

APPENDIX C
PROTOTYPES I - IV

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APPENDIX C

PROTOTYPES I - IV

This appendix provides a description of the process of applying the TRIM.FaTE methodology (Chapter 4) to cases of increasing complexity (referred to as “prototypes”). These prototypes were developmental applications of the TRIM.FaTE modeling framework that were used to test the model as additional phases, compartment types, processes, algorithms, and other aspects of the TRIM.FaTE methodology were added to the model. Four early prototypes (*i.e.*, I through IV) were developed for preliminary testing purposes. Section 1 of this appendix discusses the computer implementation of the prototypes; Section 2 describes the development process for each prototype; Section 3 addresses the features of the prototypes, including the types of compartments and links simulated; and Section 4 discusses the chemical-specific parameters and values used in prototype 4. The goals of this appendix are to: (1) illustrate the flexibility of TRIM.FaTE for application at different levels of spatial and temporal resolution; (2) illustrate how different multimedia configurations with TRIM.FaTE are set up; and (3) document the historical development of TRIM.FaTE leading up to Prototype V. More documentation of Prototypes I - IV, including a detailed description of the testing performed using Prototype IV, is presented in the initial TRIM.FaTE Status Report (U.S. EPA 1998a) and Technical Support Document (U.S. EPA 1998b).

Based on the lessons learned from testing and application of Prototypes I - IV and the 1998 comments by EPA’s Science Advisory Board, EPA developed Prototype V, the first application of TRIM.FaTE at an actual site for a metal contaminant (*i.e.*, mercury). For detailed information regarding testing and application of Prototype V, the reader is referred to the 1999 TRIM.FaTE Status Report (U.S. EPA 1999a) and Technical Support Documents (U.S. EPA 1999b,c).

C.1 COMPUTER IMPLEMENTATION OF PROTOTYPES

The concepts discussed in Chapter 4 have been implemented in all the prototypes using a combination of Microsoft Visual Basic™, Fortran, and Microsoft Excel™ software. An object-oriented architecture was implemented using Visual Basic 5 application environment imbedded within Excel 97 to model the hierarchy of components of TRIM.FaTE. This hierarchy includes volume elements, compartment types, compartments, links, and sources. The coding architecture is not tied to any specific ecosystem configuration. A preliminary algorithm library that utilized this coding architecture was also implemented.

If all transport processes are simulated as a first-order process, the result is a system of linear ordinary differential equations, as explained in Section 4.2. This system must be solved to determine the redistribution of chemical mass as a function of time. For TRIM.FaTE, this system is solved using the Livermore Solver for Ordinary Differential Equations (LSODE) (Radhakrishnan and Hindmarsh 1993), a Fortran program freely available via several online numerical algorithm repositories.

The LSODE subroutine solves systems of first-order ordinary differential equations of the form (Hindmarsh 1983):

$$dy/dt = F(t,y), y(t_0) = y_0$$

where y is an n -dimensional time-dependent vector, *i.e.*,

$$y(t) = [y_1(t), y_2(t), \dots, y_n(t)].$$

The system of differential equations can be stiff or non-stiff. In the stiff case, it treats the Jacobian matrix (Schneider and Barker 1989) as either a full or banded matrix. It uses Adams (Schneider and Barker 1989) methods (predictor-corrector) in the non-stiff case, and backward differentiation formula methods in the stiff case. The linear systems that arise are solved by direct methods. LSODE supersedes the older GEAR and GEARB packages.

The only restriction on the size of the system of differential equations is that imposed by computer memory. This code was modified so that it could be accessed by Visual Basic 5 in Excel 97. Another Fortran code was used, in a similar manner, to determine the steady-state solution to the system of linear differential equations (Barrodole and Stuart 1981).

Microsoft Excel spreadsheets were used for general preprocessing, postprocessing, and data storage (additional databases for spatial data were also created using Visual Basic and accessed by Excel). Excel spreadsheets also served as a convenient interface to the Visual Basic and Fortran subroutines.

The approach taken for testing the methodology made it possible to investigate the implications of draft algorithms and to work on the development of a flexible system for addressing conceptual site models with many compartments. The pre- and postprocessing for the ultimate implementation of TRIM.FaTE may require a more sophisticated platform. However, with some modification, much of the Visual Basic code, and all of the Fortran code, can be used in other computer programming languages.

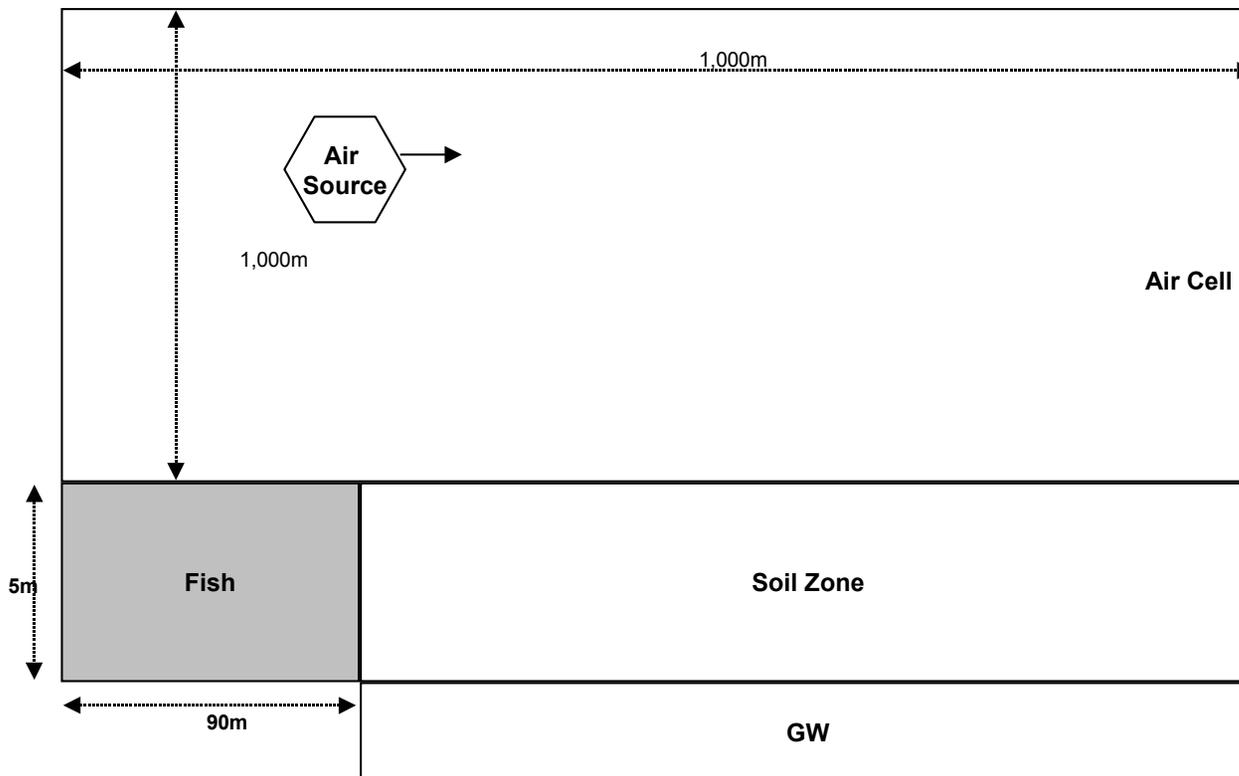
C.2 PROTOTYPE DEVELOPMENT

Multiple prototypes were developed with increasing complexity to model the movement of a chemical through an ecosystem. This section describes features of the prototypes in increasing order of complexity.

C.2.1 PROTOTYPE I

Prototype I (P1) was designed to test the mass transfer methodology (Section 4.2) and the LSODE utility. Air, surface, soil, ground water, surface water, and fish compartment types were simulated in P1 as illustrated in the conceptual site model shown in Figure C-1. P1 includes a uniform volume source emission of benzene into the air compartment volume. Benzene was selected because most of its transfer factors were readily available from CalTOX (Maddalena et al. 1995).

Figure C-1
Conceptual Site Model for Prototype I



Some transfer factors were derived independently of CalTOX for the air to air sink, soil to ground water, fish to water, and water to fish transfers. The remaining factors were taken directly from CalTOX. The dimensions of the terrain were adapted from CalTOX to facilitate comparison of results. Chemical reaction was not simulated in this prototype.

The runs produced estimates of benzene mass throughout the system, and no problems were experienced in running the LSODE subroutine. The resulting mass distribution of benzene in various compartments was examined qualitatively to ensure that the numerical routines were producing stable and realistic solutions. A quantitative analysis of the results was not performed because the input parameters were selected only to test the implementation infrastructure. The results were approximately commensurate with theoretical expectations with no unstable or anomalous values. These results prompted further testing of the modeling approach on a more complex ecosystem.

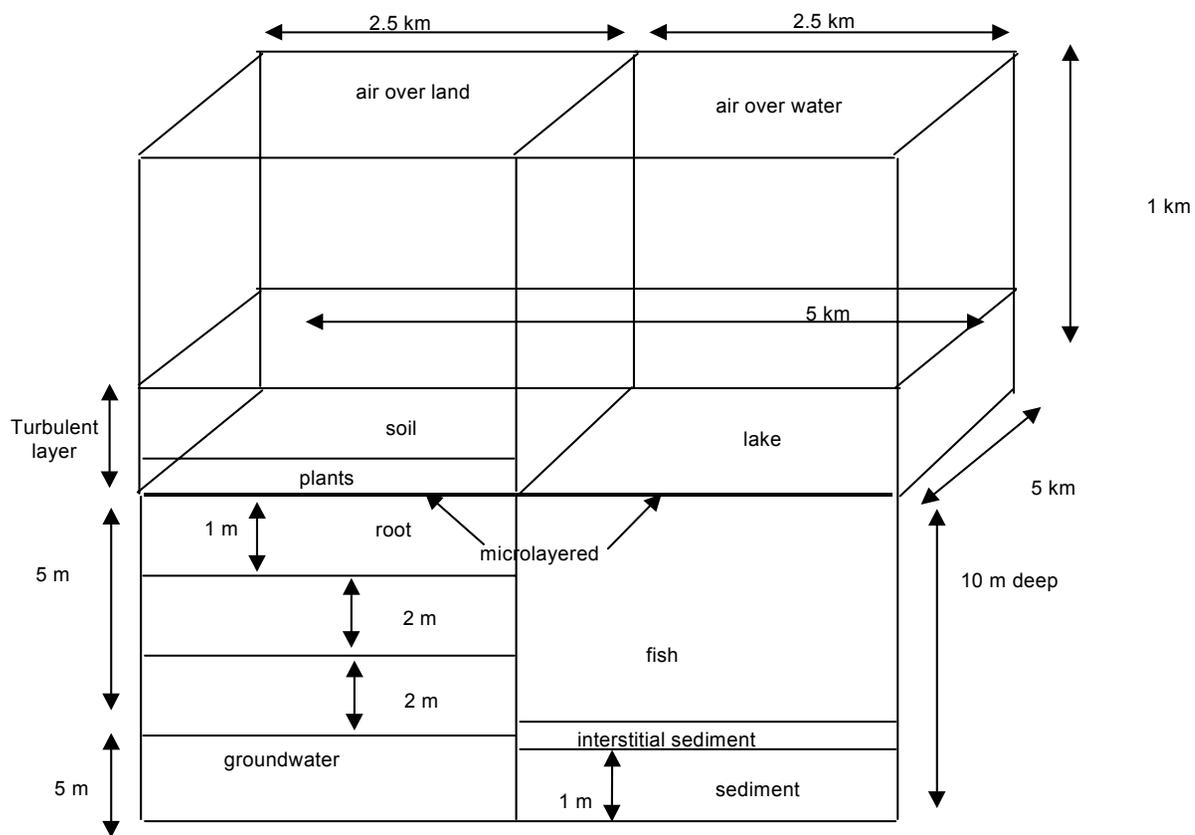
C.2.2 PROTOTYPE II

Prototype II (P2) includes more spatial detail sophistication than P1 in both the types and number of compartments used. Unlike P1, P2 included multiple volume elements for both the soil and air compartment types and included the use of plant and sediment compartments. In addition, the links between compartments had multiple-phase (*i.e.*, gas, liquid, and solid) mass transfers. P2 included a volume source emission of benzo(a)pyrene (B[a]P) into only one of the air compartment volumes. This made possible a very simple representation of spatial transport. B(a)P was selected as a test chemical for this and subsequent prototypes because of its persistence in the environment and because it is a HAP (a chemical of concern in the CAA). The derivation of the transfer factors is described in detail in the second volume of this document. The conceptual site model for P2 is shown in Figure C-2.

Multiple-phase (liquid, gas, and solid) transport within a compartment was introduced in P2. The phases are assumed to be at chemical equilibrium, with the ratios of the concentrations in the individual phases constant.

P2 was run for four different conditions that included constant source terms under pristine conditions, an artificially lower organic carbon partitioning coefficient (K_{oc}) value for B(a)P, a constant source term with non-pristine conditions in surface water, and a time-varying source-term condition. In all cases, under steady-state conditions, most of the B(a)P accumulated in the plants, with minimal penetration into the subsurface. In the water column, most of the B(a)P was found in the sediment sink, with minimal accumulation seen in the fish compartment. Decrease of the K_{oc} value resulted in corresponding increase in mass in subsurface soil. Only the air compartment type seemed to be responsive to the varying source-term condition.

Figure C-2
Conceptual Site Model for Prototype II



The transfer factors and steady-state outputs of P2 were compared to runs performed on CalTOX (Maddalena et al. 1995). Most of the transfer factors used in P2 were very similar to those in CalTOX; the mass distributions of B(a)P were similar in air, soil, and surface water compartments and differed by three orders of magnitude in plant, sediment, and ground water (aquifer) compartments. This led to refinement of the TRIM.FaTE algorithms for plant and sediment compartment types. The difference in the ground water masses was due to the fact that both TRIM and CalTOX have simple approximations to model transport in ground water.

C.2.3 PROTOTYPE III

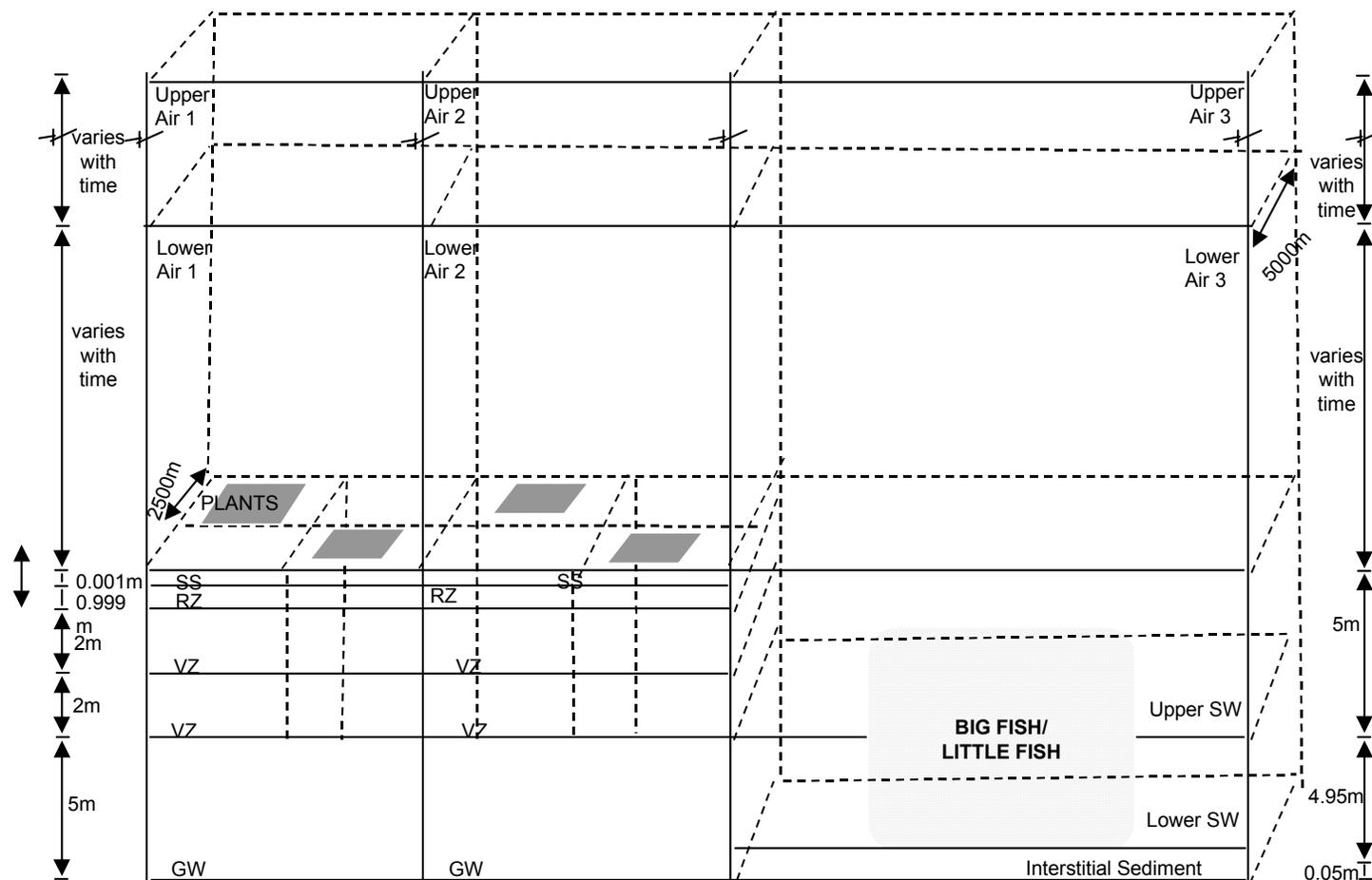
Prototype III (P3) focuses on code and input data structure refinements because the code and input data are significantly more complex than either P1 or P2. P3 was developed both to incorporate lessons learned from P2, which has a refined set of abiotic algorithms, and to set up the TRIM.FaTE model for the case study model run Prototype IV (P4). P3 includes a conceptual site that approaches the spatial scale (approximately 10-kilometer [km] radius) of the ecosystem used for the testing the full prototype (P4). The conceptual site model for P3 is shown in Figure C-3. The vertical dimensions of individual air compartments are not indicated because these dimensions were allowed to vary with time according to a set of specified meteorological conditions. The soil and surface water compartments were split into finer grid structures relative to P2, and several new biotic algorithms were added. The source term simulated in P3 was a volume-source emission of B(a)P into only one of the four air compartments. This was used to make an approximation to a continuous point-source release.

The differences of P3 relative to P2 include:

- C Addition of terrestrial earthworm, kingfisher, and mouse compartment types;
- C Addition of aquatic food-web system;
- Addition of macrophyte compartment type;
- C Addition of compartments with varying heights for air;
- C Division of soil compartments horizontally;
- C Introduction of “thermoclines” and refinement of mixing for surface water;
- C Refinement of plant algorithms;
- C Refinement of soil diffusion algorithms;
- C Addition of erosion in the soil compartment types;
- C Refinement of ground water algorithm;
- C Introduction of flexible code design; and
- C Introduction of temporal variation for a few key input parameters.

As in the case of P2, several runs were performed for P3. The results showed that the plant, macrophyte, and sediment compartments are major sinks of B(a)P in the environment. The model showed that B(a)P mass distribution in the environment is sensitive to total macrophyte volume in the water column. The model results were extremely responsive in most compartments to varying source-term conditions. Comparisons of P3 outputs with CalTOX outputs showed that B(a)P mass distributions in the ecosystem being simulated were in closer agreement than was seen in the case of P2. This was believed to be a result of refining the

Figure C-3
Conceptual Site Model for Prototype III



algorithms as previously stated and implied that the prototype was appropriate for application to a more complicated test case.

C.2.4 PROTOTYPE IV

Whereas P1 through P3 used generic inputs and were intended for evaluation simulations, P4 was designed to be applied to an actual site. P1 through P3 were used to develop and test the TRIM.FaTE algorithms. P4 was developed and used to illustrate and evaluate the likely limits of TRIM.FaTE with respect to the number of land parcels and length of time steps used. This prototype had the shortest plausible time step (1 hours), a large number of land units in the planar view (20 parcels), and 21 different biotic compartment types. This level of detail resulted in several hundred compartments, including abiotic and biotic compartments, and the sinks necessary to account for transformation and transport losses outside of the system boundary. To test the model using a realistic ecosystem, P4 was applied to an area in the northwestern region of the United States. A detailed description of the compartment layout used, the abiotic and biotic compartment types modeled, and model evaluations carried out for P4 is included in the 1998 TRIM.FaTE Status Report (U.S. EPA 1998a) and Technical Support Document (U.S. EPA 1998b).

C.3 PROTOTYPE FEATURES

The specific features modeled in the prototypes are discussed in this section. Section 3.1 presents the abiotic compartment types modeled; Section 3.2 includes the biotic compartment types modeled; and Section 3.3 discusses the abiotic and biotic links associated with the prototypes.

C.3.1 ABIOTIC COMPARTMENTS

In P1 (Figure C-1), the air, soil, and surface water each consist of a single volume element and compartment. Ground water was simulated simply as a sink to the soil compartment. P2, as shown in Figure C-2, divides the air into four volume elements (two upper air and two lower air layers); divides the soil into four volume elements (surface soil, root zone, and vadose zones one and 2); and simulated ground water, surface water, and sediment as single volume elements. In P3, (Figure C-3) the air consists of six volume elements (two lower air and two upper air over soil, and a lower air and upper air over surface water); the soil was divided into 32 volume elements (eight surface soil, eight root zone, eight vadose zone 1, and eight vadose zone 2); ground water and surface water were both simulated with two volume elements; and sediment was simulated as a single volume element. P4 simulates 129 abiotic volume elements. Parcels were defined in P4 and divided vertically based on compartment type. The 129 abiotic compartments associated with the parcels in P4 are summarized in Table C-1.

C.3.2 BIOTIC COMPARTMENTS

In P1 and P2, a single fish species is modeled and only uptake and loss of chemical through the gills is simulated. In the transition to P3 and P4, the number of biotic water column compartments was expanded from a single fish species to an aquatic food web represented by

several feeding trophic levels (compartment types). Bioaccumulation by herbivores, as well as omnivores and carnivores, is accommodated within the P3 and P4 simulations. It is important to note, however, that the trophic level representations were simplified to reflect primary uptake and loss from a single representative species from each trophic level.

Both P3 and P4 include terrestrial wildlife as compartments. Wildlife may be exposed to chemicals through food, soil, and water ingestion, and through inhalation of chemicals in air. Elimination of chemicals from body tissues may occur through metabolic breakdown of the chemical and excretion through urine, feces, milk (mammals only), and eggs (birds only). Terrestrial and semiaquatic biota were not considered in P1 and P2. Two species were introduced in P3: a white-footed mouse (*Peromyscus leucopus*) and the belted kingfisher (*Ceryle alcyon*). These species were selected because they are taxonomically dissimilar (mammal versus bird) and represent differing compartment types (terrestrial omnivore and semiaquatic piscivore, respectively). P4 simulated a more complex terrestrial, aquatic, and semiaquatic system, as summarized in Table C-2.

Table C-1
Types of Abiotic Compartments and Number of Volume Elements Modeled

Compartment Type	Number of Volume Elements ^a			
	P1	P2	P3	P4
Air	1 - Air	2 - Upper Air Layer 2 - Lower Air Layer	3 -Upper Air Layer 3 - Lower Air Layer	20 -Upper Air Layer 20 - Lower Air Layer
Soil	1 - Soil (general) 1 - Ground water	1 - Surface Soil 1 - Root Zone 1 - Vadose Zone 1 1 - Vadose Zone 2 1 - Ground water	8 - Surface Soil 8 - Root Zone 8 - Vadose Zone 1 8 - Vadose Zone 2 2 - Ground water	14 - Surface Soil 14 - Root Zone 14 - Vadose Zone 1 14 - Vadose Zone 2 14 - Ground water
Surface Water	1 - Surface Water	1 - Surface Water	1 - Upper Surface Water Layer 1 - Lower Surface Water Layer	1 - Upper Lake Layer 1 - Lower Lake Layer 5 - River Segments
Sediment	NA	1 - Interstitial Water 1 - Sediment	1 - Interstitial Water 1 - Sediment	6 - Interstitial Water 6 - Sediment
TOTAL NUMBER	4 Volume Elements	12 Volume Elements	44 Volume Elements	129 Volume Elements

^a Reaction and advection sinks are not listed in this table.

**Table C-2
 Biotic Compartments Modeled**

Compartment	P1	P2	P3	P4
Aquatic Ecosystem	Single Fish Species	Single Fish Species	C Macrophytes (Benthic Herbivores) C Aquatic Herbivores C Aquatic Omnivores C Aquatic Carnivores	C Macrophytes (Benthic Herbivores) C Mayfly (Benthic Herbivores) C Bluegill (Modeled as Herbivore) C Channel Catfish (Omnivore) C Bass (Carnivore) C Mallard (Herbivore) C Raccoon (Omnivore) C Tree Swallow (Insectivore)
Terrestrial Ecosystem	NA	NA	C White-footed Mouse (Omnivore) C Earthworm (Soil Detritovore) C Plant Leaves, Roots, Xylem and Stem	C White-footed Mouse (Omnivore) C Earthworm (Soil Detritovore) C Black-capped Chickadee (Insectivore) C Red-tailed Hawk (Predator) C Long-tailed Weasel (Predator) C Black-tailed Deer (Herbivore) C Long-tailed Vole (Herbivore) C Mink (Piscivore) C Trowbridge Shrew (Ground Invertebrate Feeder) C Insects C Plant Leaves, Roots, Xylem and Stem
Semi-Aquatic Ecosystem	NA	NA	C Belted Kingfisher (Piscivore)	C Belted Kingfisher (Piscivore) C Wetland Plant Leaves, Roots, Xylem and Stem

P3 and P4 also simulated pollutant transfer to earthworms. The concentration in earthworms was assumed to be in equilibrium with the solid, liquid, and vapor-phase concentrations of the chemical in the root zone compartments.

Plants were introduced to the TRIM.FaTE framework in P2. The plant component of the ecological model implemented for P2, P3, and P4 is comprised of leaves, roots, xylem, and stem. Plants are divided into these compartment types because: (1) the literature suggests that concentrations of non-ionic organic chemicals in foliage are primarily related to those in air and that concentrations in roots are generally related to those in soil (with stems serving as the conduit between the two), and (2) herbivores may eat part but not all of a plant. Each compartment type was assumed to be homogeneously-mixed. The plant algorithms implemented in P2 through P4 are applicable for mature plants only, and did not address plant growth.

C.3.3 LINKS

If mass can move from one compartment to another compartment without first moving through intervening compartments, then the two compartments are considered "linked." Each link is associated with an algorithm that determines the direction and rate of mass flow between the two compartments. Links may be between compartments in adjacent volume elements or compartments within a volume element. At a given spatial location, and within a single volume element, more than one compartment may exist and linkages may exist between these compartments.

Table C-3 shows examples of generalized links applied in P1 through P4. This table is generic and can be used in conjunction with Tables C-1 and C-2 to define a specific link. For example, in P2 through P4, transfer of a pollutant can occur from an upper air compartment to adjacent upper air compartments and to a lower air compartment. This is represented in Table C-3 by the air (sending compartment) to air (receiving compartment) link. A more complex example is the links associated with the kingfisher from the semi-aquatic ecosystem. As a receiving compartment, pollutant(s) can transfer to the kingfisher from air (*i.e.*, lower air), soil (*i.e.*, surface soil), surface water (*i.e.*, upper lake layer), and aquatic (*i.e.*, bluegill) ecosystems.

The links from sending compartments to sinks are not shown in Table C-3. Sinks refer to the compartments of pollutant mass leaving the modeled ecosystem through a reaction or physical process(es).

Table C-3
Examples of Links Associated with Compartments Types

Sending Compartment Types	Receiving Compartment Types
Air	Air Soil Surface Water Terrestrial Ecosystem Semi-aquatic Ecosystem
Soil	Air Soil Ground water Surface Water Terrestrial Ecosystem Semi-aquatic Ecosystem
Ground water	Ground water Surface Water
Surface Water	Surface Water Sediment Aquatic Ecosystem Semi-aquatic Ecosystem Terrestrial Ecosystem
Sediment	Surface Water Aquatic Ecosystem
Terrestrial Ecosystem	Terrestrial Ecosystem Air Soil
Aquatic Ecosystem	Aquatic Ecosystem Semi-aquatic Ecosystem Terrestrial Ecosystem Surface Water
Semi-aquatic Ecosystem	Terrestrial Ecosystem Air Soil Surface Water

C.4 PAH-SPECIFIC VALUES USED IN TESTING OF PROTOTYPE IV

This section discusses the testing approach for chemical specific parameters and values. More detailed descriptions of algorithms associated with many of the parameters discussed in this section can be found in TRIM.FaTE TSD Volume II.

C.4.1 TRANSFORMATION OF PAHs BY PLANTS

C.4.1.1 Metabolism in Plants

Few studies of metabolism of organic chemicals in plants exist. Exceptions include metabolism of: atrazine by poplar trees (Burken and Schnoor 1997); pentachlorophenol in soybean and spinach (Casterline et al. 1985); trichloroethylene in carrots, spinach, and tomatoes (Schnabel et al. 1997); PCBs in plants (reviewed in Puri et al. 1997); and bromacil, diclobenil, nitrobenzene, and 1,3-dinitrobenzene in soybean plants and barley roots. Metabolic rate constants were only calculated in the first paper. Investigations of the metabolism of polycyclic aromatic hydrocarbons in plants include: metabolism of phenanthrene and anthracene by tomato and wheat (Harms 1996), metabolism of anthracene and benz[a]anthracene in bush bean (Edwards 1988), metabolism of anthracene by soybean (Edwards et al. 1982), metabolism of anthracene in bush bean (Edwards 1986), and metabolism of various PAHs by bush bean (in progress, T. McKone, personal communication, August 1997). The first two papers are somewhat useful for the calculation of a metabolic rate constant, and the ongoing study by McKone may prove most useful when completed. Unfortunately, the two papers are dynamic studies with PAH taken up through the soil and air and degraded gradually, perhaps at a first-order rate, and with metabolites present in the nutrient solution that could also be taken up.

Thus, it is difficult to calculate the metabolic rate constant. Harms (1996) provides radioactivity (percentage of applied) of parent compound (phenanthrene or anthracene) and metabolites in culture medium; parent compound, metabolites, and nonextractable residue in shoots; and parent compound, metabolites, and nonextractable residue in roots after five days of exposure. If it is assumed that a) non-extractable residues reflect the measured proportion of parent compound to metabolite, b) metabolites produced in aseptic culture medium were produced by roots rather than by shoots, c) metabolites did not move between plant organs, and d) that most of the measured parent compound was in the plant for the majority of the five days (the rate of uptake may have been rapid because of the application of phenanthrene in liposomes), a simple calculation of a first-order metabolic rate constant can be made. (Although these are poor assumptions, it is notable that the order of magnitude variability in rate constants for metabolism of phenanthrene in shoots of two plant species (below) is probably greater than errors associated with the above assumptions.)

Thus, a calculation of a lower bound on the first-order metabolic rate constant can be made. The equation used is $\ln(N/N_0) = -kt$, where N is the radioactivity of the metabolite pool after five days and N_0 is the sum of the radioactivity of the parent compound pool and metabolite pool after five days (assumed to be the total radioactivity of the parent compound in the plant close to the beginning of the experiment). If the calculation is made, the rate constants are: 0.008/d for phenanthrene in tomato leaf and stem, 0.08/d for phenanthrene in wheat leaf and

stem, 0.24/d for phenanthrene in tomato root, and 0.28 for phenanthrene in wheat root. The half-lives range from 2.5 to 90 days.

Similarly, a calculation of a lower bound on the first-order metabolic rate constant for benzo(a)pyrene can be made using results from uptake and metabolism of benz(a)anthracene by bush beans in nutrient solution (Edwards 1988). The PAH was added continually to solution to maintain a constant concentration. In a previous experiment it was determined that most of the benz(a)anthracene absorbed by roots was taken up within one day. After 30 days 25 percent of the radioactivity was parent compound and 14 percent was in the form of metabolites; the distribution of the parent compound and metabolites in the plant is presented in the paper. Using the same assumptions as above, low estimates of the rate constants are: 0.015/d for benzo(a)pyrene in root, 0.19/d for the PAH in stem and 0.12/d for the chemical in foliage.

Randy Maddalena and Tom McKone of Lawrence Berkeley Laboratory investigated the uptake of anthracene, fluoranthene, phenanthrene, and pyrene from air by leaves of bushy beans. The following calculation is based on a personal communication from Tom McKone in September 1997. These compounds appear to have reaction rates on the order of 0.1 to 0.3 /day (half-life of three to 10 days) and thus are somewhat higher than the low estimate of the rate constant for phenanthrene metabolism in leaves described above.

It is expected that metabolism in plants is estimated within an order of magnitude in TRIM.FaTE. The parameters in Table C-4 should be used for phenanthrene and benzo(a)pyrene or as defaults for other PAHs. Different numbers may be chosen in the future as additional information is obtained. As the root and leaf compartment types are connected, the rate constant for the stem is likely to change.

Table C-4
First-order Metabolic Rate Constants (d⁻¹)

Chemical	Root	Stem	Leaf
Phenanthrene	0.3	0.08	0.2
Benzo(a)pyrene	0.02	0.2	0.2

C.4.1.2 Photolysis on the Plant Surface

The process of photolysis on the plant surface was not implemented in the PAH test case of TRIM.FaTE because the leaf and leaf surface were not separate compartment types. In future runs of the model for PAHs, photolysis on the leaf surface may be included. Few investigations of the photolysis of contaminants on plant foliage have been undertaken. An exception is the photodegradation of 2,3,7,8-tetrachlorodibenzodioxin sorbed to grass foliage ($k = 0.0156 \text{ hr}^{-1}$). It is assumed that photolysis of organic contaminants on the leaf surface occurs at a rate that is somewhat less than that of PAHs sorbed to particulate matter in air; PAHs on leaves are probably exposed to a lower light intensity than those in air. Thus, the rate constant on leaf surfaces is assumed to be one-half of the rate constant of photolysis of PAHs on particulates in

air. Kamens et al. (1987) provides measurements of the rate constant for benzo(a)pyrene when the chemical is present at a loading of 30 to 350 ng/mg particulates (0.0211 min^{-1}) and when the PAH is present at a loading of 1000 to 2000 ng/mg particulates (0.009 min^{-1}). Their more general equation for determining the rate constant (in min^{-1}) for the 30 to 350 ng/mg loading case is:

$$\ln k = -1.355 - 1.279(1/T) + 0.831(\ln(I)) + 0.816(\ln[\text{H}_2\text{O}]),$$

where:

I = the average solar intensity ($\text{cal/cm}^2/\text{min}$)
 [H₂O] = water vapor concentration in g/m^3

Kamens et al. (1987) have not investigated photolysis of 3-ringed PAHs such as phenanthrene. Behymer and Hites (1988) suggest that photolysis is independent of PAH structure for substrates with a carbon content greater than five percent. In an experiment in which fifteen fly-ash substrates were irradiated using a mercury vapor lamp (17.6 W/m^2), they investigators measured photolytic rate constants for phenanthrene ranging from $<0.00069 \text{ hr}^{-1}$ to 0.0050 hr^{-1} , with a mean of 0.0019 hr^{-1} . The mean rate constant for benzo(a)pyrene was measured at 0.0035 hr^{-1} . Thus, this measurement is more than an order of magnitude lower than the numbers in the Kamens study (note that they are presented in min^{-1}).

Without knowledge of solar intensity (and with lots of uncertainty), the following rates are suggested for photolysis of contaminants on a leaf surface during the daytime hours: 0.03 hr^{-1} for benzo(a)pyrene and 0.001 hr^{-1} for phenanthrene.

C.4.2 DISTRIBUTION, ELIMINATION, AND TRANSFORMATION OF PAHs IN WILDLIFE

The toxicological literature was reviewed to identify models or parameters to describe the absorption, metabolism, and excretion of phenanthrene in both avian and mammalian species. No data were found to describe the toxicokinetics of phenanthrene in birds. Although models to describe the toxicokinetics of phenanthrene in mammals were not found, data suitable for estimating absorption, metabolism, and excretion rates following oral exposure were available. These data, and rate estimates developed from them, are outlined below. Phenanthrene appears to be readily absorbed, metabolized, and eliminated by mammals. Rahman et al. (1986) orally dosed rats with single one mg dose radiolabeled phenanthrene. Eight hours post dose, 72.74 percent of the initial radio label dose had been recovered in bile or urine, suggesting an assimilation efficiency of approximately 73 percent.

Chang (1943) orally exposed rats to an experimental diet containing one percent phenanthrene and by oral gavage of 11 or 13 mg phenanthrene. Amount of parent compound excreted in feces was measured. Because excretion rates were comparable regardless of the mode of exposure, results from both dietary and gavage exposure were pooled. Rats excreted four to seven percent (mean equals 5.75 percent) of the original dose. Conclusions from this study are limited by the small sample size used in limited description of the methods employed.

Chu et al. (1992) exposed both rats and guinea pigs to doses of radiolabeled phenanthrene of 10 mg/kg/d via gavage. After 48 hours, rats and guinea pigs had excreted 52 percent and 47 percent of the initial radiolabel. In rats, 90 percent of the excreted radiolabel was in urine and 10 percent in feces; among guinea pigs, 95 percent of the excreted radiolabel was in urine and five percent in feces. Of the radiolabel in the urine both species, 95.8 percent and 95.7 percent consisted of metabolites of phenanthrene and 4.2 percent and 4.3 percent of unmetabolized phenanthrene in rats and guinea pigs, respectively.

Female rats were orally or dermally exposed to phenanthrene, either as phenanthrene alone or as phenanthrene adsorbed to sandy or clay soil (Kadry et al. 1995). Absorption was greatest for pure phenanthrene as compared to phenanthrene adsorbed to soil. Percent absorption of the initial dose ranged from 55.7 percent to 65.3 percent and 0.7 percent to one percent for oral and dermal pathways, respectively. After 72 hours, 47.6 percent to 52.4 percent of the initial oral dose was recovered in urine; 27.8 percent to 22.1 percent was recovered in feces. After 96 hours, 36.2 percent to 48.4 percent of the initial dermal dose was recovered in urine; 8.6 percent to 14 percent was recovered in feces.

The results of these studies are listed and summarized in Table C-5. From these data, the mean excretion (E_u), metabolic (E_m), and absorption efficiencies for phenanthrene are 3.2 percent, 63.4 percent, and 33.8.0 percent, respectively. The first-order rate constants for metabolism range from 0.1 day^{-1} to 1 day^{-1} . Because no data were found for assimilation for water, soil, or food, assimilation via all pathways is assumed to be equal, *e.g.*, $A_a = A_w = A_s = A_f$. Because no data were found concerning uptake and elimination of phenanthrene by birds, parameters developed for mammals should be used. Due to physiological differences between birds and mammals, use of mammalian values for birds will contribute significant uncertainty to the final tissue residue estimate. No studies data were found to enumerate elimination of phenanthrene via lactation (E_l) or elimination via egg production (E_e). However, transfer of contaminants from the diet to milk or eggs may be estimated using models reported in Travis and Arms (1988) and McKone (1993a, 1993b, 1993c).

C.4.3 UPTAKE OF PAHs BY BENTHIC INFAUNA

Uptake of PAHs is based on the water to benthic infauna transfers presented in Section 7.3.2.1 of TSD Volume II. Uptake of contaminants from water is primarily based on respiratory processes. (Stehly et al. 1990) have found that the clearance rate of B(a)P and phenanthrene from water by the mayfly is analogous to the clearance rate of oxygen during respiration. The uptake of these two PAHs can, therefore, be estimated similarly to the ratio of oxygen clearance to the volume of water passing over respiratory surfaces. With a known or assumed volume of water passing over respiratory membranes with known concentrations of B(a)P and phenanthrene, the extraction efficiency of these PAHs can be calculated. Generic algorithms in Section 7.4.2.1 of TSD Volume II were adapted from Stehly et al. (1990) for estimating PAH uptake and loss within the benthic invertebrate, based on the clearance rate driven by the volume of water cleared and the bioaccumulation factor (BCF). Uptake rates, as measured by a clearance rate constant, as well as the bioconcentration factor for 30, 60, and 120-day-old mayflies for B(a)P and phenanthrene, were provided by Stehly et al. (1990).

Table C-5
Summary of Assimilation, Metabolism, and Elimination Data for Phenanthrene

Percent of Total Dose Excreted as Phenanthrene or Metabolites (percent)	Days	First-order Excretion Rate (day ⁻¹)	Percent of Total Dose Metabolized ^f (percent)	First-order Metabolic Rate Constant (day ⁻¹)	Reference
72.74	0.33	3.9	69.68	3.6	Rahman et al. 1986
52 ^a	2	0.37	49.82	0.34	Chu et al. 1992
47 ^b	2	0.32	44.99	0.30	Chu et al. 1992
75.4 ^c	3	0.47	72.23	0.43	Kadry et al. 1995
76.2 ^d	3	0.48	73	0.44	Kadry et al. 1995
74 ^e	3	0.45	70.9	0.41	Kadry et al. 1995

^a rats

^b guinea pigs

^c pure phenanthrene

^d phenanthrene adsorbed to sandy soil

^e phenanthrene adsorbed to clay soil

^f assumes that 95.8 percent of total excreted dose is not phenanthrene, based on Chu et al. (1992)

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