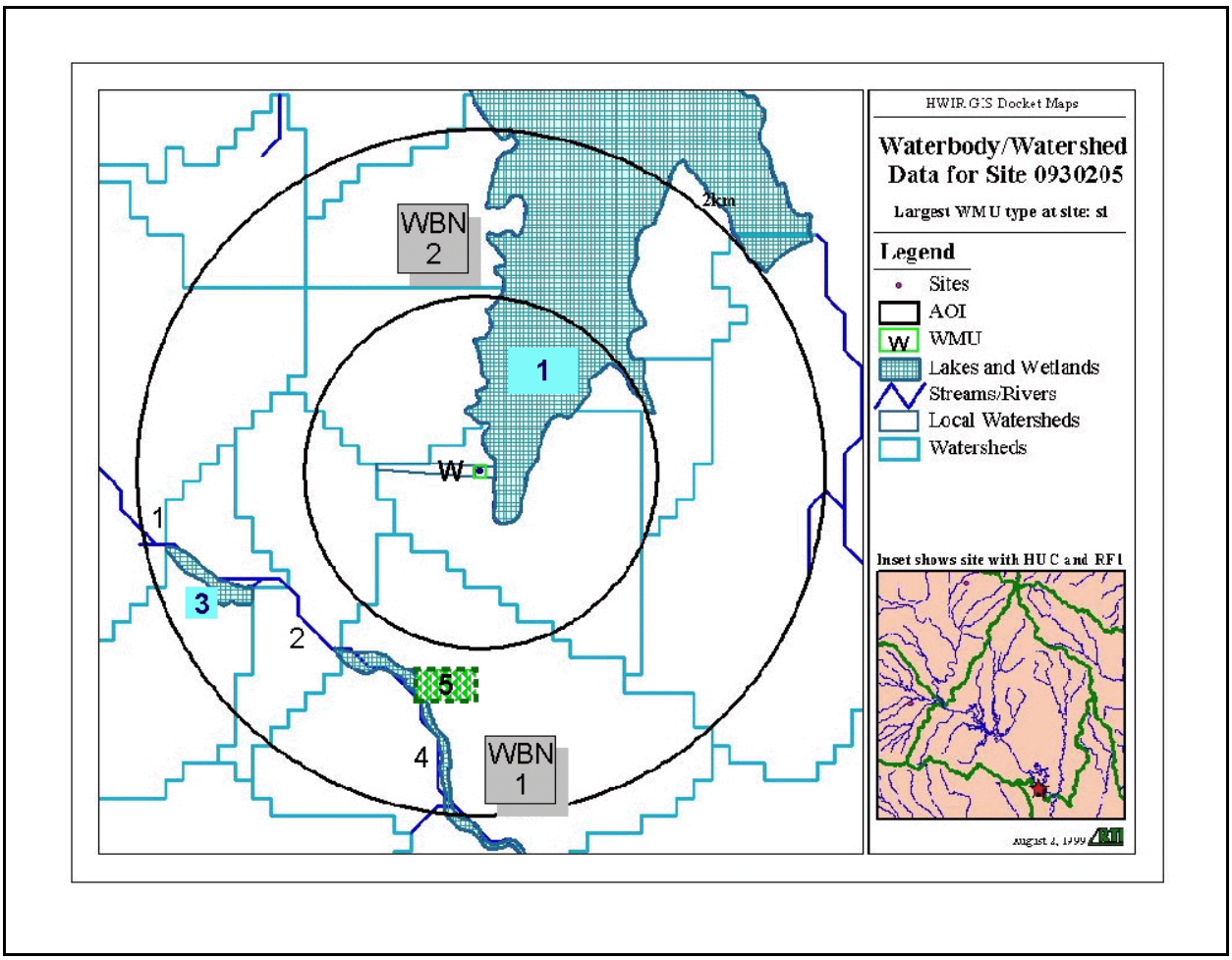

Figure B-5. Site 0930205, located in rural North Carolina near Badin.

This site (Figure B-6) contains a single waste management unit type, a land application unit (LAU). The underlying geology is sand and gravel. Two water body networks are present. The first is a two-reach 1st-order stream. The second network is a 7th-order river with two adjacent wetlands covering 630 ha and 936 ha, respectively. Runoff and leaching pathways connect the LAU to wetland reach 3.

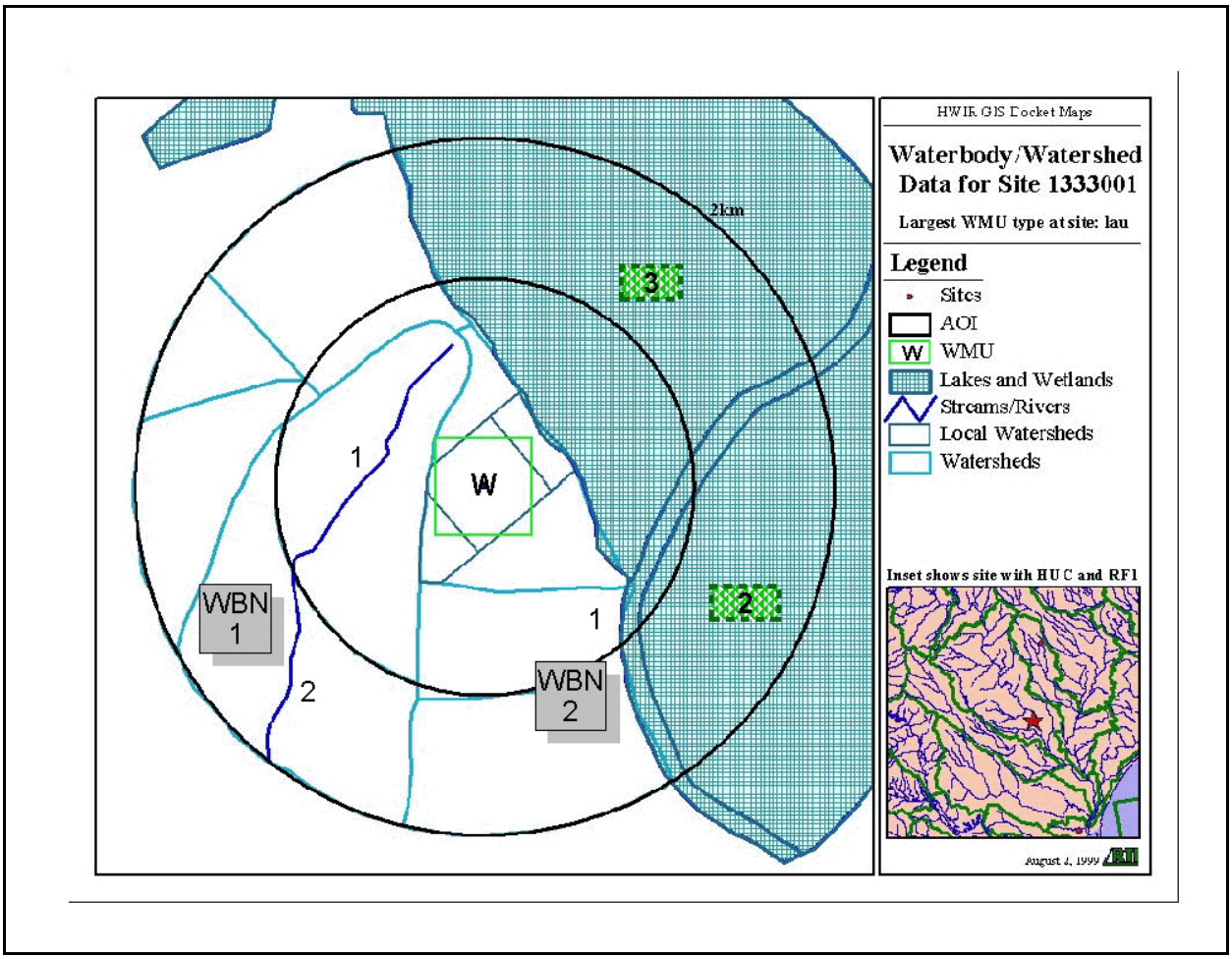

Figure B-6. Site 1333001, located in rural South Carolina near Florence.

This site (Figure B-7) contains a single waste management unit type, a waste pile (WP). The underlying geology contains unconsolidated and semi-consolidated shallow aquifers. A single water body network has 11 reaches. A 2nd order stream (reaches 3 and 5) drains directly to a 341 ha section of a large lake (reach 7). A 94 ha wetland (reach 8) also drains to the large lake. A 3rd order stream (reaches 1, 3, 4, and 6) ends in a 69 ha lake (reach 9), which spills into wetland reach 10, and then to the large lake. A small 13 ha lake (reach 11) connects to stream reach 6. Runoff and leaching pathways connect the WP to stream reach 4.

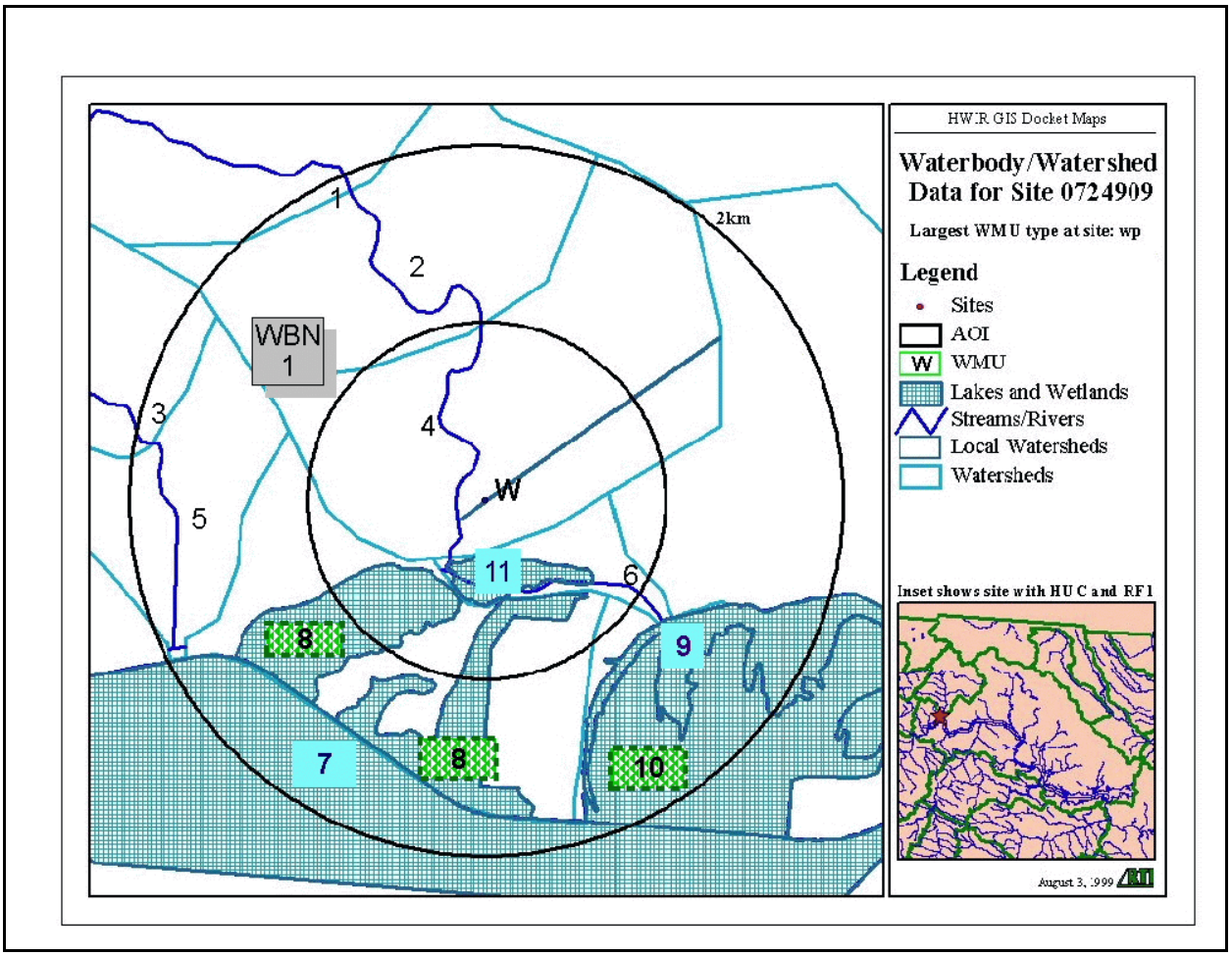

Figure B-7. Site 0724909, located in rural North Dakota near Williston.

This site (Figure B-8) contains two waste management unit (WMU) types, including aerated tank and surface impoundment. The underlying geology is sand and gravel. Two small lakes (1 and 1.7 ha) with no exiting surface flows are present. No runoff or leaching pathways are active at this site. Contaminants can reach the lakes by volatilization and atmospheric deposition.

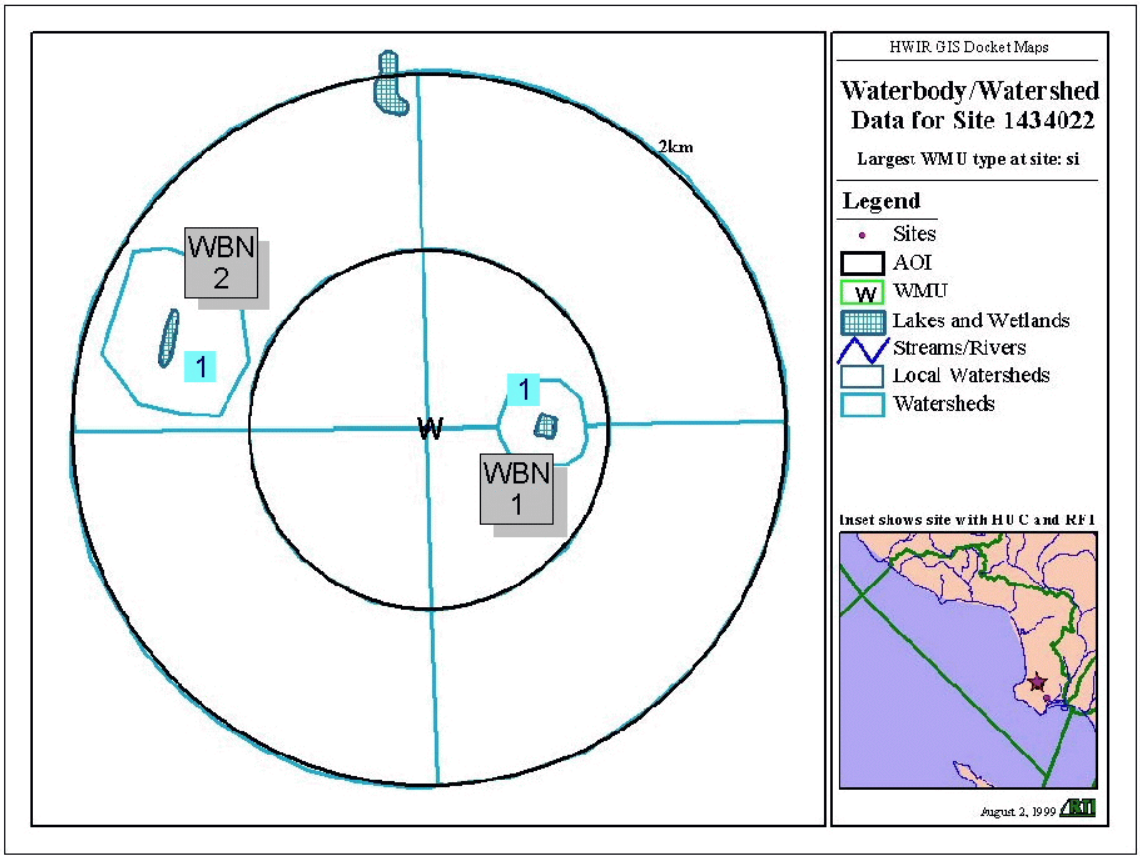

Figure B-8. Site 1434022, located in urban California near Torrance.

This site (Figure B-9) is contains four waste management unit (WMU) types, including aerated tank, landfill, surface impoundment, and waste pile. The underlying geology is bedded sedimentary rock. A single water body network has 18 reaches, including eleven 2nd through 4th order streams and seven small lakes, ranging from 1.5 to 12 ha in size. Potential runoff and leaching pathways connect the WMUs to stream reach 11.

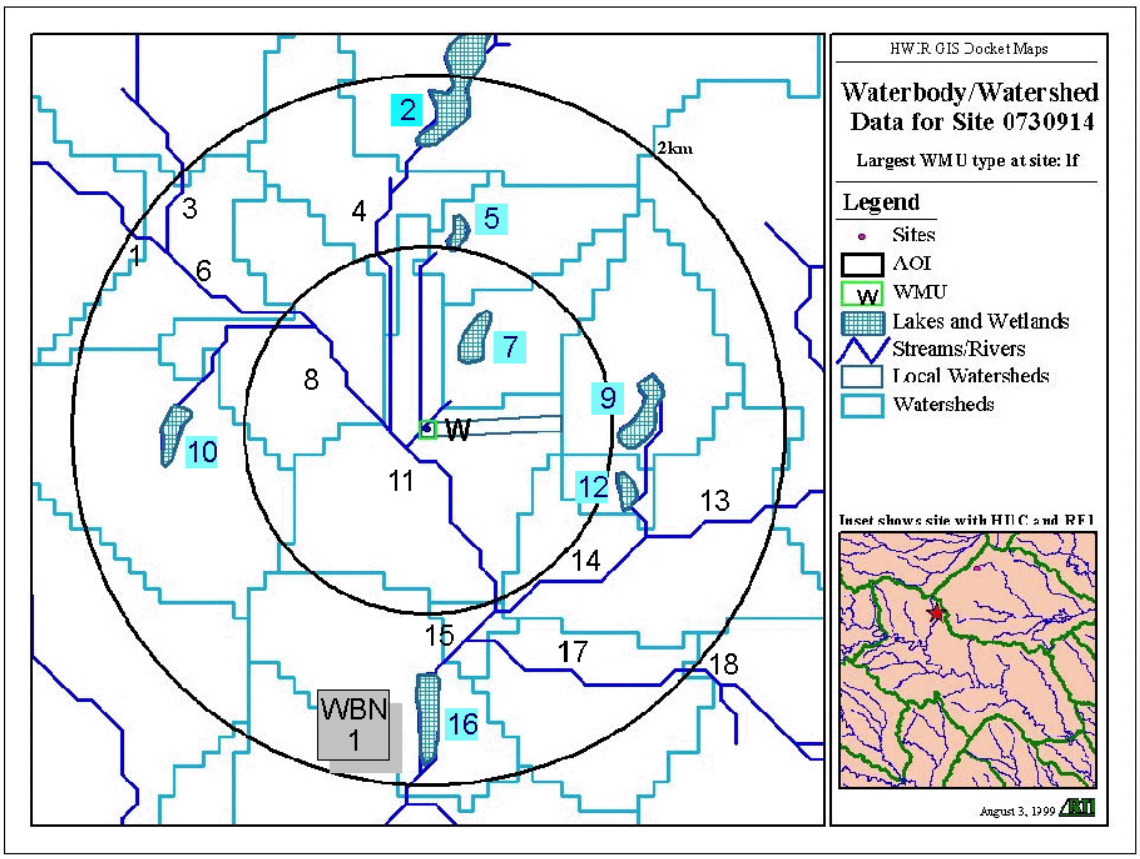

Figure B-9. Site 0730914, located in rural Texas near Elgin.

B.3. EXAMS System Validation Case Studies

B.3.1 Overview

Since EXAMS was released in 1983, there have been many applications to water bodies across the world. This chapter summarizes applications that report model performance against measured data in either a calibration or validation mode. The environments include small streams, rivers, ponds, rice paddies, and bays. Chemicals include dyes, herbicides, insecticides, phenols, and other organic chemicals with a variety of chemical properties. Fate processes include advection, sorption, sediment-water exchange, volatilization, hydrolysis, photolysis, water column and benthic biodegradation, and oxidation. Chemical coefficients have been supplied from the open technical literature and, in some cases, from site-specific experiments. The case studies are reported in chronological order, then discussed in general terms at the end of this chapter.

B.3.2 Linear Alkylbenzene Sulfonate in a Small Stream

Games, L.M., 1982. Field validation of Exposure Analysis Modeling System (EXAMS) in a flowing stream. In K.L. Dickson, A.W. Maki, and J. Cairns, Jr., editors, Modeling the Fate of Chemicals in the Aquatic Environment. Ann Arbor Science Publishers, Ann Arbor, Michigan.

EXAMS was applied to model the fate of linear alkylbenzene sulfonate (LAS) discharged in treated sewage effluent into Rapid Creek, a small mountain stream in South Dakota with relatively constant regulated flow. The model network was composed of 5 water column segments, each overlying a benthic segment. Segment lengths were set to end at stream monitoring stations, and varied from 4.7 to 39.2 km. Water column depths varied between 0.43 and 0.56 m, while sediment depths were set at a constant 3 cm. The important chemical fate reactions for LAS are partitioning to solids and biodegradation, both of which vary with the isomer chain length. Average chain length in Rapid Creek is about 12, and so measured reaction coefficients for this homolog were used in the model runs. Partition coefficients to sediment and to bacteria were 330 and 3070 L/kg. First order biodegradation rate constants measured below the discharge at 24 C were 0.021 hr^{-1} for the aqueous phase, and 0.040 hr^{-1} for the sediment-sorbed phase. These rate constants were applied to the first four model segments. Lower measured rate constants from an upstream station (0.002 hr^{-1} and 0.01 hr^{-1}, respectively, for aqueous and sediment phases) were applied to the most downstream model segment. Based on previous work, a Q_{10} temperature correction factor of 2 was applied.

The model was applied to data from an October 1980 survey, when stream flow was at a constant 1 m^3/sec and water temperature ranged between 4 C and 7 C. The upstream boundary concentration was set to the observed LAS value at the first monitoring station. The sediment-water mixing coefficient was treated as a calibration coefficient. The best fit between model results and survey data was obtained with a value of 5×10^{-5} m^2/hr (1.4×10^{-4} cm^2/sec). Qualitatively, the agreement between predicted and measured concentrations was described as excellent. The plotted results show predicted values within 10% to 50% of the water column survey data, and predicted values within 10% to 100% of the sediment data. The most sensitive model parameters were found to be the sediment-water dispersion coefficient and the sediment biodegradation rate constant. Because these are two of the least-understood parameters, the authors suggest that "wide error limits would need to be placed on predicted LAS concentrations

... using EXAMS, and probably any evaluative model in a safety assessment." Nevertheless, the authors conclude that "given the proper assumptions, EXAMS can successfully predict the concentration of LAS resulting from its steady-state input to a flowing stream."

B.3.3 Phenol in the Monongahela River

Pollard, J.E., and S.C. Hern, 1985. A field test of the EXAMS model in the Monongahela River. Environmental Toxicology and Chemistry **4**, 361-369.

EXAMS was tested against phenol data in an 18-mile reach below a steel plant discharge to the Monongahela River, Pennsylvania. The model network was composed of 5 water column segments, each overlying a benthic segment. Measured flow and depth during the two early October field surveys averaged 46.4 m^3/sec and 3.8 m. Chemical properties and rate constants for degradation of phenol were obtained from the literature, which indicates that the primary environmental pathways for phenol are biodegradation, metal-catalyzed oxidation, and photooxidation. Measured microbial levels in the river were low, averaging 935 cells/mL in the water and 3×10^{10} cells/mL in the sediment. Total oxidant concentrations could not be measured, so runs were made with high and low values from the literature (10^{-9} to 10^{-8} mol/L). Phenol loadings from the steel plant effluent were found to be variable, so the average well-mixed concentration at the first river station downstream of the plant was used to estimate the average loading rate for this study.

Survey and model results indicated that little or no phenol is present in the sediment downstream of the plant, and phenol in the water column experiences rapid decay. Observed water column phenol concentrations were highly correlated with the high-oxidant predictions (correlations of 0.93 and 0.99 for the two surveys). Chi-square tests, however, indicated a significant difference between observed data and predictions for the first survey. Comparing average concentrations by station, predictions appear to fall within a factor of 1.5 to 3 of observations in the first survey, and within a factor of less than 2 for the second survey. The authors observe that rapid phenol decay could be caused by the release of oxidants from the steel plant itself, which would undergo first-order decay downstream. Specifying spatially-variable oxidant concentrations in accordance with this scenario resulted in a nearly perfect fit of observed and predicted concentrations by station.

B.3.4 Disperse Yellow 42 Dye in a Pond

K.-W. Schramm, M. Hirsch, R. Twele, and O. Eutzinger, 1988. Measured and modeled fate of Disperse Yellow 42 in an outdoor pond. Chemosphere **17**(3):587-595.

EXAMS was tested against Disperse Yellow 42 dye introduced to an experimental outdoor pond 24.5 m^2 in area and 1.5 m deep. The model network included a water column segment and two benthic layers each 1 cm deep. Laboratory experiments were conducted to measure second order rate coefficients and environmental parameters characterizing this dye's biological and photolytic degradation. No data are given for the dye's partition coefficient. A loading of dye was added to the pond, and the concentration was tracked in the water and sediment layers over a period of 3000 hours (125 days). During this period, water column concentrations declined from 110 ppb to 10 ppb, while concentrations in the upper benthic layer first increased to 1000 ppb

over the first 12 days, then declined to 40 ppb by 70 days. Dye concentrations in the second layer increased to about 150 ppb, then declined to 15 ppb by day 50.

EXAMS water column calculations were close to observations near the beginning of the experiment, but did not decline as rapidly over time as the prototype. After about day 20, EXAMS water column calculations exceeded the observations by about 20% to 80%. In the upper sediment layer, EXAMS calculations fell below observed concentrations by about an order of magnitude at the beginning of the experiment, but declined more slowly than the observed data; EXAMS matched the final observation on day 70. In the lower sediment layer, EXAMS calculations fell below observations by over 2 orders of magnitude. The authors observe that the EXAMS transport to the sediment was not realistically simulated. They did not report the value use for the key model parameters governing this process, the sediment-water mixing coefficient and the partition coefficient. Nevertheless, they characterized the overall model performance as good.

B.3.5 Chlorophenol, Chloroquaiacol, and Chlorocatechol in Norrsundet Bay (Sweden)

K. Kolset and A. Heiberg, 1988. Evaluation of the fugacity (FEQUM) and the EXAMS chemical fate and transport models: a case study on the pollution of the Norrsundet Bay (Sweden). Wat. Sci. Tech. **20**(2):1-12.

EXAMS was calibrated and tested with three chemicals from a kraft mill effluent to a heavily polluted bay on the east coast of Sweden. The model network representing an inner and outer harbor was composed of 6 water column segments from 2.6 to 25 m deep, each overlying a 10 cm benthic segment. Based on empirical methods, water column segments were linked with estimated exchange flows ranging from 0.9 to 27 million m^3/hr. An inner harbor loop flow was estimated to be 0.072 million m^3/hr, and an outer harbor longshore current was estimated to be 11 m^3/hr. Chloroform data taken in November 1983 were used with the EXAMS to calibrate the network flows. Exchange flows in the outer harbor were reduced by a factor of 5; in the inner harboer, one exchange flow was reduced 50%, while the other was unchanged.

Four compounds identified in the effluent were used to test EXAMS–2,4,6-trichlorophenol (2,4,6-TrCP), 3,4,5-trichloroquaiacol (3,4,5-TrCG), tetrachloroguaiacol (TeCG), and tetrachlorocatechol (TeCC). Chemical properties and oxidation rate constants were specified from the literature. 2,4,6-TrCP has a Henry's Law constant of 4×10^{-6} atm-m^3/mole, a log K_{OW} of 3.61, and an oxidation rate constant of 10^{-3} hr^{-1}. 3,4,5-TrCG has a log K_{OW} of 4.13 and a Henry's Law and oxidation rate constants of 0. TeCG has a log K_{OW} of 4.42 and Henry's Law and oxidation rate constants of 0. TeCC has a log K_{OW} of 4.19, Henry's Law constant of 0, and oxidation rate constants of 0.5×10^{-2} hr^{-1}.

EXAMS was run using the calibrated network flows, measured loading rates, and the chemical data. Calculated and measured concentrations agree well for 2,4,6-TrCP, 3,4,5-TrCG, and TeCG, but not for TeCC. For the first three compounds, most predictions lie between the minimum and maximum measured within each compartment. Linear regressions yield slopes between 0.6 and 0.75, and correlation coefficients between 0.86 and 0.97. Given the uncertainty in environmental and chemical input data, the authors conclude that this agreement is good.

For TeCC, predicted concentrations are about 10 times higher than observed concentrations in the inner harbor. This compound is said to have a particularly high affinity for suspended particles from the effluent, and a significant degree of settling is likely. EXAMS does not account for this loss process, and thus overpredicts TeCC concentrations.

The authors conclude that EXAMS is capable of predicting the concentrations of some selected chlorophenolics in the Norrsundet area with reasonable accuracy. EXAMS describes all important transformation and loss processes except for sedimentation reasonably well.

B.3.6 Three Herbicides and an Insecticide in Rice Paddies

Woodrow, J.E., M.M. McChesney, and J.N. Seiber, 1990. Modeling the volatilization of pesticides and their distribution in the atmosphere. Pages 61-81 in: Kurtz, D.E., Editor, Long Range Transport of Pesticides,. Lewis Publishers, Inc., Chelsea, Michigan.

Volatilization flux was measured for three rice herbicides—MCPA, molinate, and thiobencarb—and one insecticide—methyl parathion—from a laboratory chamber and two flooded rice fields. The flux measurements were compared to predicted fluxes using EXAMS with chemical properties and chamber or field conditions as input. The chamber measured flux rates from a sample dish filled with aqueous solutions of the chemicals, with a humidified air stream velocity of 2.2 m/sec. The rice fields were 37 and 41 hectares in area with water depth maintained at 15–26 cm. Molinate and thiobencarb were applied to the fields as a dry granular formulation which sank to the bottom sediment where the herbicides slowly dissolved. MCPA and methyl parathion were applied as emulsified aqueous suspensions which remained largely in the rice water after application, followed by slow partitioning and breakdown. Chemical properties, including water solubility and vapor pressure were specified from the literature. Henry's Law constant was calculated from these two properties.

The calculated Henry's Law constants imply the following order of decreasing volatility:

molinate > thiobencarb > methyl parathion >> MCPA >> MCPA (DMA salt)

This order was observed experimentally in the laboratory chamber and predicted by EXAMS. The normalized volatilization flux values predicted by EXAMS compared well overall with the observed values, within 10%–20% for molinate, a factor of 2 for MCPA acid., and a factor of 3 for methyl parathion. The calculated flux rate for thiobencarb, however, was low by a factor of 5. The authors attribute this discrepancy to possibly incorrect vapor pressure and/or solubility data.

The model was further compared with measured diurnal variations in flux from the two rice paddies for molinate and methyl parathion. Using input field conditions (including diurnal wind speed and water temperature), EXAMS was able to reproduce the observed variations in volatilization flux for these two chemicals. The observed and predicted water and sediment concentrations were not reported in this paper. Neither EXAMS nor the laboratory chamber were able to predict the volatilization of MCPA from the rice paddies. This is attributed to the observation that MCPA mainly volatilized from dry deposits on soil and plant surfaces.

The authors conclude that EXAMS "appeared to be promising as a predictive tool for estimating volatilization, when the appropriate chemical properties and environmental conditions were used as input data."

B.3.7 Xylenes, Dichlorobenzenes, Styrene, and 4-phenyldodecane in a small lowland river in U.K.

Tynan, P., C.D. Watts, A. Sowray, and I. Hammond, 1991. The transport and the fate of organic pollutants in rivers II - Field measurement and modelling for styrene, xylenes, dichlorobenzenes and 4-phenyldodecane. In: *Proceedings of the Sixth European Symposium Organised within the Framework of Concerted Action Organic Micropollutants in the Aquatic Environment*, Angletti G. and Bjorseth A. (eds.), Cost 641 Working Party 2, Lisbon, Portugal, 22-24 May 1991.

EXAMS was tested against a variety of chemical data in a 7 km reach below a sewage treatment works effluent to a small, unnamed lowland river in England.. The model network was composed of 9 water column segments, each overlying a 10 cm deep benthic segment. A survey was conducted following a plug of water downstream. The survey date was not mentioned in this paper, nor were river flow and water column depths (except for a value of 0.4 m in the sixth reach and the observation that travel time through the 7 km reach is about 7 hours). Reach properties were given for key parameters, including pH (7.6–7.7), water temperature (15–20 C), suspended solids concentration (6–10 mg/L), water column organic carbon fraction (6%–36% near the effluent), benthic organic carbon fraction (0.4%–1.1%), and sediment bulk density (1.9–2.1 g/mL).

A larger than expected mass fraction of each chemical was found to be sorbed to suspended solids, suggesting non-equilibrium partitioning. This violates the assumption in EXAMS of local equilibrium. By contrast, bed sediment concentrations were found to be closer to equilibrium with the water column. Theoretical calculations indicate that several days would be required for these chemicals to reach a new sorption equilibrium following discharge to the river. To handle these observations, the K_{OW} value for each compound was increased by 3 orders of magnitude, while the bed sediment organic carbon fractions were decreased by 3 orders of magnitude. This enabled EXAMS to calculate proper chemical concentrations on both suspended and benthic solids.

In general, EXAMS predictions are described as being reasonably close to measured values, with "fairly close predictions" for styrene, m-dichlorobenzene, and p-dichlorebenzene.

Total water column concentrations illustrated in the figures in the study appear to be within 50% or better for these compounds at most river stations. Predictions of 4-phenyldodecane concentrations are within an order of magnitude of observations, but do not match the rapid downstream decline that was observed. The authors attribute this to a lack of data on this compound, leading to an unquantified degradation process. They conclude that EXAMS produces quantitative predictions that compare well with observations for those chemicals for which reliable rate data exist.

B.3.8 Aniline and Lindane in River Calder

Cousins, I.T., C.D. Watts, and R. Freestone, 1995. Field measurement and modelling the fate of aniline and lindane in a UK lowland river. Environmental Technology, **16**, 515-526.

EXAMS was tested against aniline and lindane data in a 7 km reach below a sewage treatment works effluent to the large lowland River Calder in West Yorkshire, England.. The model network was composed of 9 water column segments, each overlying a benthic segment. Surveys were conducted in April and August, 1991. Measured river flow and depth were not described in the article. The river is described as turbid, with suspended solids concentrations between 15 and 40 mg/L in the two surveys. Chemical properties for aniline and lindane were specified from the literature. The loss pathways for aniline are biodegradation and photolysis. Specified properties were Henry's Law constant of 2.53×10^{-4} atm-m^3/mole, log K_{OW} of 0.90, first-order biodegradation rate constant of 6.85×10^{-3} hr^{-1}, and first-order surface photolysis rate constant of 2.57×10^{-3} hr^{-1}. The loss pathways for lindane are hydrolysis and biodegradation. Specified properties were Henry's Law constant of 1.87×10^{-3} atm-m^3/mole, log K_{OC} of 3.43, first-order hydrolysis rate constant of 4.5×10^{-3} hr^{-1}, first-order biodegradation rate constant of 4.0×10^{-4} hr^{-1}, and first-order surface photolysis rate constant of 4.0×10^{-4} hr^{-1}.

EXAMS predicted very slight losses for both chemicals, a result consistent with both surveys. Fairly good correlations were achieved between measured and predicted dissolved water column concentrations, with predictions falling within a factor of 2 of station means. Measured suspended particulate concentrations in the river were significantly higher than predicted, probably because of limitations in the equilibrium partitioning assumption. The measured high particulate concentrations from the STW appeared to be either irreversibly or strongly bound with a slow desorption rate. By contrast, predicted bed sediment concentrations were "a little lower than measured," all falling within an order of magnitude of observations. From this study, the authors conclude that EXAMS is useful for predicting the fate of non-ionic organic chemicals in rivers, provided that adequate physicochemical and environmental data are available.

B.3.9 Bensulfuron Methyl and Azimsulfuron in Rice Paddies

Armbrust, K.L., Y. Okamoto, J. Grochulska, and A.C. Barefoot, 1999. Predicting the dissipation of bensulfuron methyl and azimsulfuron in rice paddies using the computer model EXAMS2. J. Pesticide Sci. **24**(4), 357-363.

EXAMS was first calibrated to bensulfuron methyl (BSM) and azimsulfuron (AZM) data taken in experimental lysimeters that contained 5 cm of water overlying 50 cm of paddy soil. Initial simulations were run assuming that these pesticides are degraded by hydrolysis and direct photolysis in the water, and by hydrolysis and biological metabolism in the soil. Initial results led to the specification of an additional water column degradation pathway, indirect photolysis, which photochemically produces hydroxyl radicals that degrade the pesticides. An average hydroxyl radical concentration of 7.6×10^{-16} M was inferred from calibration of EXAMS to the lysimeter studies, as was the water - soil dispersion coefficient of 3.8×10^{-6} m^2/hr.

EXAMS was then set up for two field sites, Ushiku (0.09 ha) and Nihonmatsu (0.10 ha). Soil organic carbon content for these paddies was 9.74% and 1.55%, respectively. Water

column and soil depths were 5 cm each. Initial pesticide applications of BSM and AZM were 30 g/ha, and 6 g/ha (active ingredients). Chemical properties of the pesticides were specified, along with the two calibrated variables. EXAMS successfully predicted the partitioning and degradation reactions that led to the observed 3–4 day chemical half-lives in paddy water. The indirect photolysis rate using calibrated hydroxyl radical concentration accounted for a significant fraction of the degradation. Predicted water column concentration responses generally matched the observed data. EXAMS overestimated soil concentrations by factors of 2 to 4. The authors conclude that a "definitive characterization of the rate of degradation and mobility of the two chemicals at a specific site would require additional information on environmental parameters and site-specific soil-chemical interactions."

B.3.10 Discussion of Case Studies

EXAMS requires a combination of environmental, chemical, and loading data in order to properly specify the model parameters. Erroneous, uncertain, or missing data can result in improper model parameterization, which leads to errors in model predictions. Overly-simple process equations can also lead to errors in model predictions. The case studies here highlight both parameter uncertainty and model uncertainty. Despite these sources of uncertainty, it appears that EXAMS is able to predict the concentrations of most organic chemicals within a factor of 2 or better in the water column, and within an order of magnitude in the sediment.

Advection and dispersion are transport processes that affect all chemicals. The first step in a model application is characterizing the water body network, including geometry, flows and exchanges. Specifying geometry and flows is often straightforward, such as for gaged rivers or simple ponds. For some water bodies such as bays, however, gaps in the basic hydrogeometry and transport data present a large degree of uncertainty. In such cases, flows were inferred from tracer studies or from comparing predicted chemical concentrations to observations. For almost all aquatic environments, sediment-water column exchange is a poorly-characterized process that is quantified by uncertain parameters, including dispersion coefficient and sediment mixing depth. This process is often an important contributor to chemical fate. Best results are achieved when the coefficients are calibrated with site-specific data.

Sorption is another process that significantly affects the fate of many chemicals. For many organic chemicals, the assumption of local equilibrium between phases governed by the organic carbon partition coefficient and the solids organic carbon content is robust. Some case studies, however, highlight the limitations of this equilibrium partitioning process model. When the discharge is characterized by strong chemical sorption and the travel time through the water body is relatively brief, the partitioning model tends to underpredict the sorbed phase concentration in the water column. This can be described as a model error rather than a parameterization error, although clever assignment of partition coefficients can improve model performance satisfactorily.

Volatilization is a process that significantly affects a subset of chemicals characterized by a high Henry's Law constant. The case studies indicate that EXAMS is able to predict volatile fluxes reasonably well (within a factor of 2 or 3) if the relevant chemical parameters are accurate. These parameters include Henry's Law constant, solubility, and vapor pressure.

Any of the chemical transformation processes can become important if their reaction half-lives are short compared with the residence time in the water body. Biodegradation was most often measured and applied in these case studies as a first-order reaction. Measuring and applying benthic biodegradation rate constants seems to be relatively uncertain. Oxidation rates are a function of the environmental oxidant concentrations, which can be specified or calculated by a set of photolysis algorithms. These environmental parameters are relatively uncertain, with typical values varying perhaps an order of magnitude among water bodies. Consequently, site-specific calibration seems necessary to improves model performance when this reaction is controlling chemical fate. First-order hydrolysis and photolysis rate constants were used in some of these case studies with low apparent uncertainty.

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Tynan, P., C.D. Watts, A. Sowray, and I. Hammond, 1991. The transport and the fate of organic pollutants in rivers II - Field measurement and modelling for styrene, xylenes, dichlorobenzenes and 4-phenyldodecane. In: *Proceedings of the Sixth European Symposium Organised within the Framework of Concerted Action Organic Micropollutants in the Aquatic Environment*, Angletti G. and Bjorseth A. (eds.), Cost 641 Working Party 2, Lisbon, Portugal, 22-24 May 1991.

Woodrow, J.E., M.M. McChesney, and J.N. Seiber, 1990. Modeling the volatilization of pesticides and their distribution in the atmosphere. Pages 61-81 in: Kurtz, D.E., Editor, Long Range Transport of Pesticides, Lewis Publishers, Inc., Chelsea, Michigan.

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