ABSTRACT

MULTIMEDIA MODELING OF ORGANIC CONTAMINANTS IN THE PASSAIC RIVER WATERSHED

by
Lansana Coulibaly

A dynamic fate and transport multimedia environmental model was developed and applied to assess the release of five priority contaminants in the Passaic River Watershed, including: napthalene, toluene, trichloroethylene, 1-1-1 trichloroethane and xylene. The model uses the current releases of contaminants as well as cross-boundary advection to determine the fate and environmental distribution of these chemicals in the watershed. The model was developed using a dynamic fugacity approach in order to allow for scenario analysis such as source reductions and no-action alternatives. This modeling effort is expected to achieve a comprehensive assessment of contaminants not only in the proximity of their release but on the scale of the entire watershed, or even larger areas.

This new modeling approach is based on the partition of chemicals between homogeneous and adjacent compartments (i.e. water, air, soil, sediment and vegetation) in order to determine their final distribution in the environment. The effect of spatial resolution on model prediction was addressed in this study by comparing the modeling results of Passaic River Watershed as one environmental unit versus considering the watershed as several sub-watershed units. Other points addressed in the present model include: the determination of the likelihood and the required time for environmental contamination to reach steady state and the consistency of the intermedia transfer rates in estimating actual environmental processes. As part of the model development, the linking of the multimedia model to the available Geographical Information System (GIS) database was

successfully demonstrated. A procedure was developed for deriving relevant data that can be used for other environmental applications. This mode of data manipulation identified the need for recording available and future data in a manner and units useful for multimedia modeling applications. This consistency in data representation would ultimately result in wider use of multimedia models and for their validation.

The current unsteady state Level IV fugacity model was successfully validated using the widely referenced ChemCAN model. Applications of this model to the watershed environment provided more information on the fate of contaminants, thus allowing for better decisions in controlling their releases. The inclusion of spatial resolution was found to improve the results of the multimedia models by several orders of magnitude, especially for high molecular weight non-volatile organic contaminants. Furthermore, considering the soil compartment as three separate and distinct layers was found to significantly improve the estimation of the contaminant distribution as a function of depth. Finally, it was observed that the organic contaminants used in the multimedia model displayed different behavior in their distribution and intermedia mass transfer rates based on their physical and chemical properties. Non-volatile contaminants like naphthalene show a preferential distribution in the soil layers irrespective of their point of release and as a result they may persist in the environment for long period, especially if the degradation rate in that compartment is low. Volatile contaminants such as toluene tend to move more freely and distribute evenly between the different environmental compartments and as a result they do no persist in the environment for long period of time.

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This dissertation is dedicated
to my parents
Maimouna Coulibaly and Mamadou Coulibaly

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TABLE OF CONTENTS

Chapter **Page**

TABLE OF CONTENTS
(Continued)

Chapter **Page**

TABLE OF CONTENTS
(Continued)

Chapter **Page**

TABLE OF CONTENTS
(Continued)

Chapter **Page**

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

Table **Page**

LIST OF TABLES
(Continued)

Table **Page**

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Environmental exposure models are developed and used by scientists and regulators to estimate the level of contamination resulting from accidental or continuous releases of chemicals in a landscape. They are very important in helping shape regulations and providing an understanding of the behavior of contaminants in a complex environmental setting. The scope and level of complexity of these models vary greatly from screening level and small application area (e.g. small landfill) to very comprehensive and medium specific model applicable to continental size (RIVM, 1994). Every model developed for environmental assessment of pollutants has its set of limitations, which must be understood by the users for a good interpretation of its results. These models can also be used to interpret the results of monitoring programs and field observations as well as to define an analysis of different scenarios on how to best address a particular contamination problem.

The tasks involved in assessing the effect of a contaminant on the environment include defining the properties of the contaminant and quantifying the environmental releases of the contaminant. Exposure assessment is accomplished either through monitoring programs where the contaminant concentration in each pathway (the intake from a given medium) to humans is measured, or through the use of predictive models capable of representing key environmental processes. Different approaches to modeling the environment have been developed during the past 40 years. Based on the intended application, these models are classified as either spatial (also called one-medium model with high spatial resolution) or as multimedia (many media but with low or zero spatial resolution). Traditional environmental models that have been used to address environmental contamination were based for the most part on a single medium (water, air, soil, sediment, aquatic or terrestrial biota).

Numerical and empirical models grew in complexity and spatial resolution as computational speed and cost decreased with the advent of computers. Early large-scale environmental models date back to 1970s. The goals of such models were to determine the fate of pesticides such as DDT (Randers, 1973) and the impact of nuclear particles fall-outs on the environment and the human population date back to World War II (Reist, 1993). However, these large-scale numerical models are now considered to be less useful because of their large input data requirements and their deficiency in providing useful information regarding the rate of the processes that control the fate of the contaminant.

Other approaches have focused on retrospective analysis, which consisted of conducting large scale monitoring studies in order to derive empirical models (Calamari, 1992). The drawbacks of the latter modeling approach are the inconsistency introduced by data gaps and the prohibitive cost of monitoring programs. Other single medium models have been linked to account for the inter-phase transport of contaminant in different environmental media as in the case of UTM-TOX (Unified Transport Model for Toxicant), ALWAS (Air, Land, Water Analysis System) and TOX-SCREEN. However, since these models were based on using results of one part such as the air module for calculations of another part such as the land module, the results were not obtained simultaneously and required large input data (Cohen, 1990). In spite of its limitations, the latter approach presented new insights in environmental modeling with a view of the environment as a complex and inter-related system. In such a system the contaminants movement is dictated not only by the nature of the contaminant in a specific medium, but also the interactions between different environmental media.

It is necessary to note that the above spatial modeling to environmental problems have had significant regulatory implications. For example current regulations have focused on one medium and one medium only (i.e. clean water act, clean air act etc.) Thus pollution problems have been addressed by limiting discharges to the medium of concern (i.e. water bodies) without much regards for the impact that adjacent media or phases (i.e. air) may have on the concentration levels. It has recently been estimated that air sources account for over 20% of lead (Pb) contamination of the Delaware Bay (U.S. EPA, 1994). Therefore, the results of this single medium modeling approach have resulted, in many cases, in noticeable over-regulations of a target medium without proper accounting for the contribution of other media to the pollution. The reasons for these shortcomings in the above models are numerous and may also include a lack of relevant representation of the environmental processes. This can mostly be attributed to the inherent difficulties in linking complex models to account for the inter-transfer of contamination between various media. In the current research we have developed a model that can represent a complex environment such as the Passaic River Watershed using a multimedia approach.

The multimedia media approach to environmental modeling was first used by Hamaker (1972) to predict the distribution of contaminant in the different sub-compartments of a soil (solid soil, water and air). The Hamaker's description of the environment was later extended to a macroscopic application by introducing the 'evaluative environment' concept (Baughman and Lassister, 1978). An evaluative environment is best described as a theoretical unit of the world in which the behavior of a particular contaminant can be described and quantified. This was achieved by reducing complex phenomena into simpler and more manageable ones. For example, lumping the laminar and turbulent diffusion coefficients in a fluid phase into one coefficient which is representative of an average environmental process such as bulk diffusion between air and water. Thus a "new environment" along with its properties can be defined and used to determine the fate and distribution of chemicals. Many multimedia models have appeared since the introduction of the unit world concept; the most promising and popular of which is the Mackay's equilibrium model (Mackay, 1979; 1983; Neely, 1979; and Cohen, 1990).

The above equilibrium model, also known as "fugacity model" is based on well-understood thermodynamic principles. According to such principles, a contaminant introduced into an environment will reach equilibrium among the different environmental compartments and thus satisfying the conditions of 'equal fugacity'. Fugacity itself has been described as the tendency of a chemical compound to escape from one phase to another based on its vapor pressure in these phases. This principle can be applied to an evaluative environment consisting of many different phases between which the chemicals will move and reach equilibrium. The different phases can be represented by boxes or compartments, which are then linked together through the fugacity of the chemical and the transport parameters. This organization of the model gave rise to the appellation "box-model" which is commonly used for this approach. Furthermore, each box is described as a CSTR (Completely Stirred Tank Reactor) or homogeneous and well mixed compartment.

In order for multimedia models to be useful, accurate representation of the physical, chemical and biological transformations is necessary (Cohen, 1986). These models can be very useful to environmental managers because of the large amount of information they generate regarding the macro-behavior of the environment being studied. In other words, it is possible to compare individual inter-media processes such as deposition to water vs. direct discharge to water to determine which of these processes dominates the movement and the fate of the contaminants in the water environment. This type of analysis becomes particularly critical in evaluating emission data. For example, industries can reduce their responsibility by moving emissions from one medium (highly regulated) to another (less regulated) without a net reduction to the pollution. The multimedia approach will provide us with the necessary tools to determine the effect of every contribution to a given compartment, and thus allow us to assess the impact of the contaminant on the total environment.

An illustration of the multimedia model, along with different compartments and processes controlling the fate of contaminants in the environment, is provided in Figure 1.1. The figure includes five major compartments, namely: air, soil, water, sediment at the bottom of water bodies, and groundwater. These compartments are in turn subdivided into sub-compartments as follows:

1. The air compartment consists of pure air phase and aerosols.
2. The soil compartments consist of solid soil and terrestrial plant.
3. The water compartment consists of pure water phase, suspended sediment, and aquatic biota including fish, plant and other aquatic populations.
4. The sediment compartment includes just the deposited sediment layer.

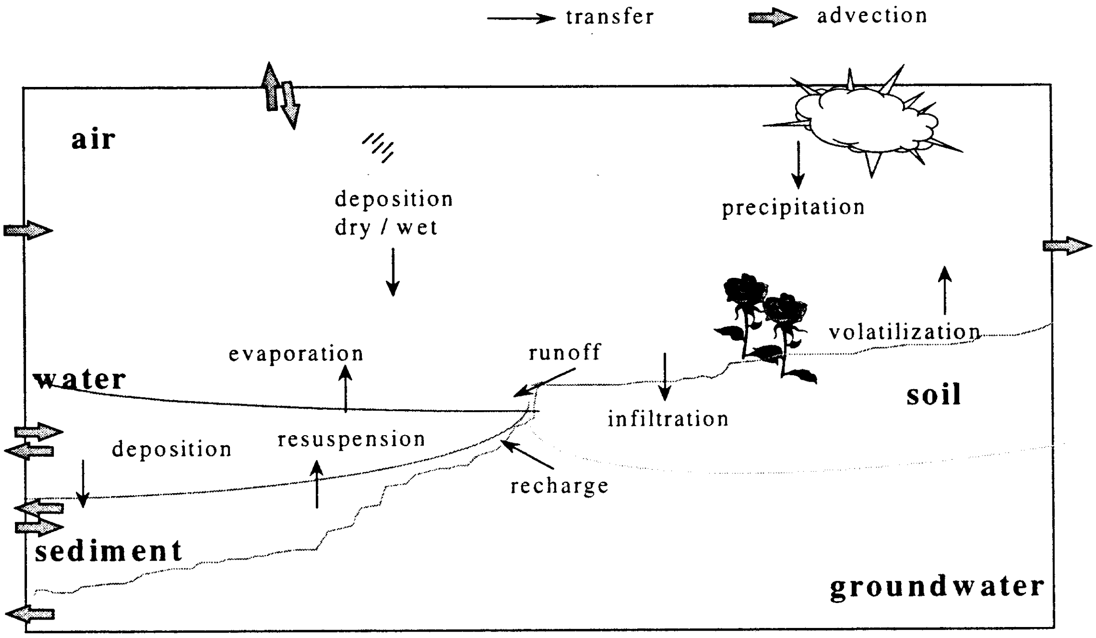


Figure 1.1 A Schematic Representation of a Unit Watershed Environment

The above subdivisions are necessary to accurately model the entire behavior of a contaminant in different environmental compartments. Such behavior depends on the nature of the chemical under consideration. An example of such differing behavior is the case of hydrophobic chemicals such as dioxin, which has a higher affinity for organic carbon than for pure water and air, thus it will mostly partition into the soil, aerosols and water sediment. More examples are described later in this dissertation.

1.2 Research Objectives

The multimedia model developed in this research will be used to determine the fate of five prominent chemicals being released in the Passaic River Watershed in New Jersey. The intended use of this model is as a screening tool in the management of contaminant releases in the watershed environment. The useful and interpretative outcome of this modeling effort is possible providing the emission rates of the chemicals in the environment and an accurate estimate of the chemical transport across the watershed boundaries are quantified. Because the predicted chemical concentration sought after can potentially be used for risk assessment purposes and for providing an understanding of the relative sources of the organic pollutants, the average concentration of such chemicals in each medium would be sufficient. This is possible since average exposure concentrations are directly used in the risk calculations.

The main point of contention in using the multimedia equilibrium approach, which is the lack of spatial resolution, will be investigated by introducing an element of spatial resolution in the multimedia representation of Passaic River Watershed contamination by organic chemicals. Two levels of resolution are introduced using two different representations of the Passaic River Watershed environment: treating the watershed as one unit, and using a sub-watershed unit division of this landscape. For the latter representation, the watershed hydrological unit characteristics, HUC11, as defined by the N. J. DEP, are used as unit environments. Recalling that the unit environment consists of different phases, such as air, water, soil layers, vegetation, sediment, all assumed to be uniformly mixed, the HUC units will be linked together using the inter-phase transfers of the contaminant. A comparison of the total distribution of the contaminant using the above two levels of spatial resolution will follow. Since no reported comparisons between different (spatial scales) applications of the same model exist, a major contribution to the validity of the equilibrium approach will be to determine the impact of spatial resolution on the model results. This point is underlined by the fact that the major criticism of the approach is not the science of the physical inter and intra-phase transfers, but rather the lack of spatial resolution that they provide. The following points represent a summary of the goals of this research:

1. To develop a multimedia box-type model to predict the fate and transport of five prominent organic chemicals in the Passaic River Watershed. As a result, the average concentrations in various media will be determined; also an understanding of the different environmental processes that determine the ultimate fate of the five chemicals used will be predicted. Furthermore, the chemical concentrations predicted by the model can be easily incorporated into the risk assessment of the contaminants and therefore, potentially prioritize them based on availability and toxicity. One possible outcome of this effort is to make recommendations regarding present and future releases of such chemicals.

2. To model the Passaic River Watershed as a unit environment and introduce a sub-watershed division (11 units division) of the watershed environment to determine the impact of higher resolution on the multimedia equilibrium model results. In this framework, the watershed landscape will be completely characterized for future use, and the methodology developed can be applied to other watersheds in New Jersey and elsewhere.

3. To provide a substantial validation effort of the modeling results. The end results are expected to be the average concentrations on which risk assessment calculations may be performed. These averages should be within the range of measured concentrations, where available, in New Jersey Department of Environmental Protection (NJDEP) monitoring studies or compare well with other established models.

4. To determine the distribution of contaminants in the environment, using a level IV (unsteady state) fugacity model. Although the level III model is sufficient for most assessment purposes of low concentration contamination, it does not provide an

appreciation for the time required to reach this state. Furthermore, the environmental processes, which drive the fate of the contaminant, are continuously changing based on the different state of fugacity in environmental media. The unsteady level IV representation can be used to perform long term scenario analysis and no-action alternatives. It also permits us to determine the environmental response times or how long it would take the contamination to be reduced to acceptable levels.

It is believed that accomplishment of the above goals would contribute substantially to the field of environmental engineering and to the solution of pollution problems. This approach may also lead to viewing environmental pollution problems in a different way, not as stand-alone issues to be addressed on a medium specific basis but as inter-related mechanisms between the properties of the chemicals and the nature of the environment in which it is released. Finally, the goal of the current research is not to obtain a high spatial resolution of contaminant distribution, but to determine the overall understanding of the chemical fate and the processes that dominate its final distribution in the environment.

1.3 Research Justification and Applicability

To overcome the inability of present numerical and analytical models to account for the cross-medium transfer of contamination, a multimedia approach is proposed in the current research. This multimedia model is to be used to assess the contamination of the Passaic River Watershed environment from the releases of different chemicals. Five prominent chemicals are chosen for this study based on their toxicity to humans, persistence in the environment and magnitude of their use. These chemicals are: trichloroethylene (TCE), 1-1-1 trichloroethane, naphthalene, toluene and xylene. Additionally, since these chemicals are released at a relatively low concentration with little spatial variation, it is appropriate to use a multimedia equilibrium model to predict their fate.

This new approach to represent different spatial scales of an environmental unit is different from the previous attempts which have focused on using a single environmental unit such as a contaminated site, a state, or a region. Typically, the units are then divided into bulk compartments and sub-compartments to represent a local or regional transport (Wania 1996, Diamond 1990 and Cohen 1990). In the current research, a much higher spatial resolution is sought at the watershed division. The watershed division is chosen herein because it presents several benefits including a more coherent data collection since current NJDEP regulated facilities and environmental monitoring stations are made on watershed basis. Also, the watershed unit provides a more "natural unit" for the different environmental processes, especially water flows. As such each watershed will constitute a complete environmental unit consisting of 7 compartments (air, water, sediment, surface soil, terrestrial vegetation, root zone soil and vadose zone soil) and 18 different sub-compartments. The latter classification is critical to the model developed and used in this study.

A significant obstacle that must be overcome in this research is the ability to provide an accurate distribution of contaminants in the environment including an accurate characterization of the contaminant sources and landscape parameters. Preliminary review of the state and federal databases on environmental reporting has determined that the present methodology of reporting chemical releases is increasingly favorable for the application of this model. The latter is specifically possible through the dissemination of the Toxic Release Inventory (TRI) of major chemicals in the air (via stack emissions, fugitive emission etc...), water (discharge through publicly owned treatment works or POTW) compartment, and land disposal. However, soil sources will not be characterized with any accuracy since disposal of contaminants to landfills predates most regulatory permitting. Therefore, the mass of contaminants present in site soils or even their chemical species are not readily quantifiable. It should be noted that current efforts addressing this issue are underway at the NJDEP. Although this information will not be available during the development of the current model, the latter can still be tested using reported disposal mass in the TRI database to determine the relative contribution of all sources to the watershed contamination. The present research is believed to be the first attempt of its kind not only for Passaic River Watershed, but also for any northeastern areas with similar physiographic or hydrogeologic properties. Thus, the Passaic River Watershed landscape will be established in detail and will constitute a major effort in this research. It is intended to establish this landscape listing from the current NJDEP GIS (Geographical Information System) and other available published databases. This constitutes a major milestone in linking the state GIS resources and other database sources to perform detailed multimedia environmental assessment of contaminants.

To test the objectivity of this effort, a similar multimedia model, QWASI (quantitative water-air-sediment interchange), developed by Mackay (1989) was used to predict the fate and transport of two prominent chemicals (dioxin and PCB) in the New York Harbor environment. The predicted water, sediment and fish concentrations of these chemicals were found to be within measured values in the harbor. A detailed explanation of this case study on the applicability of multimedia model is presented in Section 1.6. It should be noted that a number of researchers, using this approach to environmental modeling, have successfully predicted the fate of chemical release from contaminated soils and assessed human risk from such contamination. The model known as "CalTOX" is enjoying an increasing popularity and is directed to smaller contaminated soil sites of total area in the order of 1 square kilometers (CEPA, 1993). Other studies include the prioritization of chemicals released in air in the State of Minnesota using human risk-based concentrations (MPCA, 1992). Using this multimedia model in the State of Minnesota, over 126 priority chemicals that are emitted via air have been ranked according to the risk they present to human health and to the environment in the State of Minnesota. Finally, a new regulatory use of multimedia model has been implemented in the European Economic Community (EEC). This model is the Netherlands Uniform System for the Evaluation of Substances (USES), and it is used to prioritize the newly manufactured and existing chemicals used in the Netherlands (RIVM, 1994) and throughout the EEC. The prioritization is based on the same multimedia compartment model to predict the fate and transport of contaminants in air, soil, water, and other compartments.

1.4 Historical Account and State-of-the-Art in Multimedia Environmental Modeling

Environmental models have been developed and used for many decades to address the ever-increasing pollution problems. Chemical pollutants are released from manufacturing waste streams, agricultural sources, mining industries, and human activities. Although some of these pollutants are occasionally released in large concentration (such as in accidental oil spills), the largest mass is due to the continuous release over time. The effect of these chronic releases on human health has been the subject of intense exposure and toxicity assessments by EPA researchers and academics. Exposure assessment is usually achieved with the use of environmental models that can predict the level of contamination to which humans are exposed. These models have traditionally been based on "one" environmental medium such as the transport of contaminant through water. However, in the past two decades another type of environmental modeling approach based on the multimedia approach and more specifically the fugacity approach has emerged.

Multimedia modeling has been introduced as a new tool to track the distribution of a contaminant in all environmental compartments connected together. This approach first appeared in the late seventies under the terminology 'environmental chemodynamics' and environmental distribution of a contaminant was predicted using the concept of the 'evaluative environment' (Baughman and Lassiter, 1978). The advantage of reducing the complex environment to an evaluative unit world was the result of the development of a comprehensive understanding of the contaminant's movement in the environment and the driving forces behind such movement. Also, the new approach provides a quantitative approach to estimating the exposure to contaminants and thus can be used as a tool for assessing the risk to human and environment.

Subsequent developments of this modeling approach resulted in an increased number of publications on this subject according to Vighi (1993) culminating with the publication of the Organization of Economic Cooperation and Development report on the practical approaches for the assessment of environmental exposure (OECD, 1986). Of these new approaches to environmental modeling, the fugacity or Mackay type model have been widely recognized as potentially the most useful (or popular) model (Cowan, 1994). The fugacity model is based on the simple thermodynamic 'fugacity', a principle introduced by the American chemist G. N. Lewis in 1901. Lewis proposed to use fugacity to characterize chemical equilibrium and partitioning to assess the distribution of a chemical compound in different phases. As such, a fugacity model should predict the amount of contaminant that will partition in each phase or compartment (Mackay, 1991).

1.4.1 Approaches to Environmental Modeling

As cleanup efforts and their costs have increased dramatically over the past three decades, there has been a noticeable increase in the number of mathematical models developed to address past and present pollution. These models vary both in scope and application. Some models are essentially used to assess the for-seen risk to human and environment due to toxic chemicals. The validation of these multimedia models is as varied as their scope, however, the most prominent ones had some successful field validations. There are two basic approaches to model the environment, namely: the spatial approach and the equilibrium approach.

1.4.1.1 Spatial Environmental Models: Spatial models have been the traditional approach to modeling pollutants in the environment. The first comprehensive attempt of such modeling effort was possible with the introduction of the computer as a calculating tool. Instead of finding analytical solutions to complex partial differential equations, approximate solutions using either finite difference or finite element representation of the equations were developed. These models were first developed in the 1950's to predict the exposure of human to global fallout of nuclear fallout and were more extensively developed in the middle of 1970 (OECD, 1977; Eliassen and Saltbones, 1975) and more recently by Petersen (1993). They consist of solving numerically the partial differential equations that represent the movement of chemicals in an environmental phase (such as air, water, sediment and soil layers). Such models include air dispersion models that predict the movement of pollutants in the air using Eulerian equations and large input data. The recent model HMET (Heavy Metal Eulerian Transport) was designed to track long range transport and deposition of heavy metals such as mercury and lead (Bartnicki, 1996).

Extension of the above approach was applied to contaminated sites. The most popular of such models include the Jury Volatilization model (Jury et al.; 1983 and 1990) which is an extension to the analytical solution of the one dimensional diffusion equation formulated by Carslaw and Jaeger (1959) and Mayer et al. (1974). Here the diffusion equation is solved for a uniformly mixed layer of soil where the volatilization occurs at the soil surface (EPA, 1996). The Jury model has been used for both finite and infinite sources, and was based on assumptions such as no boundary layer at the soil-air interface, no water flux through the soil and an isotropic soil column contaminated uniformly throughout. Some of these assumptions and attributes made this spatial model similar to some extent to those proposed in multimedia approach, but without the consideration of interface fluxes as in the multimedia models. The Jury model is discussed here because it has been extensively validated at the bench scale and in field studies (Balbour, 1984; Radian Corporation, 1984 and 1989; and Kienbush, 1986), and has been proposed as an accepted soil model in the EPA soil screening guidance (EPA, 1996).

These spatial models have the advantage of providing a high resolution simulations of contaminant transport. Their major limitation is usually longer computational times since the higher resolution is based on discretizing the environment into smaller sub-units in which the differential equations are solved simultaneously. The smaller the sub-units, the larger the number of equations that must be solved. To arrive at a solution of these equations, boundary values are necessary and these are obtained using either monitoring data or making assumptions. As such these models are extremely useful in dealing with site specific situations. Additionally, the spatial models are mostly geared toward the transport of a contaminant in one medium. Examples include the EPA groundwater model MODFLOW and air dispersion model ISC2 (Industrial Source Complex). Other fate and transport models used for regulatory purposes include the SESOIL (Seasonal Soil Compartment Model), CMLS (Chemical Movement in Layered Soils) and PRZM-2 (Pesticide Root Zone Model).

SESOIL is a numerical model developed to simulate finite source contaminant movement in soil (Criscenti, 1994). It uses a volatilization module coupled with a hydrodynamic dispersion module and accounts for such processes as diffusion, sorption, biodegradation, metal complexation, cation exchange and hydrolysis. It also includes a soil erosion, runoff and infiltration for surface water inputs. The limitations of using this model are the excessive need for input data that makes its use inappropriate for screening level applications when large and complex areas are considered.

The CMLS is an analytical finite source model developed to represent hydrodynamic movement of contaminant in the unsaturated zone (Nofziger, 1994). Although the CMLS model does not include as many processes in its fate and transport as the SESOIL, it does include multiple soil layers (up to 20 different layers) for better characterization of site heterogeneity. Also, in this case the need for detailed input data limits its utility to site specific situations. Additionally, the model does not calculate the leachate concentration which is left to the user to estimate through other means (EPA, 1996). The objective of this model is limited to predicting the time required for a contaminant to reach the water table from contaminated sites.

Another complex model developed to simulate most of the environmental processes is the numerical model PRZM-2. This model also included an uncertainty analysis using the Monte Carlo analysis and attempts to couple a leaching model (PRZM) and a soil transport model (VADOFT). In this case, the transport and transformation of contaminant are predicted by running the transport model VADOFT, and then uses its result as boundary conditions for the leaching model PRZM. This awkward coupling, along with the need for large input data, make the use of this model difficult. Cohen (1990) made similar conclusion in this regard. According to these researchers, existing spatial multimedia models including UTM-TOX (Unified Transport model for toxicant), ALWAS (Air, Land, Water Analysis System) and TOX-SCREEN are all single medium models linked in series. The consequences of this approach are cumbersome models that are unable to account for all the environmental processes simultaneously. Furthermore, input requirements of such models restrict their use to site specific contamination.

1.4.1.2 Equilibrium/Fugacity Models: The shortcomings of the spatial modeling and the lack of inter-media transfer processes prompted the development of new multimedia approach. Some of the first of such approach include the U. S. EPA EXAMS (Exposure Analysis Modeling System) model (Burns, 1981), a lake eutrophication model (Schnoor, 1980), and the Great Lakes model (Thomann, 1984 and Dolan, 1982). Of these models, the EPA Exams model has been used extensively in regulatory decision-making and has been reviewed to a greater extent. EXAMS is a dispersion model that uses water and sediment flow to predict chemical concentration in the aquatic (water and sediment) environment only. It includes advective processes in water, suspended sediments, losses through air and mobile biotic materials between compartments and takes into account the chemical transformation, direct photolysis, hydrolysis and oxidation. The EXAMS was the first step in recognizing the advantages of the multimedia approach; however, it did not include all the environmental compartments required for a comprehensive multimedia modeling effort. These shortcomings were subsequently addressed by Donald Mackay in the early 1980s in what is called the fugacity approach. A fugacity multimedia model uses the equilibrium concept of a chemical introduced in an environment with its partitioning properties among different phases (air, water, soil, sediment, and biota) and transport vectors to predict distribution of the chemical in all phases.

The fugacity model was first used in the QWASI (Quantitative water, air and sediment interaction) model which was applied to assess the distribution of contaminants in the Great Lakes (Mackay, 1983). Other successful applications of the fugacity approach to an aquatic environment included the determination of the fate of 17 chemicals in the Bay of Quinte in Canada (Diamond, 1994), a surface water runoff application (Di Guardo, 1993), PCBs studies in Lake Ontario (Fox, 1996), heavy metals contamination in Hamilton Harbor in Canada (Diamond, 1996). The model was also used to estimate the pesticide loading to surface water from agricultural watershed in Chile (Barra, 1994). These aquatic models vary in their scope and levels of complexity. While the homogeneous box model or zero spatial variability has been sufficient for most environmental applications, few efforts have focused on introducing a spatial variability to represent the inherent heterogeneity of the environment. Two causes have been attributed to this variability in environmental distribution of contaminant (Wania, 1996):

1. The first relates to the spatial proximity and accessibility of the source of contamination, the difference in source strength from one location to another and impartial mixing of the environmental compartments. Examples of this case include the heterogeneity of chemical concentration between areas receiving direct discharge versus remote areas, and distribution of chemicals in a river system between shelf areas versus other areas. This particular heterogeneity is more noticeable for local discharge of immobile and reactive contaminants and has little or no effect on non-point sources.

2. The second cause relates to the variability of the processes that control the fate and transport of contaminant caused by the variation in different locations of an environmental compartment. One example of this type of variability is the different rates of biological degradation due to the variable concentration of microbes in the soil compartment. The same analogy can be made for the type of soil at a site since clay soils will behave as sinks for certain chemicals compared to sandy soils.

Similar conclusions were made by Cohen (1990 and 1994) regarding the need to include some spatial resolution in the SMCM model (Screening-level Spatial Multimedia Compartment Model). This author proposed to divide the environment into two types: uniformed and well-mixed compartments (air, water and suspended sediment) and non-uniform compartments (soil and sediment layer). The non-uniformity can be introduced by subdividing the compartment into smaller sub-compartments. For example, dividing the soil into a top-soil sub-compartment and a deep soil sub-compartment. Other authors proposed to remedy the lack of spatial resolution by subdividing the soil compartment based on its use (such as agricultural, natural and industrial; Maddalena, 1995). Also, variable transport rates between sub-compartments based on the level of heterogeneity were proposed (Mackay, 1990 and Devillers, 1995). Similarly, dividing a larger environmental unit into smaller multiple compartments such as different reaches of a river, or nesting the compartments, such as using a smaller compartment within a larger compartment were proposed by Van De Meent (1995).

Finally, the current state of the art in multimedia modeling is well demonstrated in the California State EPA CalTOX model (CEPA, 1993). The CalTOX model represents not only all relevant processes, but also include an exposure module that determines the human risk level for most organic contaminants present at a specific site. It is currently being worked into the framework of California State pollution remediation as a tool for responsible parties to assess the human risk of their discharges. However, the CalTOX model is limited to an area extend to 1000 m^2, thus effectively reducing its utility to only small contaminated sites.

1.5 Description of the Generic Fugacity Model

Since the beginning of the industrial revolution, we have enjoyed an ever- increasing use of new chemicals to better our lives. In the process, the amount of chemicals being released into the environment has also been increased. In response to the need to assess the impact of the disposal of these chemicals on both human and the environment, environmental models have been developed. For the most part, the models that have been used for this assessment were based on a single medium such as water transport model or air dispersion model. These models, although accurate and possessing great spatial resolutions, do not account for the transfer of chemical from one medium to another, and thus do not reflect actual environmental processes. For instance, it is estimated that over 90% of the lead, PCBs and Benzo(a)pyrene in Lake Superior come from air sources (USEPA, 1994). To overcome these limitations, multimedia approaches are required.

The multimedia approach proposed in this research predicts the fate and transport of contaminants by incorporating not only the single medium fate and transport but also the inter-medium transfers in the form of a comprehensive model. A contaminant is thus modeled using not only its chemical-physical characteristics, but also by considering the characteristics of the environment (including all phases that are present). One popular multimedia model that is used by researchers is the Mackay model which has received substantial peer review (Cowan, 1994). The Mackay type model is to be used as the framework of this research. These models are based on the well-accepted thermodynamics concepts such as fugacity and equilibrium.

A detailed analysis of the fugacity notion can be found in most chemical engineering texts (Lyman, 1982; Thibodeaux, 1996). Fugacity is denoted by the symbol f, and has units of pressure (Pascal). It is related to concentration as follows:

$$C = f * Z \tag{1.1}$$

where,

C is the concentration in mole/m^3

f is the fugacity in Pa

Z is the fugacity capacity in mole/m^3.Pa

1.5.1 Fate and Transport Component of the Model

The contaminant may enter and leave an environmental unit by a number of mechanisms or processes. A comprehensive accounting of these processes is needed to properly model the real environment. In the present research, all relevant processes will be represented as to allow a complete understanding of the contaminant journey into the evaluative environment. The processes that drive the fate and transport of the contaminant are divided in three types, advection, decay and inter-media transfers. A detailed description of such processes is provided below.

1.5.1.1 Advective Processes: Contaminant movement across state boundaries has been the focus of current environmental dispute between neighboring states. Examples are the contemptuous disputes between the United States and Canada, Germany-England and Scandinavian countries, and between the former USSR and its European neighbors.

Attempts to address such pollution at a local level will undoubtedly lead to failures. An example of such case is the assessment of chlorobenzene in the southern region of Ontario, Canada. Researchers have found that the sources of this contamination was not due to the Canadian sources, but due to the United States through particles drift (Renner, 1995). In this case, the United States sources contributed the chlorobenzene pollution about 300 times more than the local sources. Other pertinent example of pollutant drift is the detection of DDT and other pesticides in animal tissues in the North Pole. Such chemicals were never manufactured nor used in these areas, but were transported there via dust particle deposition.

Contaminant gains and losses through such advective processes are discussed in the present study with the conservation of mass. These processes include advective air, water, suspended sediment, air particulate inflow and outflow from the evaluative environment. One way to quantify these processes is to introduce a rate of advection, N (mole/h) where N is the product of the flow rate G (m^3/h) and the concentration of the contaminant in that medium C ($mole/m^3$). Thus flows of contaminant across a watershed boundaries (i.e. through water) will be calculated with ease by knowing the in-flowing water concentration and the water flow measurements.

$$N = G * C \tag{1.2}$$

Recalling that the goal of the modeling exercise is to predict average concentrations of a contaminant, the above equation needs further manipulations. From the first equation presented above

$$C = f * Z \tag{1.3}$$

Thus,

$$N = G * f * Z = f * (GZ) = f * D_a \tag{1.4}$$

where D_a is called the advective transfer coefficient. D_a has mole/h.Pa units. It is possible to use this form of representation for all advective processes shown below. A list of advective processes to be represented in the current multimedia models includes:

1. Transfer of air between the troposphere and the stratosphere (vertical movement of air out of the evaluative environment)

2. Inflow and outflow of air in the air compartment. This is considered with only the pure air phase (not including aerosol particles). Estimates can be made from wind speed measurement.

3. Inflow and outflow of aerosol particles in the air compartment. Fractional relationships have been developed between the pure air phase and the aerosols in the bulk air compartment by Mackay (1991) and MPCA (1993). One such relation has the aerosol concentration in air to be close to 10^{-11} per volume fraction. Thus the aerosols flow rate can be estimated from the airflow rate in the air compartment.

4. Inflow and outflow of surface water in the air compartments.

5. Inflow and outflow of suspended sediment in the water compartment. Similar to the aerosol case, fractional relationships between suspended sediment and water flow can be used to estimate the sediment inflow or outflow rates into the water compartment.

6. Inflow and outflow of biota in water compartment. Here only fish will be considered as the primary aquatic biota; an implicit food chain model will be included to account for the bio-concentration and the bio-magnification of contaminant in fish tissue.

7. Deposition of suspended sediment from water column to the sediment layer.

8. Re-suspension of sediment particles from the sediment layer to the water column. Such movement may be caused by turbulence in water, or by movement of biota through the sediment (bioturbation). The net difference between the latter two processes is the amount of chemical lost through sediment burial. This process is very important in many waterways, especially those used for shipping lanes. The continuous burial does eventually fill the channels and may require dredging which may cause subsequent re-contamination of the water. This is a significant problem in the New York Harbor, for instance.

9. Infiltration of the water from the air phase to the soil phase (i.e. rainfall).

10. Leaching of soil moisture to the water table accounting for the aquifer recharge. This is significant since many of the contaminated sites are underlined by aquifers.

11. Inflow and outflow of groundwater through the evaluative environment. This will account for transport of the contaminant from up-gradient sources.

12. Possible recharge of surface water by intermittent rises in water table elevation. It is not certain if such phenomenon occurs in New Jersey but it may be accommodated in the model, if needed.

1.5.1.2 Reaction Processes: Another mechanism through which contaminant gains and losses take place in the environment is due to degradations and other forms of transformations. Not all reactions are degradations. For example some reactions just change a chemical from one compound to another but do not lead to degradation. The reaction rate, k is derived in most chemical references as the radioactive decay and is usually represented as:

$$k = 0.693 / t_{1/2} \tag{1.5}$$

where, $t_{1/2}$ is the time required for the depletion of 50% of the contaminant present initially. Furthermore, this degradation time has been the subject of substantial research, and environmental rates have been derived and are widely available in the literature. For example, the half-life ($t_{1/2}$) of 2,3,7,8-TCDD (tetrachloro-dibenzo-p-dioxin) has been suggested as 170 hours in the air compartment, 550 hours in the water compartment, 17000 hours in the soil compartment and 55888 hours in the sediment compartment (Mackay, 1992). It is clear that if no remediation is chosen as an alternative, reduction in pollution level is to be expected only in the air and water compartments. Furthermore, the persistence of the dioxin once introduced into the soil and sediment is very prolonged.

As for reactions that do not follow the first-order kinetics, a pseudo first order reaction can be assumed. This is necessary since higher order reactions are much difficult to handle and require two or more rate constants. One such reaction is the microbial rate of decay which is proportional to the concentration of all organisms and the rate applicable to each organism. However, under real environmental conditions, most reactions are second order. Using the above simplification, the second order reaction rates are lumped into one reaction rate as follows:

$$N = V * C * k_1 * k_2 \tag{1.6}$$

with N the advective rate in mole/h, V the compartment volume in m^3, C the phase concentration in mole/m^3, k1 and k2 representing the reaction rates in h^{-1}. Introducing a new rate constant k such that $k = k_1 * k_2$, the above equation can be rewritten as transfer coefficient, D_r as follow:

$$N = V * C * k = f * D_r \tag{1.7}$$

The environmental processes that are classified as reactions include:

1. ***Biodegradation***: This applies to most naturally occurring chemicals and some synthetic chemicals with the exception of high molecular weight compounds. The rate of degradation depends on the amount and concentration of the chemicals present, amount of nutrients, the properties (i.e. toxicity) of the contaminant and the amount of organisms present to convert the chemical. Biodegradation is therefore not applicable to the free-phase contaminant but to the low-level contaminant which is considered in the present research. Also some synthetic compounds have shown to be formidable to this degradation due to their physical and chemical properties. Such is the case for highly chlorinated solvents that are necessary ingredients to numerous manufacturing processes. In these cases where biodegradation has shown powerless, special degradation half-lives will be closely examined to ensure proper reaction rates. These degradation rates have been estimated for many aerobic and anaerobic processes at environmental temperature (Mackay, 1991 and 1992). Numerous databases relating the chemical properties to their degradation rates have been compiled by many researchers (Howard and Banerjee, 1984; Alexander, 1985; Neilson, 1985; Painter, 1985 and Brown, 1987). This is especially true for petroleum-based chemicals introduced in the environment as a result of oil-spills (National Academy of Sciences, 1985).

2. ***Hydrolysis***: A reaction process caused by the addition of water, i.e., hydrogen ion and hydroxyl ion to a chemical species. Mabey and Mill (1978) have co-related the half-life degradation rates of ester to the pH. The hydrolysis reaction is found to be strongly dependent on the pH and is found to apply to a small number of organic chemicals. Of

the organic compounds encountered in the environment, alkyl halides, amides, amines, carbamates, carboxylic acid esters, epoxides, nitriles, phosphonic and phosphoric acid esters, and sulfonic and sulfuric acid esters have been found to be the most responsive to hydrolysis (Schnoor, 1996).

3. ***Oxidation***: A process by which the dissolved oxygen in the environment oxidizes the organic chemical. This oxidation process may also be caused by singlet oxygen, ozone, hydrogen peroxide or other hydroxyl radicals. The latter are very abundant in nature and have large oxidizing power (Schnoor, 1996). Additionally, there is a wealth of literature on the reaction half-lives of the oxidation of organic compounds and these will be used to predict the degradation of chemicals in the proposed model. Very often, redox reactions are dominant under anaerobic conditions (absence of oxygen) and are specially relevant to soil contamination.

4. ***Photochemical Transformation Reactions***: These transformations occur in the presence of sunlight, which causes rupture in chemical bonds. This process occurs in two forms, as a direct photolysis where the organic molecule absorbs photons and becomes exited with the ensuing release of electron thus changing the molecule. The other form of phtolysis involves indirect photolysis. This proceeds with the energizing of an intermediate molecule which reacts with the organic chemical of interest. Photolysis reactions are important for degrading organic compounds in the upper atmosphere as well as in shallow aquatic environment (Sawyer, 1994). The United States Environmental Protection Agency (U. S. EPA, 1983) has devised specific guidelines to estimate the transformation rates of photolysis along with the other processes. Application of this reaction process is incorporated into U.S. EPA environmental

EXAM (Exposure Assessment Model) model (Burns, 1985). Other researchers have studied this process in marine and freshwater photolysis (Zafriou, 1984; Payne and Philips, 1985 and Mudambi, 1988).

In a given compartment, advection and reaction are the two processes that control the loss of contaminant. It should be noted that these two processes can also be added through the transfer coefficient D_r and D_a, defined above. This addition is possible because of the common fugacity assumption in a compartment. The net loss of the contaminant through these two processes in water for example is defined as:

$$N = (f_w * \sum D_a + f_w * \sum D_r) = f_w * D_T \qquad (1.8)$$

with f_w, the water fugacity of the chemical and D_T the overall transfer coefficient. Additionally, the above loss quantification can be used to estimate the overall residence time or persistence of the contaminant in an evaluative environment. Assuming that the total amount of contaminant in the environment is known to be M (mole). Thus:

$$M = \sum f * V * Z \qquad (1.9)$$

$$t = M / N \qquad (1.10)$$

where t is the total residence time (in hours), M is the total mass (in moles) and N is the loss of contaminant (in mole/h). Rewriting the last equation:

$$1 / t = N / M = f (\sum D_a + \sum D_r) / f * \sum(V * Z) = \sum D_a / \sum(VZ) + \sum D_r / \sum(VZ) \qquad (1.11)$$

$$1 / t = 1 / t_a + 1 / t_r \qquad (1.12)$$

with t_a and t_r being the residence times attributed to the advective and reactive processes, respectively. Although the two quantities are treated independently, reaction and advection are related in an environmental compartment. The rate at which the contaminant degrades in a compartment depends strongly on its availability or the loss of that contaminant via advection. As demonstrated above in Equation 1.12, the residence times add reciprocally and the dominant loss mechanism will have the larger influence on the overall persistence of the contaminant.

1.5.1.3 Inter-Media Transfer Rates: Contaminant fate and transport are determined not only by advection and transformation, but also by other inter-media transfers such as non-diffusive and diffusive transfers. Diffusion itself can be divided into two phenomena, diffusion within one medium (i.e. dilution) and diffusion between two adjacent media (i.e. volatilization). In the real environment the diffusive transport is very slow and difficult to quantify. This process (diffusive in a single medium and diffusive across two media) have been and continue to be the focus of scientific investigation as much doubt remain regarding the transfer coefficient of chemicals under various environmental conditions. Each of these processes will be discussed in more detail.

1. ***Diffusion within a single compartment*.** This type of diffusive transfer is driven by the presence of a concentration gradient and is generally termed 'molecular diffusion within a phase'. This process is the result of the continuous movement and mixing of the molecules from one distribution to another. Also, this movement has been described as random in nature and has been expressed mathematically as Fick's First Law of diffusion:

$$N = -B*A*dC/dy \tag{1.13}$$

where B is the diffusivity (mole/h), A is the area of diffusion (m^2), C is the concentration of the diffusing compound (mole/m^3), and N is the flux of compound (mole/h) as, previously defined. The term dC/dy represents the concentration gradient responsible for this molecular diffusion from high to low concentration. This process is well described in most transport phenomena texts under the term Brownian movement. The diffusivity B has been related to the molecular displacement y and the time of that displacement t (Bird, 1960) as:

$$y = (2Bt)^{1/2} \tag{1.14}$$

Since y, dy or B are not known in most situations, a new term was devised to incorporate them and thus effectively decreasing the number of unknown parameters.

The same diffusivity formula can be extended to cover turbulent or Eddy currents. The random molecular diffusion described above generally applies to stagnant fluid bodies. However, under most environmental conditions, these fluids (air, water) are in motion. In cases of wind induced movements in water or river flows in steep channels, the turbulent diffusion becomes more dominant and the molecular diffusion can be neglected (Thibodeaux, 1996). One pragmatic approach to model these two processes into one is to describe the turbulent diffusion in the same manner as that of the molecular diffusion. The new diffusivity is as follow:

$$N = -A(B_m + B_t)dC/dy \tag{1.15}$$

where B_m and B_t represent the molecular and turbulent diffusivities, respectively. Thus, depending on the diffusive process (river flow, thermocline layer of a lake) one of the above two diffusivities will dominate.

Finally, this molecular diffusion is applicable to contaminant movement in porous media. The reason lies in the extremely slow movement of groundwater since the hydraulic conductivity ranges from 1E-6 m/s for sandy aquifers to less than 1E-9 m/s for clay layers. These low conductivities translate in about a transport of contaminant 30 meters downstream in a year. Also it has been established that the pores (containing water) are interconnected to allow not only advective transport, but also diffusive transport. The slow movement of groundwater makes the molecular diffusion an important process. The retardation in this case is caused by two factors: the tortuosity factor F_y which causes the fluid and contaminant to travel a longer distance, and an area factor F_a which accounts for the decrease in diffusive area caused by the presence of soil particles (Satterfield, 1970). Furthermore, F_a is defined as the void fraction v (fraction of total volume which is fluid) and F_y has been related to the void fraction by the inverse square root. The effective diffusivity B_p of these two factors has been related to the molecular diffusivity B_m as:

$$B_p = B_m F_a / F_y = B_m v^{1.5} \tag{1.16}$$

It should be noted that the diffusivity B_p applies to only concentration in the diffusing medium and where sorbed phases are absent (inert matrix as sand). In situations where the contaminant may be sorbed to the matrix (organic and clayey materials), a correction must be applied to the diffusivity based on the sorption strength of the contaminant on organic compounds. Such correction can vary from 1 (for relatively hydrophilic chemicals) to 1000 or more (for hydrophobic chemicals).

2. ***Diffusion between phases***: This type of diffusion represents the advantage of the multimedia approach over the spatial approach in environmental modeling. Although it is often difficult to characterize, many analogies exist in other engineering fields. Processes that are described by inter-phase diffusion include volatilization (air-water transfer), sorption and de-sorption (water-sediment), absorption (soil-air), and water to aquatic biota transfers. While diffusion in a single medium has been described using a concentration gradient, the case is not true for inter-phase diffusion. The diffusion (i.e.

volatilization) between water and air will approach completion without the need for the concentrations to be equal. However, at this non-equilibrium state, the fugacity in both water and air will be equal. Thus, the inter-media diffusion is driven by the fugacity gradient and not by the concentration gradient. Inter-phase diffusion has been described using the Whitman Two-Resistance mass transfer coefficient (MTC) approach (Whitman, 1923). This approach has been applied to atmosphere-ocean water interchange by Liss and Slater (1974) and organic solute transfer by Leinonen (1975). The fugacity formulation of this process has also been formulated and applied to various scenarios of environmental transport (Mackay, 1991). Examples of inter-media diffusive transfers that are important in contaminant transport include:

- Air-water transfers: The volatilization of certain contaminants from water to the atmosphere is significant. This is the principle behind the air-purging of waste water treatment plant or the passing of contaminated water through aerated towers. Oxygen transfer between the atmosphere and the ocean is considered to have the highest overall mass transfer coefficient in nature in the order of 20 cm/h (Schnoor, 1996). There are other contaminants that readily volatilize from water to air: they include PCBs, and dieldrin.

- Soil-air transfers: The volatilization and absorption from and to surface soils can be modeled using the inter-media diffusion. This process is important for chemicals with high vapor pressures such as TCE (trichloroethylene).

- Sediment-water transfers: This includes the re-diffusion of contaminants from the buried sediment layers to the water column. A major concern that arises in dredging water bodies is not only the re-suspension of sediment particles but also the availability of buried contaminant for back diffusion to the water compartment.

- Biota-water transfers: This relates to the diffusion of contaminant across the skin, stomach and gills of aquatic biota (Clark, 1990). Through this process a low concentration of a contaminant becomes concentrated in fish tissues (usually several order of magnitude for chemicals with high K_{ow}). This phenomenon is referred to as bio-concentration; for example, DDT may be found in fish at concentration one million times that of water.

1.5.2 Different Types of Fugacity Models

Based on the level of complexity desired and on the goal of the modeling efforts, all these advective, reactive and diffusive processes can be accounted for in multimedia models. These considerations were the basis of distinguishing four different levels of fugacity models. The different levels are presented below.

1.5.2.1 Fugacity Level I: Level I is the simplest and quickest fugacity calculation that can be used to assess the case of an environmental contamination. It uses only the partition coefficient and an evaluative environment, as shown in Figure 1.1, to predict the chemical distribution between all the phases present. A level I calculation may be useful for a rapid prediction of an accidental release of chemicals. Since it does not account for any losses (transport, degradations), it can only be used for relatively simple assessment.

1.5.2.2 Fugacity Level II: Level II calculations account for all the environmental losses described above. These include advection in and out of the compartments, sediment burials, degradation and reactions. Furthermore, since these processes have been described in a similar fashion, it is possible to combine them in an input-output mass balance calculation. Also, level II chemical equilibrium is assumed to exist between all phases, and thus inter-phase diffusion is not included in the calculations. From the combination of the different processes, residence time or persistence can be estimated for a given contamination.

1.5.2.3 Fugacity Level III: A realistic modeling effort should include representation of all processes that are important to the fate and transport of the contaminant. While the inter-phase transfers are ignored in level II, they may be very important to the fate of certain chemicals, especially for those with high vapor pressure. A new level of fugacity model is devised to include the non-equilibrium condition that appears in inter-phase diffusions. Thus a level III model predicts the steady state concentration of a chemical in all compartments as a result of its partitioning properties and the environmental processes acting on it. A typical mass balance for a level III fugacity applied to the water-atmosphere environment is presented in Figure 1.2 as follows:

Change in contaminant mass is equal to the total input minus the total output:

$$dM/dt = V_iZ_i df_i/dt = I_i + \Sigma(D_{ij}f_j) - \Sigma(D_{Ti}f_i) \tag{1.17}$$

where V_i represents the volume, Z_i the bulk fugacity capacity, D_{ij} the inter-media input transfers, D_{Ti} the inter-media output transfers and I_i the direct input in the compartment i. The subscript j represents the other compartments contributing to the mass input into the compartment of interest i. Since steady state conditions are assumed, the first term df_i/dt is equal to zero and the resulting system of equations can be solved for the different fugacity parameters. Using the example of Figure 1.2, these equations are written as:

In the water compartment where the fugacity is f_w:

$$EW + \{f_{iw}(DI + DX) + f_a(DC + DQ + DM + DV)\} - f_w(DY + DS + DJ + DV) = 0 \quad (1.18)$$

In the air compartment where the fugacity is f_a:

$$EA + \{(f_{ia}(DP + DY) + f_w(DV)\} - f_a(DU + DQ + DA + DQ + DC + DV) = 0 \quad (1.19)$$

Also in the above equations, EW and EA are the emission rates into water and air in mole/h, f_{iw} and f_{ia} stand for the fugacity in the water inflow and air inflow, respectively; these can be estimated from the background air and water concentrations. The task in Level III models is thus reduced to solving the above two equations for f_w and f_a.

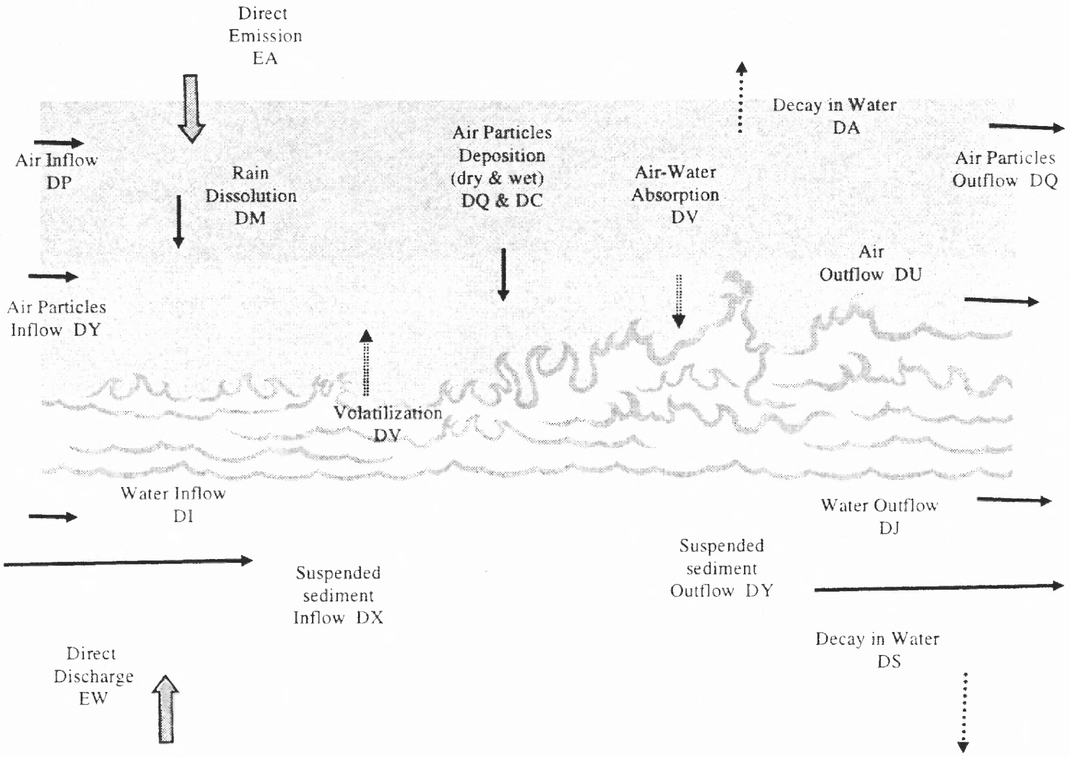


Figure 1.2 A Water-Air Evaluative Environment

1.5.2.4 Fugacity Level IV: The level III fugacity model used to solve a steady state problem can be extended to handle unsteady state situations. The additional complexity has the cost of more input data as initial conditions are now required to perform the simulation. Level

IV can be very advantageous, especially when long-term scenarios need to be considered. Also it may indicate to decision-makers the required time for an environment to return to an acceptable level of contamination. The term $V_iZ_idf_i/dt$ is not zero in the unsteady state level IV, thus the chemical fugacity and concentration are allowed to change with time.

The inter-media transfers discussed above constitute the main difference between the multimedia models and the spatial models. The advantages in using a multimedia approach include the ability to add and compare all the D values (MTC) individually while keeping computations relatively easy to follow. Also, all the MTCs can be added in series or in parallels to determine the overall contaminant fate. These MTCs values contain a great deal of information as to which process would dominate the ultimate fate of the contaminant and thus lead to effective decision making.

1.6 Case Study of Multimedia Modeling in the New York Harbor and Illustration of the Model

As stated in this chapter, a case study using the multimedia approach to environmental modeling was performed to investigate the applicability and merit of such models. This work involved the study of pollution in the New York Harbor and was recently published (Coulibaly et al, 1998).

The New York Harbor has received large amounts of contamination since the beginning of this century. The level of contamination increased as the number of chemicals and manufacturing plants multiplied upstream of the harbor. Although the discharge of contaminants such as PCB and dioxin has been curtailed in recent years, the level of such chemicals in the harbor sediment continues to persist. In this study, we have attempted to quantify contaminant contributions from all sources using multimedia modeling to assess the current situation in the harbor. The water and air concentrations of both chemicals in the harbor area are above the national average (NJDEP Incinerator 2000 Report and U.S. EPA, 1994). In our study we have accounted for all contamination sources, including: direct discharge into the harbor, contaminant loading from the tributaries and ambient air sources. To assess the transfer of contaminants across different environmental compartments, a multimedia modeling based on the fugacity approach was employed. The selected geographical area was divided into three separate compartments - air, water and sediment. These compartments were linked together through transport parameters (diffusion and advection) as per Level III fugacity model developed by Mackay. The fugacity model used here is a modified QWASI (Quantitative Water-Air-Sediment Interaction) model developed by Mackay (1991).

1.6.1 Characteristics of the Environmental Compartments

The area of study covers an approximate area of 7.26E8 m^2 and is comprised of three major compartments of equal area but varying volume: air, water and sediment. Each compartment in turn consists of different sub-compartments i.e. air compartment comprises of pure air and aerosols. The inflow and outflow rates for the New York Harbor were estimated to be 2.59E6 m^3/h and 2.89E6 m^3/h, respectively (Thomann, 1989). From the same reference, mean sediment depth was taken to be 2.29 cm, the inflow water particles to be 64.63 mg/L, the solid volume fraction of 0.15 in sediment and a lipid volume fraction of 0.07 in fish.

Other significant parameters include the fraction of organic carbon of 0.072 and 0.036 in water particles and sediment, respectively. The deposition rate of suspended sediment was estimated to be 1.4 g/m^2.day and the re-suspension to be 0.58 g/m^2.day. The rainfall rate of 1.08 m/y with the aerosols deposition rate of 7.2 m/h and aerosol scavenging ratio of 200000 were used (Mackay, 1991). Finally, densities of 1 g/cm^3, 1.5 g/cm^3 and 2.4 g/cm^3 were used for water and fish, aerosol particles and sediment particles, respectively. Of these parameters, the organic carbon content is the most critical since it influences the different partition coefficients between the phases present. Other references used to characterize the harbor environment include the National Oceanography Series and the default environmental parameters provided by Mackay (1991) for the evaluation of the generic fugacity model. The relevant landscape data are summarized in Table 1.1.

In the above Table 1.1, most of the transport values were estimated from the environmental data of the Hudson River Estuary, which includes the New York Harbor. For the most part these data were weighed on the area basis to account for the heterogeneity present at these sites. For the purpose of this case study, these values were assumed appropriate, however, more accurate data on the environmental compartments will be obtained through the NJDEP GIS (New Jersey Department of Environmental Protection Geographical Information System) databases to model the Passaic River Watershed environment. The linking of this modeling effort to the above GIS database is an important phase of this study. Other assumptions made in the determination of the environmental parameters include an estimated air residence time of 10 hours (i.e. the air parcel entering the compartment will exit within 10 hours). All other parameters were extensively characterized in the Thomann's report, thus allowing for a detailed analysis of these parameters.

Table 1.1 Environmental Compartments and Flow Rate Descriptions

[3]Water area (m2)	7.26E+08
[3]Sediment solids volume (m3)	2.49E+06
[3]Sediment pore-water volume (m3)	1.41E+07
[3]Mean water depth (m)	7.34E+00
[3]Mean active sediment depth (m)	2.29E-02
[3]Water inflow (m3/h)	8.41E+06
[3]Water outflow (m3/h)	2.89E+06
[1]Rain rate (m3/h)	8.98E+04
Rain rate (m/year)	1.08E+00
Total inflow rate of particles (m3/h)	2.26E+02
[2]Sediment deposition rate (m3/h)	1.76E+01
[2]Sediment deposition rate (g/m2.day)	1.40E+00
[2]Sediment re-suspension rate (m3/h)	7.32E+00
[2]Sediment re-suspension rate (g/m2.day)	5.81E-01
[2]Sediment burial rate (m3/h)	7.42E+00
[2]Sediment burial rate (g/m2.day)	5.89E-01
Particle outflow (m3/h)	2.41E+00
[4]Aerosol deposition velocity (m/h)	7.20E+00
[4]Scavenging ratio Q	2.00E+05
[4]Wet particle deposition rate (m3/h)	3.59E-01
[4]Dry particle deposition rate (m3/h)	1.04E-01
[4]Total particle deposition rate (m3/h)	4.64E-01

1 National Oceanography Series
2 Mackay (1991) for a generic environment
3 Thomann (1989)
4 Mackay (1992)

1.6.2 Physical-Chemical Properties of Dioxin and PCB

The fate of a chemical compound is largely dependent on its basic properties such as its partitioning among different media, its partial vapor pressure, molecular weight, and mass transfer coefficient at environmental temperature. For these two chemicals there is a wealth of chemical and physical data available from numerous studies undertaken to determine their toxicity. The references used in this research are those compiled by Mackay and Wan (1992, 1993). These properties drive the contaminant to move from one medium to another based on its relative affinity in the two media (for example, PCB, which is hydrophobic will freely transfer from water to the organic sediment). Also of interest are the different degradation rates, since they determine the persistence of the contamination in the environment. These properties are summarized in Appendix A.

1.6.3 Summary of the Chemicals Input

The Dioxin and PCB chemicals have been introduced into the harbor environment from the surrounding industries prior to 1970. A major source of dioxin was the Diamond-Alkyli Company located on the Passaic River, which directly discharged to the harbor and from the New York City metropolitan POTWs (Publicly Owned Treatment Works). As for PCB, it originates mainly from the different industries on the upstream confluence of the Hudson River and other major tributaries of the harbor and also from the POTWs. The industries discharged the PCB in the past decades before its manufacture was banned in 1977. The upstream section of the Hudson River is believed to contribute up to 85 percent of the harbor PCB load (Thomann, 1989).

Table 1.2 summarizes the mass contaminant input into the harbor environment. These data were obtained from Thomann (1989) and the NYSDEC Incineration 2000 Report. Additionally, it is believed that the air sources were not well characterized thus the ambient air concentration is used as the atmospheric contribution. Furthermore, two separate ambient air concentrations are available for PCBs, including a published monitoring concentration and an estimated concentration based on aerosol deposition. The first provided an ambient air concentration of 1.34E-4 ng/m^3 of PCB and 5.93 E-4 ng/m^3 of dioxin over Bergen and Essex counties in New Jersey. These monitoring sites are located sufficiently close to the harbor area to allow the use of their data. The second ambient PCB air concentration of 7.77e-3 ng/m^3 is estimated from Hudson Estuary air sources with the assumption of advective air residence time of 10 hours. In investigating these two scenarios, the multimedia model sensitivity to this parameter will be characterized.

The water sources are divided into two components, loading from inflow water bodies (Upper-Hudson, Passaic and Raritan rivers and local runoffs which account for 24165 cfs), and the direct discharges (through POTW and CSO - Combined Sewer Overflow which accounts for 3643 cfs). Similar values have been reported by Brosman (1996) with 21865 cfs for inflow and 4058 cfs for direct discharge. Using PCB loading from Thomann (1989), these flows translate into 5185 kg/y via inflow water or 228.53 ng/L and 509 kg/y via direct discharges. The dioxin sources are not as well characterized as the PCB sources, therefore, the limited available monitoring data is used to estimate the inflow water concentration. A survey of 20 representative communities in New York State determined an average dioxin concentration of 1.7 ng/m^3 (Meyer, 1989). Other significant sources that have been identified include wastewater from domestic laundry (EPA, 1994), thus POTW discharges may be important. The only data available on dioxin discharge to the harbor through POTWs did not report any concentration above the reporting limit (NYC DEP, 1995). However, detected values of 0.012 to 0.027 ng/L were reported and are used to estimate direct discharges of 65 g/y in this case study.

Table 1.2 Chemical Input Summary

	Dioxin	PCB
Air concentration ng/m^3	5.93 E-4*	7.77 E-3$^@$ & 1.34E-4*
Inflow water (bulk) concentration ng/m^3	1.7$^\#$	2.28E5$^@$
Direct discharge g/year	65**	5.09 E5$^@$

* NYSDEC Incineration 2000

** NYCDEP, 1995

\# Estimated from EPA/600/6-88/005Cb-c

@ Thomann (1989)

1.6.4 Mass Balance

The summation of the inflow, outflow and residing contaminant in the environment is conserved at all time. A non-equilibrium fugacity model, which accounts for the above mechanisms (advection, decay and inter-phase transfers) and is in steady state, is called a level III fugacity model. The mass balance is as follows:

$$V_i Z_i df_i/dt = I_i + \Sigma(D_{ji} f_j) - \Sigma(D_{Ti} f_i) = 0 \tag{1.20}$$

For the biota (fish) sub-compartment, the fugacity f_f is calculated assuming the fish to be in equilibrium with the bulk water compartment. The biota mass balance is written as:

$$V_f Z_f df_f/dt = D_{vg}(f_w - f_f) - D_m f_f - D_g f_f + E_o D_a f_a - E_o D_a f_f/BMF = 0 \tag{1.21}$$

with D_{vg} representing the gill ventilation, D_m the metabolism, D_g the growth/dilution, D_a the food uptake, E_o the uptake efficiency and BMF the bio-magnification factor. Once the water fugacity has been calculated, the latter equation is then used to estimate the fish fugacity/concentration.

1.6.5 Results of Model

The results of this case study are presented below in Table 1.3 and in graphical format in Figures 1.3 and 1.4. Table 1.3 includes different compartments and sub-compartments concentrations and the distribution of the chemicals in each phase. The graphical representation of the results includes all the different processes through which the chemicals degrade and move in and out of the harbor environment.

The distribution of both dioxin and PCB is presented along with the dominant processes that determine their fate in the environment (Figures 1.3 and 1.4). It is clear that the fate of dioxin is driven by its hydrophobic properties as most of the chemical is transferred to water and sediment through deposition and is removed by either sediment

Table 1.3 Environmental Compartments Concentration of Dioxin and PCB

	Dioxin	**PCB**	
		Ambient Air Conc.	Ambient Air Conc.
Total air (ng/m3)	5.93E-04	1.34E-04	7.77E-03
Total water (ng/L)	1.49E-03	2.14E+02	2.14E+02
Inflow water (ng/L)	1.70E-03	2.28E+02	2.28E+02
Particulates (ng/g)	3.78E-01	4.22E+04	4.22E+04
Sedt solids (ng/g)	1.44E-01	3.49E+04	3.49E+04
Sedt pore water (ng/L)	1.55E-03	5.95E+02	5.95E+02
Rain (ng/L)	5.34E-02	5.16E-04	2.99E-02
Fish (whole) g/m3	3.51E-05	5.168	5.168
Fish (lipid) g/m3	5.01E-04	73.84	73.84

Dioxin Ambient Air Conc. of 5.93E-4ng/m3 & Direct Discharge of 65 g/year

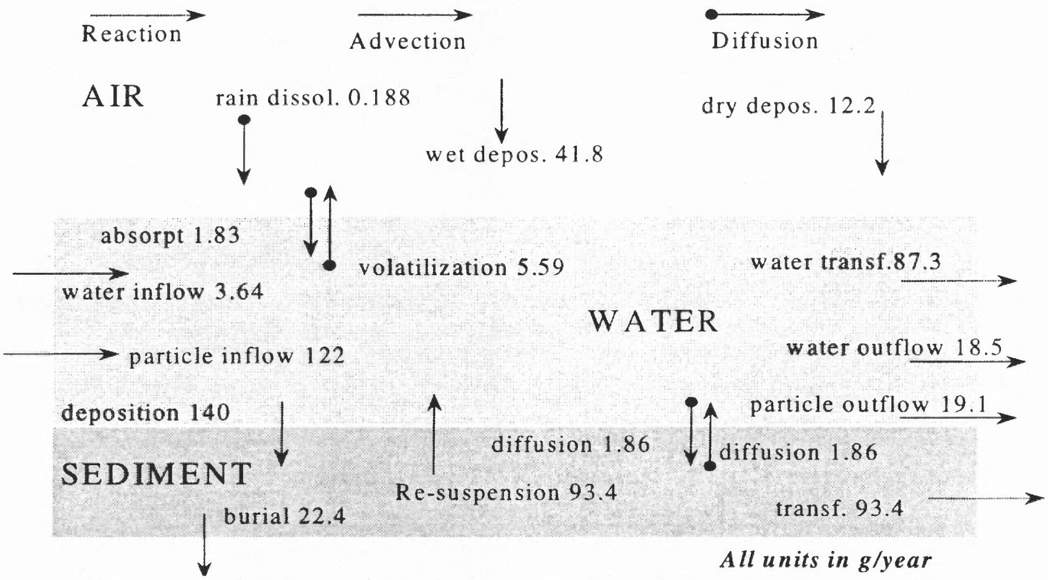


Figure 1.3 Environmental Processes Driving the Fate of Dioxin in the New York Harbor.

burial or degradation in water. So in a sense, the harbor is effectively cleaning the dioxin from air and transferring it to the sediment. The monitoring data on this compound are very limited because the environmental concentrations are often below the detection limits. However, the dioxin can bio-accumulate in aquatic biota, which provides an exposure pathway to humans. The predicted fish dioxin concentration using the above data is 3.5E-5 μg/g for the whole fish body and 5.01E-4 μg/g for the fish lipid.

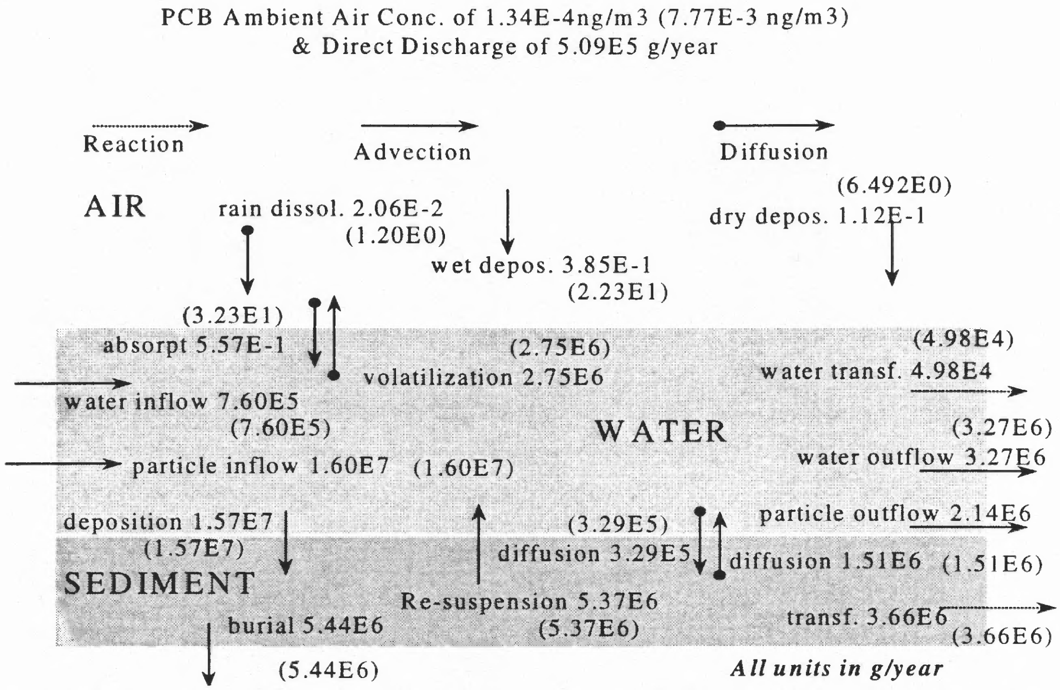


Figure 1.4 Environmental Processes Driving the Fate of PCB in the New York Harbor.

Figure 1.4 illustrates the fate of PCB in the New York Harbor. Here, the dominant inter-phase transfers are volatilization and sediment burial with each process being important. And unlike dioxin, the air compartment is being contaminated by the volatilization of the PCB from the harbor water. The two scenarios of PCB modeling resulted in similar concentration as shown in Table 1.3. Therefore, the hydrophobic characteristic of this chemical dominates its fate in the harbor environment and the air sources have little or no influence on the water, sediment and subsequently biota concentrations. The bulk water concentration predicted from the model (0.214 μg/L) compares very well with the measured value of 0.09 to 0.24 μg/L from NYC 208 Data and 0.1 to 0.5 μg/L from USGS 1978 Data. These data were reported in Thomann (1989). Similar concentration (0.0819 to 0.2 μg/L) was also obtained from NYSDEC monitoring data for 1991-1992 (Litten, 1995). Finally, computed bulk water concentration at different locations in the harbor ranged from 0.1 to 0.28 μg/L (Thomann, 1989).

The predicted PCB concentration in sediment of 34.9 μg/g slightly overestimated the reported values of 0.3 to 10 μg/g (Achman, 1996), and 0.1 to 8 μg/g (Thomann, 1989). Finally, the fish (Striped Bass) concentration (5.16 μg/g for whole fish and 73.84 μg/g for fish lipid) predicted by the present model strongly agree with the reported data. Sloan (1988, reported in Thomann, 1989) reported Striped Bass concentration in the New York harbor to be between 3 and 7 μg/g. Also reported in the Thomann (1989) study is the lipid base concentration of PCB in Striped Bass from the NYSDEC Data (1984) which ranged from 25 to 150 μg/g and total fish concentration from 2 to 15 μg/g. A summary of the above results is presented in Table 1.4.

Table 1.4 Model Results versus Measured Values

Compartments	Dioxin	PCB	
	Predicted	Predicted	Measured Range
Water (bulk) μg/L	1.49E-06	0.214	0.09-0.24[*], 0.1-0.5[*]
Sediment μg/g	1.44E-04	34.9	0.3-10[&], 0.1-8[*]
Fish (whole) g/m3	3.51E-05	5.168	3-7[##], 2-15[**]
Fish (lipid) g/m3	5.01E-04	73.84	25-150[**]

* Thomann, 1989
& Achman, 1996.
Sloan, 1988
** NYSDEC Data, 1984

From the above figures, the dominant process controlling the fate of the contaminants is the deposition of suspended sediment. Additionally, the most significant process to the reduction of both contaminants is the decay or transformation in the sediment compartment. It is interesting to note that more contaminant is leaving the harbor environment through degradation than through advective flow. Also included below in

Table 1.5 is the relative distribution of dioxin and PCB in the water and sediment compartments. It is observed that the bulk of the contaminant is residing in the sediment compartment.

Table 1.5 Distribution of PCB and Dioxin Between the Harbor Compartments

Total Mass (g)	Dioxin	PCB
Bulk Water	7.91E+00	1.14E+06
Sediment	8.60E+02	2.09E+08
Harbor System	8.68E+02	2.10E+08

In conclusion it can be argued that the multimedia approach can be successfully used as a screening tool to determine the fate of contaminants in larger environments. This may not be the case for spatial models because the requirement for input data would make their use prohibitive for such applications. Additionally, unlike their spatial counterparts, multimedia models can determine not only average contaminant concentrations, but also the relative importance of each environmental process to the contaminant fate. Therefore, better management decisions can be made to address current and future pollution issues. Finally, it is recommended that future contaminant source data should be reported to allow the use of multimedia models. Such reporting format should include not just measured concentration, but an estimate of the contaminant mass and some key physical properties of the environment (for example organic carbon content of the soil and sediment, and deposition velocities of particles).

CHAPTER 2

FORMULATION OF THE FUGACITY MULTIMEDIA ENVIRONMENTAL MODEL

2.1 Introduction

In the present study a fugacity model was developed to predict the fate and transport of organic contaminants in the Passaic River Watershed in northern New Jersey. In this chapter, the landscape parameters are incorporated into the formulation of the general non-equilibrium fugacity mode (Level III and IV). Additionally, the fugacity calculations, partition coefficients and mass transfer coefficients as they pertain to the present multimedia model are presented. Finally, the numerical analysis used to solve the resulting mass balance equations is provided. The flow diagram of this formulation is in Figure 2.1.

The model is expected to estimate the environmental concentrations of the chemicals released within the watershed in seven bulk compartments and eighteen separate sub-compartments. The main compartments are as follow:

1. Bulk Air Compartment, (1): The area extent of this compartment covers the entire sub-watershed. This compartment is further divided into two sub-compartments; the pure air phase, 1-1, and the aerosol particles, 1-3.
2. Bulk Water Compartment, (2): The entire Passaic River Watershed coverage is 4.8% water. This compartment is also divided into 3 sub-compartments; pure water phase, 2-2, suspended water particles, 2-3, and aquatic biota, 2-4.
3. Surface Soil Compartment, (3): The very top layer of the ground surface has much different characteristics than the deeper layers, both physically and chemically. It has higher organic matter content because of the surface vegetation and detritus and much

more void space. It is divided into 3 sub-compartments; the soil air, 3-1, the soil water, 3-2, and the soil solid particles, 3-3.

4. Bottom Sediment Layer, (4): With an area extent equal to that of surface waters, this compartment is very active in exchanging contaminants with the overlying water column. In the present model, it is divided into the sediment pore water, 4-2, and the sediment particles, 4-3.
5. Terrestrial Vegetation, (5): The vegetation is modeled as a separate compartment because it represents a significant portion of the land bio-mass in the Passaic River Watershed. It is divided into foliage plant, 5-1, and the plant roots, 5-3.
6. Root Zone Soil Compartment, (6): The physical location of this compartment is between the surface soil and the deep soil. It is also composed of soil air, 6-1, soil water, 6-2, and soil solids, 6-3.
7. Vadose Zone Soil, (7): This deep soil compartment is divided into 3 sub-compartments, soil air, 7-1, soil water, 7-2 and soil solids, 7-3. It is in direct contact with the groundwater and transmits the contaminant to the groundwater via seepage.

This model would serve as a tool to make informed management and regulatory decisions by providing the distribution of contaminant in the environment and the relative importance of the many environmental processes that drive fate and transport. Being fully dynamic, the model is expected to assess the impact of multiple scenarios on the exposure concentrations. These decisions include the reduction of current releases, the media in which the contaminant is released and the time required to reach acceptable levels.

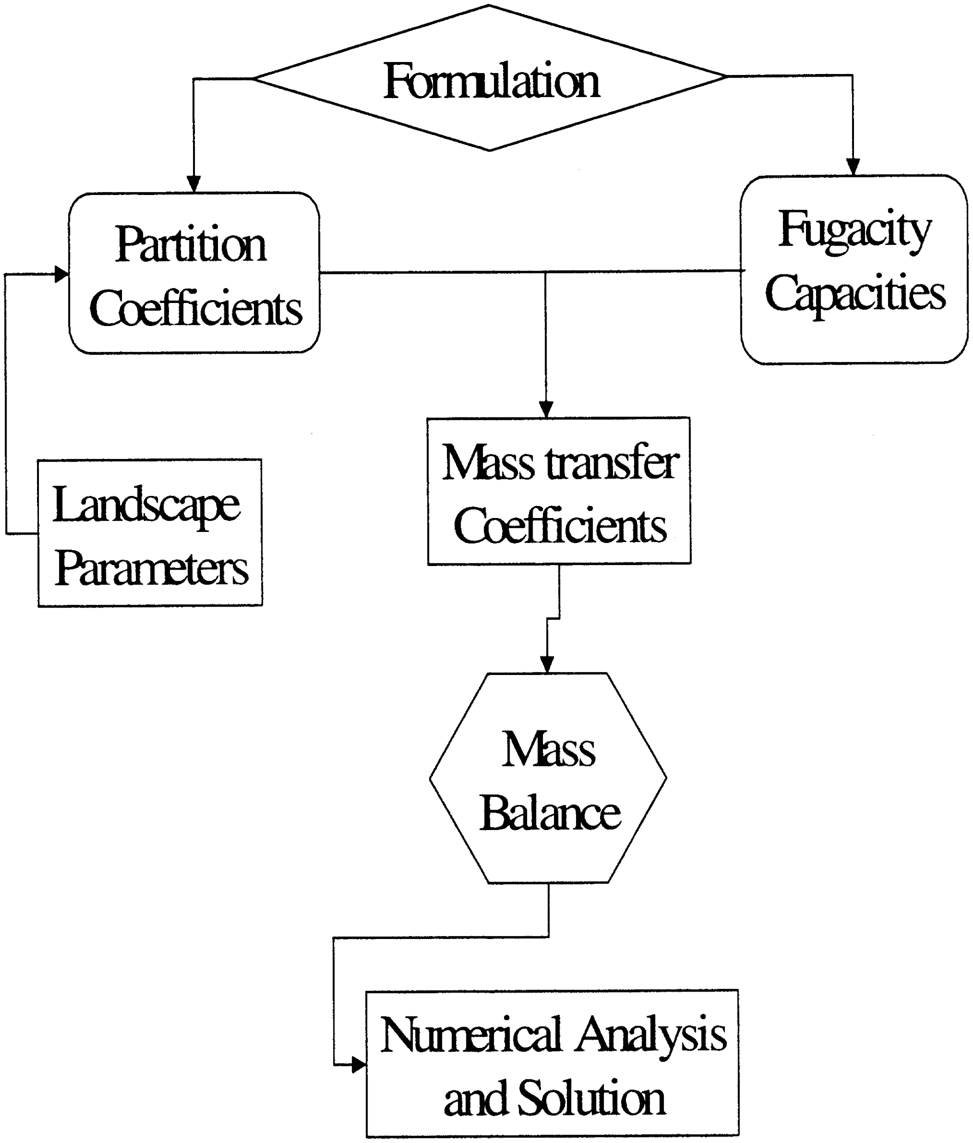
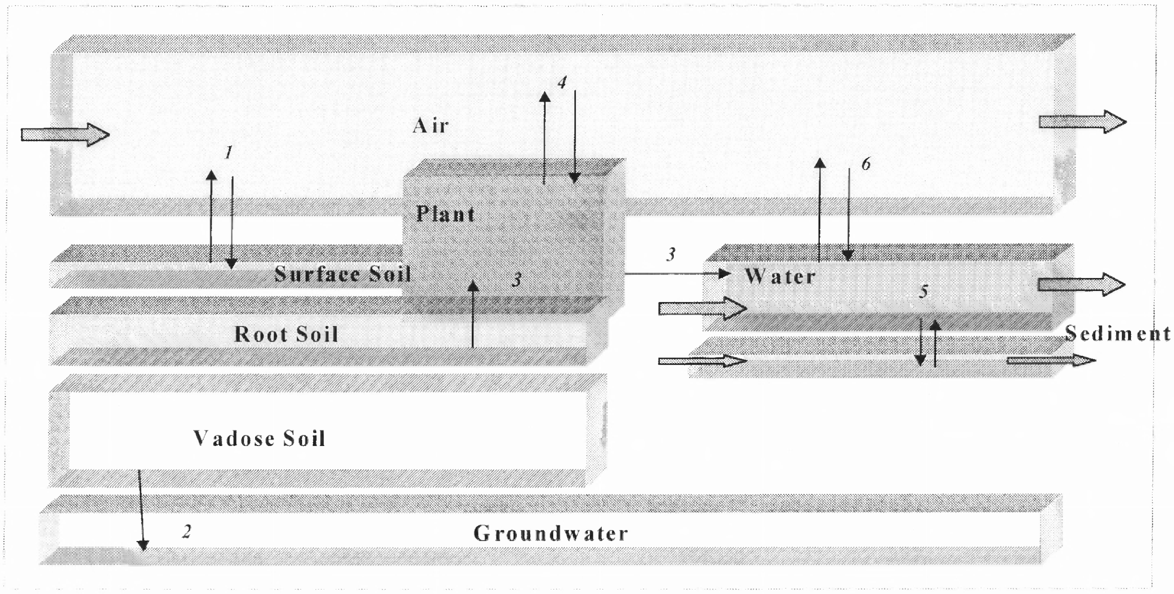


Figure 2.1 Flow Chart of the Watershed Multimedia Model Formulation.

The fugacity based models are divided into different levels of complexity, both in spatial and temporal scales. The first applications include steady state models with application to one unit environment. These steady state models are also known as Level III fugacity model. The unsteady state or dynamic fugacity models, known as Level IV, have received little development and are investigated as to their application to different scales in this research and will be a significant contribution to this emerging area of environmental modeling. The fugacity approach is discussed further below. Shown below in Figure 2.1 is a single unit world (e.g. watershed) with selected transport vectors shown for illustrative purposes.



→ Inter-media transfers

⇨ Advective Inflow/outflow

1 - soil-air absorption/volatilization/deposition (wet/dry)
2 - soil-groundwater recharge
3 - soil-surface water runoff, infiltration
4 -groundwater-surface water recharge
5 - surface water-sediment deposition/re-suspension/diffusion/burial
6 -surface water-air volatilization/absorption/deposition (dry/wet)

Figure 2.2 A Representative Watershed with the 7 Compartments and Selected Transport Vectors.

2.2 Fugacity Model Formulation

The fugacity model includes representation of all the processes that are important in the fate and transport of a contaminant including the inter-phase transfers. A model is devised to include the non-equilibrium condition that appears in inter-phase diffusions. Thus a level III model predicts the steady state concentration of a chemical in all compartments as a result of its partitioning properties and the environmental processes acting on it. A mass balance is written between the different compartments that comprise the environmental unit being modeled.

A contaminant is modeled based on its chemical-physical characteristics and on those of the physical environment. The latter includes all 7 bulk compartments and 18 sub-compartments in the present model. The model itself is based on the universally accepted thermodynamic concepts of fugacity and equilibrium, as first developed by Mackay (1991). A detailed analysis of the fugacity notion can be found in most chemical engineering texts. Fugacity is related to the concentration as follow:

$$C = f * Z \tag{2.1}$$

The fugacity, f, is analogous to temperature in heat transfer process (Mackay, 1991), i.e.,

Heat content/mass = temp. * heat capacity

with units J/kg = °K * J/°K.kg

The heat content per unit mass can be described as the heat concentration. Temperature is equivalent to fugacity and the heat capacity is synonymous with the fugacity capacity. Equation 2.1 can thus be re-written as:

Concentration = fugacity * fugacity capacity

The fugacity, f, is a characteristic of the contaminant and the fugacity capacity Z is that of both the contaminant and the medium. The fugacity equation is not necessarily linear in a real environmental setting (Mackay, 1991), and this non-linearity can be represented in the fugacity capacity, Z. Fugacity capacity is found to be a function of temperature, properties of the contaminant, properties of the physical environment or the compartment, pressure and concentration of the contaminant. Thus any estimation of Z will allow us to calculate the concentration of the contaminant by assuming equilibrium criteria. Therefore, the main task of finding a contaminant concentration in one or more compartments given the concentration in another compartment, has been made easier with the use of this method.

When equilibrium is established between two adjacent environmental compartments, their fugacity will be equal. This principle of equal fugacity implies equilibrium and not equal concentration is the first major property of this concept. Since fugacity is easily related to concentration, the above approach of equilibrium allows the properties of each compartment to be treated separately. This should provide an understanding of the processes or the driving force behind the equilibrium between the different compartments. It should be noted that 'same fugacity or equilibrium' is different treatment from the simple partition of a chemical between different compartments since the fugacity capacity is medium specific.

2.2.1 Partition Coefficients and Fugacity Capacity Calculations

In order to obtain the mass transfer coefficients needed to set up the mass balance equations, the fugacity capacities, Z, and partition coefficients are needed for each compartment and sub-compartments. The starting point of these calculations is to estimate the air and water fugacity capacities using standard thermodynamics equations. The remaining Z values for all other media are then obtained by relating the air and water Z values to their partition coefficients.

2.2.1.1 Pure Air Fugacity Capacity Z_a: Fugacity, *f*, is synonymous to the partial pressure, P for the vapor phase of a chemical. The latter expression can be derived as follows:

$$PV = nRT \tag{2.2}$$

$$C = n / V = P / RT = f^*Z \tag{2.3}$$

Thus,

$$Z = 1 / RT \tag{2.4}$$

This will be taken as the pure air fugacity capacity, or Za. Here P represents the vapor pressure of the chemical, V its molar volume, n the number of moles, R the universal gas constant, 8.314 Pa-m^3/mol-K and T the absolute temperature in Kelvin. Using the equilibrium criteria (common fugacity among all phases present):

$$f_1 = f_2 = f_3 = \ldots.= f_i \tag{2.5}$$

Considering two compartments (i.e. water and air),

$$f_a = f_w \tag{2.6}$$

$$C_a / Z_a = C_w / Z_w \tag{2.7}$$

$$C_a / C_w = Z_a / Z_w = K_{aw} \tag{2.8}$$

where K_{aw} is the air-water partition coefficient. For organic chemicals with appreciable vapor pressure, this coefficient takes the form:

$$K_{aw} = H / RT \tag{2.9}$$

where H represents the Henry's Constant. Thus these equations can be written to relate the fugacity capacities of two compartments (*i* and j) knowing their partition coefficients K_{ij} as:

$$Z_i = K_{ij} * Z_j \tag{2.10}$$

2.2.1.2 Pure water Fugacity Capacity Z_w: The relationship between air and water becomes:

$$Z_w = Z_a / K_{aw} = 1 / H \tag{2.11}$$

The Henry's law constant H is estimated from the chemical vapor pressure, VP in Pa and the aqueous solubility, S in mol/m^3 as:

$$H = VP / S \tag{2.12}$$

The solubility, S, can be estimated from regression relationships taking into account the state of the chemical at environment temperature (298 K) and its octanol-water partition coefficient (PKOW). However, it has been noted that these values vary from experimental values by as much as a factor of 5 (Verhaar & Hermens, 1990). Thus only experimentally derived values are used in the present model. For these values to be accurate, all parameters must be measured at the same environmental temperature and physical state (liquid, solid, etc.), otherwise, a correction must be applied (MPCA, 1992). For chemicals that are solid at environmental temperature, the vapor pressure must be corrected using fugacity ratio, FR (Mackay, 1991).

$$\text{If Tmelting (TMK)} > \text{Tenvironment (TME)} \tag{2.13}$$

$$FR = e^{6.79*(1-\frac{TMK}{TME})}$$

Else FR = 1

Therefore, the corrected vapor pressure for solid chemicals is written as:

$$VPQ = VP / FR \tag{2.14}$$

Certain chemicals are solid at environmental temperature, therefore, their physical properties such as aqueous solubility, SE, vapor pressure, VPE, and corrected vapor pressure, VPQE, must be adjusted from the liquid phase.

$$SE = S * e^{\frac{10000}{RG} * (\frac{1}{TK} - \frac{1}{TEK})} \tag{2.15}$$

$$VPE = VP * e^{\frac{50000}{RG} * (\frac{1}{TK} - \frac{1}{TEK})} \tag{2.16}$$

$$VPQE = VPQ * e^{\frac{50000}{RG} * (\frac{1}{TK} - \frac{1}{TEK})} \tag{2.17}$$

In these equations, TK, TMK and TEK are the chemical property temperature, the melting point and environmental temperature, respectively. Thus starting with air or water compartment, the Z value for all other compartments can be estimated knowing the chemical partition coefficient between water (or air) and that compartment. It should be noted that these partition coefficients are dimensionless and must be estimated before the fugacity capacities can be calculated.

2.2.1.3 Organic Carbon – Water Partition PKOC: This coefficient together with the octanol-water partition coefficient are the most important parameters describing the fate of organic contaminants in the environment. Many relationships have been developed over the years to estimate the organic carbon partition coefficients (PKOC) and for the most part empirical in nature thus requiring care before using them for modeling purposes. Different chemical types require different relationships thus using them in the model would have required writing as many relationships as chemicals (Karickhoff, 1985). To alleviate this difficulty a simpler relationship is used (Karickhoff, 1981).

$$\mathrm{PKOC} = 0.41\ \mathrm{PKOW} \tag{2.18}$$

For the five chemicals used, TCE, 1-1-1 trichloroethane, toluene, naphtalene and xylene, the PKOW vary from $10^{2.29}$ for TCE to$10^{3.68}$ for toluene.

2.2.1.4 Aquatic Biota-Water Partition Coefficient: Aquatic biota uptake of a contaminant has been the subject of numerous studies. Primarily, because biota represents a significant pathway by route of edible fish and crabs (Spacie and Hamelink, 1982; Neely, 1979 and Mackay, 1982). The mechanism of the biota-water partitioning is based on the fact that a hydrophobic contaminant will greatly dissolved in the lipid or fatty tissue of the biota thus reaching much higher concentration compared to bulk water. Mackay (1982, 1991) proposed a simpler relationship relating biota-water partition, K_{bw}, to the octanol-water partition, K_{ow}, by assuming lipid content of the fish of about 5% by volume.

$$K_{bw} = 0.048\ K_{ow} \tag{2.19}$$

This relationship is derived from bio-concentration data measured in fish tissues and thus should be used for only aquatic biota similar to that of the fish above.

2.2.1.5 Sorption Coefficient PK_{i3}: These non-dimensionless sorption coefficients represent affinity of the contaminant to partition between the solid fraction (3) of the *i* compartments (water, sediment, surface, roots and vadose zone soils, respectively). A similar relationship is used to estimate the sorption coefficient for the aquatic biota (Mackay, 1982). They are related to the one very important landscape parameter, the organic carbon content (f_{oc}) as follows:

$$PK_{i3} = PKOC * f_{oci} \tag{2.20}$$

$$PK_{biota} = 0.048\ PKOW \tag{2.21}$$

The other important parameter controlling the fate of a contaminant is the fraction organic carbon f_{oc}. A major contribution to this type of modeling was achieved by deriving the measured f_{oc} values for each soil type in the Passaic River Watershed. Additionally, these partition coefficients can be rewritten in a dimensionless form PD as:

$$PD_{i3} = PK_{i3} * \rho_{i3} \tag{2.22}$$

where the solid phase, *i* is density in g/m^3.

2.2.1.6 Aerosol-Air and Aerosol-Water Partition Coefficient: Aerosol particles represent an important environmental vehicle for the fate of a contaminant through dry and wet deposition, and through long range transport. An aerosol deposition model is not a trivial exercise, as the properties of these particles vary largely, both temporally and spatially. The size of the aerosol particles is the dominant factor in determining its fate in air as per its settling or continuous suspension. It has been estimated that deposition rates with coarse versus gaseous aerosols can result in differences in deposition of as much as 4 order of magnitude (Thibodeaux, 1996, Slinn & Slinn, 1981). The air-aerosol partition coefficient is not generally known primarily because of the complex characteristics and non-uniformity of these particles and their adsorption characteristics.

The fraction of the chemical in the air compartment that is associated with the aerosols f_{ap} has been estimated by researchers (Junge, 1977).

$$f_{ap} = \frac{c * \Theta}{VPE + c * \Theta} \tag{2.23}$$

where c is the Junge's constant, approximately estimated to be 0.173m-Pa and Θ represents the total suspended particle surface area concentration (m^2/m^3). The latter parameter is very difficult to measure, showing variations in both space and time. Mackay (1991) proposed a simpler version in which the partition coefficient was directly correlated to the vapor pressure as:

$$K_{xa} = 6 * 10^6 / P^s_L = PD_{xa} \tag{2.24}$$

$$Z_x = K_{xa}Z_a = 6 * 10^6 / P^s_L RT \tag{2.25}$$

where P^s_L is the sub-cooled liquid vapor pressure in Pa and is different from the solid vapor pressure. Similar relationships were found with the partition coefficient being proportional to the inverse of the sub-cooled liquid vapor pressure through a constant $3*10^6$ (CEPA, 1993). Aerosols are important components of the contaminant distribution due to their large surface to volume ratio. They have been found to account for as much as 25% of the pure phase concentration (Mackay, 1991). The aerosol water partition is thus deduced from the above equation using the corrected air-water partition coefficient K_{awc} as follow:

$$K_{xw} = K_{xa} * K_{awc} = PD_{xw} \tag{2.26}$$

2.2.1.7 Plant Interface with the Air and Soil Compartment: The plant or terrestrial vegetation is an important part of the multimedia environmental modeling. Since the land bio-mass is 99.9% vegetation, it is unavoidable that the food we eat (not accounting the aquatic food) is almost certainly derived from the plant compartment. Additionally, the edible plant concentration has been shown to be several orders of magnitude higher than that of water in both the US and Western Europe. Thus the ingestion of plant is a major pathway of exposure to environmental contaminants (Trapp and Matthies, 1998). In spite of this fact, contaminant transfer to and from terrestrial vegetation has received little attention due to the difficulty of representing this compartment in terms of fugacity. Furthermore, there are numerous routes of chemical transfer into the plant.

It has been suggested that a complete partition plant model must include the uptake and loss of aqueous and solid particles at the surface of the cuticle; additionally, the vertical translocation through the stem and the dilution by growth must be represented (Riederer, 1990). For the sake of simplicity, we have limited the uptake processes to the unidirectional uptake from the root zone soil and to the deposition and diffusion from the air compartment as shown in Figure 2.3.

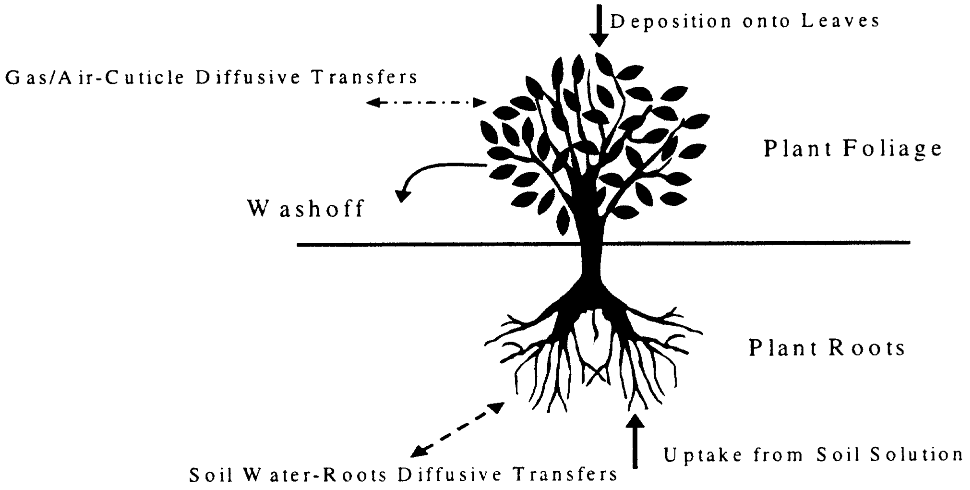


Figure 2.3 Fugacity Representation of Contaminant Movement in Plant

The partitioning between plant and air compartment is not trivial, it must account for both the gaseous air-leaf, K_{pa} and the air particles-leaf, K_{px}, the partitioning of which occurs before the particles are washed off the leaves. The leaf air partition coefficient, K_{pa} is deduced from the plant solute (in the root zone) partition, K_{pw} by using the air water partition K_{awe} (Riederer, 1990) or vice versa.

$$K_{pa} = [0.5 + (0.4 + 0.1K_{ow})R.T.Z_w] / \rho_p \tag{2.27}$$

$$K_{pw} = [0.5 + (0.4 + 0.1K_{ow})H.Z_w] / \rho_p \tag{2.28}$$

where 0.5, 0.4 and 0.1 represent the volume fraction of the plant tissue that is air, water and lipid, respectively. Also in K_{pw}, the air-water partition is just replaced by its value H/R.T. ρ_p is the density of the plant tissue.

A similar approach was used by Trapp and Matthies (1998), and by Patterson (1991) using slightly different volume fractions. The plant leaf-aerosol particle partition is found to be independent of chemical species and is estimated using a deposition and wash off rates of 3000 mol/kg(plant) per mol/m^3(air) (McKone and Ryan, 1989). With these partition coefficients and their dimensionless part, we can now calculate the remaining fugacity capacities. The plant root tissue soil solid partition coefficient is also called the root concentration factor, RCF and is estimated from Briggs (1983).

$$RCF = K_{ps} = 0.82 + 0.03PKOW^{0.77}Z_w \tag{2.29}$$

2.2.1.8 Sorbed Phase Fugacity Capacities Z_{i3}: The solid sorbed phases include the soil solid particles in the surface 3_3, root 6_3 and vadose zone 7_3, the suspended solids 2_3 in the water column and the soil solids in the sediment compartment 4_3 as shown in Figure 2.1. They are estimated as follow:

$$C_{sorbed} = K_{i3}C_w \tag{2.30}$$

$$Z_{sorbed} = K_{i3}Z_w \tag{2.31}$$

with the K values in mole/m^3 solid per mol/m^3 water; or in dimensionless term:

$$Z_{i3} = PD_{i3}Z_w \tag{2.32}$$

2.2.1.9 Aquatic Biota Fugacity Capacity Z_b (i.e. fish):

$$Z_b = K_{bw} Z_w = \rho_b K_{bw} / H \tag{2.33}$$

Here K_{bw} is the biota-water partition coefficient on the dry weight basis. This is also known as the bio-concentration factor. ρ_b represents the density of fish in g/m^3.

2.2.1.10 Foliar Plant Fugacity Capacity Z_{pf}: The following analysis can be found in the technical background document of the CEPA CalTOX (CEPA, 1993). Dividing the plant into two distinct parts provides certain advantages with respect to representing the plant interaction with the air and soil compartments. The air-plant interaction takes the form of direct deposition of particles onto the leaf surface, the subsequent diffusion of the chemical bound deposited materials through the leaf, the wash off form the leaf representing chemical losses, and the gaseous diffusion between leaf and air. For organic compounds these interactions are summarized as follows:

$$Z_{pf} = K_{pa} \rho_p Z_a + K_{px} \rho_p Z_x \rho_{ba} / \rho_x \tag{2.34}$$

with ρ_x being the aerosol particles density. The first term represents the gas phase component and the second term the aerosol component. ρ_{ba} is the density of the bulk air or dust load (gas and aerosols) and K_{pa} and K_{px} are partition coefficients as defined in Section 2.2.1.11.

2.2.1.11 Plant Roots Fugacity Capacity: Plant roots interacts with the contaminant in the root zone soil. We assume that the gas exchange between the soil and the plant is negligible and that the uptake is uni-directional from the soil (soil pore water) to the plant root tissue. Additionally, in this calculation, one should consider the soil compartment to be composed of at least four components, namely, soil air, soil water, soil solid and soil roots. Thus, different volume fractions should be applied as follows:

$$Z_{pr} = \frac{K_{ps}\left[\alpha_s Z_a + \beta_s Z_w + Z_{33}(1-\alpha_s - \beta_s)\right]}{\rho_s(1-\alpha_s - \beta_s)} \tag{2.35}$$

α_s, β_s, ρ_s are the soil volume fractions in air, water and solid, respectively (in kg/m^3).

Once the sub-phase fugacity capacities are obtained, we can proceed to calculate the bulk phase fugacity capacity for the 7 main compartments. This is achieved by simply using a different volume fraction for each compartment. For each compartment, *i*, there are up to 3 different phases, each with a volume fraction ϕ_{ij} where *i* varies from 1 to 7 and j varies from 1 to 4. Thus the bulk phase fugacity capacity, Z_{Bi} is written as:

$$Z_{Bi} = \sum_{1}^{4} \phi i_{ij} Z_i \tag{2.36}$$

2.3 Fate and Transport Component of the Model

2.3.1 Advective Processes

The advective MTCs are driven by the carrying medium, which is solely responsible for the transfer of the chemical. The derivation of the MTCs used in this study is shown below.

2.3.1.1 Surface Soil to water Bodies MTC: This one directional process of contaminant movement from surface soil to water bodies includes non-point sources such as urban runoff and agricultural runoff. In these cases both contaminant dissolved in water, D_{ww} and those attached to soil particles, D_{sw} are moved downstream after rainfall. Designating the runoff rate as k_{run} and the erosion rate as k_{eros}, the fugacity MTCs are shown below:

$$D_{ww} = A_{soil} k_{run} Z_w \tag{2.37}$$

$$D_{sw} = A_{soil} k_{eros} Z_{3\_3} \tag{2.38}$$

$$D_{SS\_W} = D_{ww} + D_{sw} \tag{2.39}$$

2.3.1.2 Root Soil to Vadose Soil MTC: This process is also considered as one directional, mainly the vertical seepage v_{sep} or the leaching rate, the resultant fugacity MTC D_{ssi2} is as follows:

$$D_{ssi2} = A_{rsoil} v_{sep} Z_w \tag{2.40}$$

$$D_{RZ\_VZ} = D_{ssi2} \tag{2.41}$$

The justification for this one way transfer includes the fact that for most areas where the fluctuation of the groundwater do not reach the root zone soil, the movement of the water is only downward. Also, the pore volume in the vadose soil is not significant to allow appreciable diffusive fluxes.

2.3.1.3 Vadose Zone Soil to Groundwater: Also considered as a vertical transfer, this process is important since groundwater is used in many areas as a source of potable water. In this research, the transport in the groundwater is not modeled, however, an estimate of the contaminant to it from the contaminated soils is provided. With the use of a dilution factor, an average groundwater concentration can be estimated, this methodology has been in the Soil Screening Standards Guidance (EPA, 1996). The fugacity MTC is:

$$D_{sgw} = A_{vsoil} v_{sep} Z_w \tag{2.42}$$

$$D_{VZ\_GW} = D_{sgw} \tag{2.43}$$

2.3.1.4 Root Zone Soil Plant Uptake MTC: The transpiration of soil water through vegetation constitutes a transfer mechanism of chemical contaminant present in the soil. The plant is believed to also transfer some of its chemical to the root soil through the flow of phloem (CEPA, 1993). However, since this flow is only a fraction of the transpiration and is very plant specie dependent, it is not included in the present model. The remaining MTC is estimated from:

$$D_{psw} = A_{plant} v_{transp} Z_w \tag{2.44}$$

$$D_{RZ\_PLANT} = D_{psw} \tag{2.45}$$

2.3.1.5 Advective Inflows and Outflows: One way to account for cross boundary transfers of contaminant between adjacent watershed is to include advective exchanges. These exchanges are in the form of air and aerosols transport and water flow from the upstream reaches of a river. The Passaic River Watershed has been studied extensively and there exists a wealth of knowledge on its landscape characteristics. The predominant wind is from the northwestern direction, approximately 7 to 8 months in a given year and from the southwest for the remainder of the year. Additionally, a reported yearly wind speed of 9.7 mph (U.S. COE, 1972) is used to calculate the advective inflow and outflow rates of air and thus contaminant. Additionally, the particles' concentration or total suspended particles is used to estimate the aerosols' influx in different watersheds.

The inflow and outflow of surface water and the suspended particles in the water column are obtained from the extensive stream gage stations throughout the Passaic River Watershed as well as the USGS water year report (USGS, 1996). These advective inflows have an added advantage of allowing to link the different sub-watersheds, thus providing a tool to assess the impact of the cross boundary contribution to an area (watershed) contamination.

2.3.2 Reaction Processes

Not all reactions are degradations. For example, reactions that just change a chemical from one compound to another. This the case of Chromium which can transform from one oxidation state (i.e. Cr+3) to a higher oxidation state (Cr+6) with the latter being more toxic than the former. Thus, some reactions perform the opposite of chemical degradation in that the daughter product is more unpleasant than the parent chemical. These types of reactions are not included in the current study.

The reaction processes as presented above account for only losses, thus the persistence of the contaminant in the environment. This can be quantified using first order kinetics as follow:

$$N = V * C * k \tag{2.46}$$

Here, V is the volume of the compartment in m^3 and k is the degradation reaction rate in h^{-1}.

$$N = V * f * Z * k = f * D_r \ \text{(or } D_r = VZk\text{)} \tag{2.47}$$

with D_r being the reaction transfer coefficient in mole/h.Pa. The reaction rate k is derived in most chemical references as the radioactive decay usually represented as:

$$dC/dt = -Ck \tag{2.48}$$

Integrating this equation with an initial condition C_0, it follows that:

$$\mathrm{Ln}\ (C / C_0) = -kt \tag{2.49}$$

$$C = C_0 \exp\ (-kt) \tag{2.50}$$

$$k = 0.693 / t_{1/2} \tag{2.51}$$

Where $t_{1/2}$ is the time required for the depletion of 50% of the contaminant present initially.

It is clear that if no remediation is chosen as an alternative, a reduction in pollution level is to be expected only in the air and water compartments. As for reactions that do not follow first order kinetics, a pseudo first order reaction can be assumed. This is necessary since higher order reactions are much difficult and require two or more rate constants. One such reaction is the microbial rate of decay which is proportional to the concentration of all organisms and the rate applicable to each organism. Under real environmental conditions, most reactions are second order. Using the above simplification, the second order reaction rates are lumped into one reaction rate as follow:

$$N = V * C * k1 * k2 \tag{2.52}$$

Introducing a new rate constant k such that k = k1*k2, the above equation becomes

$$N = V * C * k = f * D_r \tag{2.53}$$

The environmental processes, that are classified as reactions, include: biodegradation, hydrolysis, oxidation, and photochemical transformation.

2.3.3 Inter-Media Transfer Rates

The third part of the contaminant fate and transport is described in the following section as inter-media transfers. These are also called diffusive mass transfers and can be divided into two phenomena, diffusion within one medium (i.e. dilution) and diffusion between two adjacent media (i.e. volatilization). In the real environment, the diffusive transport is very slow and difficult to quantify. The concept of equilibrium (common fugacity) will need to be revised as diffusion introduces a non-equilibrium situation. These processes (diffusive in a single medium and diffusive across two media) continue to be the focus of scientific investigation since uncertainty remains regarding the transfer coefficient of chemicals under various environmental conditions. Each of these processes can be described in fugacity terms; however, only the inter-media transfer is of interest in the current research, as each phase is considered to be uniformly well mixed. Diffusion within a single compartment is briefly described in Section 2.3.3 but is not included in the present model.

The diffusion between phases represents the advantage of the multimedia approach over the spatial approach in environmental modeling. Although it is often difficult to characterize, there exist many analogies in other engineering fields. Processes that are described by inter-phase diffusion include volatilization (air-water transfer), sorption and desorption (water-sediment), absorption (soil-air), and water to aquatic biota transfers. While diffusion in a single medium has been described using a concentration gradient, the same is not applicable to inter-phase diffusion. The diffusion (i.e. volatilization) between water and air will approach completion without the concentrations being equal. However, in this non-equilibrium state, the fugacity in both water and air will be equal. Thus the inter-media diffusion is driven by the fugacity gradient and not by the concentration gradient.

Inter-phase diffusion has been described using the 'Whitman Two Resistance Mass Transfer Coefficient' (MTC) approach (Whitman, 1923). This approach has been applied to atmosphere-ocean water interchange by Liss (1974), and organic solute transfer by Leinonen (1975). An illustration of a water-air diffusion transfer is presented in Figure 2.4. At the interface, the turbulence is damped and the diffusion process slows down considerably (Mackay, 1991). Here, a larger concentration gradient is required to maintain a steady flux since the molecular diffusion is slow. A new MTC (k_w) is assigned to this water side transfer. Similarly, the same process can be thought to apply to the air-side with a MTC (k_a). Assuming that equilibrium is established at the interface as seen in Figure 2.4, a relationship between concentration in the two phases can be written as:

$$C_{ai}/C_{wi} = K_{aw} = Z_a/Z_w = H/RT \tag{2.54}$$

where C_{ai} and C_{wi} represent the chemical concentration in the air-side and water-side of this interface, respectively. Furthermore, the flux of the chemical in either phase is written as:

In the water side of the transfer process:

$$N = k_w A(C_w - C_{wi}) = k_w A Z_w\,(f_w - f_i) = D_w(f_w - f_i) \tag{2.55}$$

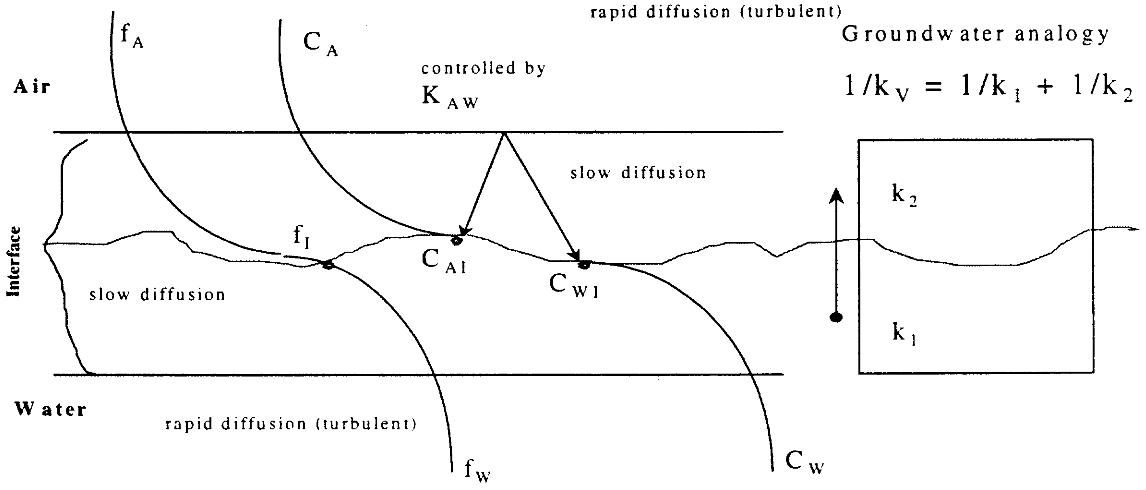


Figure 2.4 Illustration of an Inter-Phase Diffusion Process (Air-Water MTC)

And in the air side of the transfer process:

$$N = k_a A(C_{ai} - C_a) = k_a A Z_a\,(f_i - f_a) = D_a(f_i - f_a) \tag{2.56}$$

In Equations 2.55 and 2.56, the term f_i represents the interface fugacity. Although this parameter is not measurable and is not of interest to the process itself, it can be eliminated by adding the above two equations.

$$f_w - f_a = N(1/D_w + 1/D_a) = N/D_v \tag{2.57}$$

Thus,

$$N = D_v(f_w - f_a) = D_v \Delta f \quad (2.58)$$

where, D_v is mass transfer coefficient (MTC) and is determined either experimentally, or by calculation given the different partition coefficients (air-water) and the values of k_a and k_w. In the above equations, the transfer coefficient terms $1/D_w$ and $1/D_a$ represent the effective resistance which can be added in series to obtain the total resistance, $1/D_v$. This analysis of transfer coefficients is similar to the equivalent vertical hydraulic conductivity between two layers of different conductivities in groundwater flow. The term $D_v f_w$ can be used as an estimate of the net volatilization and the term $D_v f_a$ as the net absorption. Further manipulations result in:

$$D_v = AZ_a k_{oa} = AZ_w k_{ow} \quad (2.59)$$

$$k_{ow}/k_{oa} = Z_a/Z_w = K_{aw} \quad (2.60)$$

Here k_{oa} and k_{ow} are the MTC values on the air-side and water-side, respectively.

$$1/k_{oa} = 1/\ k_a + K_{aw}/k_w \quad (2.61)$$

$$1/k_{oa} = 1/k_w + 1/K_{aw} k_a \quad (2.62)$$

Examples of inter-media diffusive transfers that are included in the present multimedia model are:

1. Air-water transfers: The volatilization of certain contaminants from water to the atmosphere is significant. For example, the oxygen transfer between the atmosphere and the ocean is considered to have the highest overall mass transfer coefficient in nature, of the order of 20 cm/h (Schnoor, 1996).

2. Soil-air transfers: The volatilization and absorption from and to surface soils can be modeled using the inter-media diffusion. This process is important for chemicals with high vapor pressures such as TCE (trichloroethylene).

3. Sediment-water transfers: This includes the re-diffusion of contaminants from the buried sediment layers to the water column. A major concern that arises in dredging water bodies is not only the re-suspension of sediment particles but also the availability of buried contaminant for back diffusion to the water compartment.

4. Biota-water transfers: This relates to the diffusion of contaminant across the skin, stomach and gills of aquatic biota (Clark, 1990). Through this process, a low concentration contamination becomes concentrated in fish tissues (usually several order of magnitude for chemicals with high K_{ow}). This phenomenon is referred to as bio-concentration, for example DDT may be found in fish at concentration one million times that of water.

2.3.4 Summation of Fate Parameters

In a given compartment, the processes, advection, reaction and intermedia transfers, that control the loss of contaminant are additive through the MTC values reactive, D_r, transfer between compartments *i* and j, and advective, D_a. This addition is possible because of the common fugacity assumption in a compartment. The net loss of the contaminant through these two processes in water for example is defined as:

$$N = (f_w * \Sigma D_a + f_w * \Sigma D_{ij} + f_w * \Sigma D_r) = f_w * D_T \qquad (2.63)$$

Additionally, the above loss quantification can be used to estimate the overall residence or persistence of the contaminant in an evaluative environment. Assuming that the total amount of contaminant in the environment is known to be M, thus:

$$M = \sum f * V * Z = t * N \tag{2.64}$$

where t is the total residence time (in hours), M is the total mass (in moles) and the N is the loss of contaminant (in mole/h). Rewriting the last equation:

$$1 / t = f * D_T / f * \sum(V * Z) = \sum D_a / \sum(VZ) + \sum D_{ij} / \sum(VZ) + \sum D_r / \sum(VZ) \tag{2.65}$$

$$1 / t = 1 / t_a + 1/ t_{ij} + 1/ t_r \tag{2.66}$$

with t_a, t_{ij}, and t_r being the residence times attributed to the advective, intermedia and reactive processes, respectively. Although they are treated independently, reaction and advection are related in an environmental compartment.

2.4 Multimedia Fate and Transport – Derivation of the MTCs

In this section, the methodology used to derive the mass transfer coefficients is discussed. The essential parameters used throughout this section are the chemical air and water diffusion coefficients. These coefficients depend on the properties of the chemical contaminant and the physical characteristics of the environment.

2.4.1 Diffusivity Coefficients

Based on the detailed works of Lyman (1982) and Marrero (1973), the diffusion coefficient in air, D_{air} is related to the molecular weight and molecular volume of the chemical, and the air temperature. According to Lyman (1985), organic contaminants have air diffusivity between 0.1 and 1 m^2/d. A typical value within this range is usually used in most multimedia models reviewed during this research (Mackay, 1991; RIVM, 1994). However, differences in chemical air diffusivity of over ten folds have been reported in measured data. To curtail this inconsistency, we opted for using a chemical specific diffusivity under normal environment conditions for both air and water. With these diffusivities available, the diffusivity in porous media is easily estimated.

2.4.1.1 Diffusion in Porous Media – Soil Layers and Sediment: The above analysis applies to chemical in bulk air or bulk water. To extend it to bulk sediment and soil layers require further refinements. Using the surface soil layer as an example, this compartment is divided into 3 sub-compartments or phases: soil air, soil water and soil solid. Thus the diffusion in such a compartment can be thought of as the sum of the diffusion of the carrying phases, air and water in this case. Millington and Quirk (1961) proposed the effective diffusivity in the carrying phase using its volume fraction in soil as follows:

$$D_{eff} = \frac{w^{10/3} D_{pure}}{\phi^2} \tag{2.67}$$

with w representing the volume fraction of the phase (i.e. water) and ϕ the total void fraction (water and air).

2.4.1.2 Diffusion in Bulk Compartments – Air, Water, Soil Layers: The bulk air compartment consists of pure air and aerosol particles. This bulk diffusion is estimated using the respective fugacity capacities and volume fraction as follows:

$$D_a = \frac{Z_a D_{air}}{Z_{Ba}} \tag{2.68}$$

Recalling that Z_{Ba} represents the bulk air fugacity capacity calculated Section 2.2.1. The bulk water fugacity capacity is also estimated using the pure water values as:

$$D_w = \frac{Z_w D_{water}}{Z_{Bw}} \tag{2.69}$$

where Z_w and Z_{Bw} are the pure water and bulk water fugacity capacities, respectively and D_{water} is the diffusion coefficient in water. Finally, the bulk soil (all 3 layers) or sediment fugacity capacities are calculated using the moving phases' capacity (air and water) and their volume fraction in the soil and sediment. For the surface, root zone and vadose zone soils, the diffusion coefficients proposed by Jury (1983) are used.

$$D_{ss} = \frac{\alpha_{ss}^{10/3}}{\phi_{ss}^2}\frac{Z_a}{Z_{ss}}D_{air} + \frac{\beta_{ss}^{10/3}}{\phi_{ss}^2}\frac{Z_w}{Z_{ss}}D_{water} \tag{2.70}$$

$$D_{rs} = \frac{\alpha_{rs}^{10/3}}{\phi_{rs}^2}\frac{Z_a}{Z_{rs}}D_{air} + \frac{\beta_{rs}^{10/3}}{\phi_{rs}^2}\frac{Z_w}{Z_{rs}}D_{water} \tag{2.71}$$

$$D_{vs} = \frac{\alpha_{vs}^{10/3}}{\phi_{vs}^2}\frac{Z_a}{Z_{vs}}D_{air} + \frac{\beta_{vs}^{10/3}}{\phi_{vs}^2}\frac{Z_w}{Z_{vs}}D_{water} \tag{2.72}$$

The above equations are extended to the sediment layer as follow:

$$D_{sd} = \phi_{sd}^{4/3}\frac{Z_w}{Z_{sd}}D_{water} \tag{2.73}$$

In Equations 2.70 through 2.73, the subscript ss, rs, vs, and sd represents surface soil, root zone soil, vadose zone soil and sediment. The mass transfer coefficient can now be estimated using these diffusivity values and the boundary layer thickness between adjacent compartments.

2.4.2 Air Water MTC

As shown above, the mass transfer coefficients are important parameters at the compartment interface and they are used to provide us with rate of volatilization and adsorption between air and water. The thickness of the boundary layer at this interface is also an important factor for controlling the rate of transfer. This thickness depends on the average wind speed, Vw above the water surface, the water current or velocity of the flowing water and the depth of the water body (Southworth, 1979). In our analysis an average surface water current of 0.224 m/s is used. The air side, δ_{aw} and the water side, δ_{wa} boundary layer thickness are estimated from:

If Vw + Current < 0.5 m/s

$$\delta_{aw} = D_{air} \Big/ 5.833\sqrt{\frac{32}{MW}} \tag{2.74}$$

Else

$$\delta_{aw} = D_{air} \Big/ 11.375(Vw + Current)\sqrt{\frac{32}{MW}}$$

For the water side, this thickness is:

If Vw + Current < 1.9 m/s

$$\delta_{wa} = D_{water} \Big/ 0.235\left(\frac{Current^{0.969}}{d_{w}^{0.673}}\right)\sqrt{\frac{32}{MW}} \tag{2.75}$$

Else

$$\delta_{wa} = {D_{water}} \Big/ 0.235\left(\frac{Current^{0.969}}{d_{w}^{0.673}}\right)\sqrt{\frac{32}{MW}}\,e^{0.526(Vw-1.9)}$$

where the diffusivities are in m/h and MW represents the molecular weight of the chemical contaminant. The conditional statements are well justified since rapid mixing in streams and lakes contribute significantly to the inter-media exchanges such as volatilization. The resultant air-water k^{a}_{aw} in the air-side and k^{w}_{aw} in the water side in m/h are:

$$k^{a}_{aw} = {D_{a}} \Big/ {\delta_{aw}} \tag{2.76}$$

$$k^{w}_{aw} = {D_{w}} \Big/ {\delta_{wa}} \tag{2.77}$$

The fugacity mass transfer coefficient or D values shown earlier can now be calculated. These fugacity MTCs are true indicator of the contaminant movement between adjacent phases via diffusion or advection. The air water diffusion D_{vw}, the dissolution into rain drops or wet deposition D_{rw}, and the aerosol dry deposition to open surface water D_{qw} are shown below.

$$D_{vw} = A_{water}\left(\frac{1}{k^{a}_{aw}Z_{air}} + \frac{1}{k^{w}_{aw}Z_{water}}\right)^{-1} \tag{2.78}$$

$$D_{rw} = A_{water}(k_{rain}Z_{water} + k_{rain}Z_{x}v_{dep}\phi_{x}Q) \tag{2.79}$$

$$D_{qw} = A_{water}v_{dep}\phi_{x}Z_{x} \tag{2.80}$$

A_{water} is the area of surface water in m^2, k_{rain} is the rate of rainfall in m/h, Q the scavenging ratio of aerosols by rain drops, ϕ_x, the aerosol concentration in the air compartment and v_{dep}, the deposition velocity of aerosol particles. The resulting fugacity MTC has mole/Pa.h units. The overall air to water transfer D_{A_W} and water to air transfer D_{W_A} are summarized below:

$$D_{A\_W} = D_{vw} + D_{rw} + D_{qw} \tag{2.81}$$

$$D_{W\_A} = D_{vw} \tag{2.82}$$

2.4.3 Air Ground Surface Soil MTC

In these two compartments, we will consider the diffusion via soil air and soil water. However, due to lack of mixing, the thin layer approach is less applicable in this case. Numerous approaches came out of efforts by researchers to estimate the diffusion within the soil compartment (Cohen, 1986, 1990; Jury et al., 1983; Mackay and Paterson, 1991; Mackay, 1991). Of these approaches, the Jury volatilization model has enjoyed a greater level of use because it has been validated in numerous field studies and has received numerous peer reviews. Additionally, it is presented as an analytical solution thus making it easy to incorporate in existing models and can be used for contaminant present at varying depth. In the multimedia model developed in this research, the contaminant, if present in soil, is introduced in the root zone. This assumption avoids having the contaminant exposed to the open air and to the flowing groundwater. Additionally, the disposal of contaminants in soil requires a soil cover and care taking to avoid polluting the groundwater. Therefore, the soil contaminant is only allowed to be transported to the other layers, air and groundwater via gaseous diffusion and infiltration.

The diffusive path length or boundary layer thickness in the soil used here is based on the analysis of the Jury Model in the CalTOX Technical Background Documents and are as follows:

$$\delta_{ss} = 0.108 D_{ss}^{0.229} \tag{2.83}$$

$$\delta_{rz} = 318.4 D_{rz}^{0.683} \qquad (2.84$$

$$\delta_{vz} = 318.4 D_{vz}^{0.683} \tag{2.85}$$

Here these diffusive lengths are in m and the diffusivities D_i in m m^2/day instead of m/hour. The thickness of the boundary layer above the ground surface soil δ_{ag} is taken as 0.005 m (Hanna et al., 1982). This thickness accounts for both the volatilization and the atmospheric deposition. The MTC in the air at the air surface soil interface is estimated using the above values and are presented below. It should be noted that the MTC in the soil layers presented below account for both diffusions via water and air. Furthermore, it is assumed that there is no diffusion between the root zone and the vadose zone soil because of the depth and limited void space for an effective diffusion.

$$k_{ass}^{a} = {D_{air}}\big/{\delta_{ag}} \tag{2.86}$$

$$k_{ss} = {D_{ss}}\big/{\delta_{ss}} \tag{2.87}$$

The fugacity MTCs include the soil-air volatilization, D_{vs}, the transfer of rain dissolution into the soil, D_{rs}, and the dry and wet deposition, D_{qs}.

$$D_{vs} = A_{soil}\left(\frac{1}{k_{ass}^{a} Z_a} + \frac{1}{k_{ss} Z_{ss}}\right)^{-1} \tag{2.89}$$

$$D_{rs} = A_{soil}(k_{rain}Z_{water} + k_{rain}Z_x v_{dep}\phi_x Q) \tag{2.90}$$

$$D_{qs} = A_{soil}v_{dep}\phi_x Z_x \tag{2.91}$$

The resulting fugacity MTC has mole/Pa.h units. The overall air to water transfer D_{A_SS} and water to air transfer D_{SS_A} are summarized below.

$$D_{A\_SS} = D_{vs} + D_{rs} + D_{qs} \tag{2.92}$$

$$D_{SS\_A} = D_{vs} \tag{2.93}$$

2.4.4 Surface Water Sediment MTC

Similar to the surface soil air interface, the mass transfer through the sediment water interface is solved using the boundary layer thickness above the sediment layer and the diffusive path length inside the sediment layer. The water-side boundary layer thickness, δ_{wd} is estimated as 0.002 meter (Formica et al., 1988) and the sediment side boundary layer thickness, δ_{dw} and the ensuing MTCs are calculated as follow:

$$\delta_{dw} = 318.4D_{sd}^{0.683} \tag{2.94}$$

$$k_{wd}^{w} = D_{water}/\delta_{wd} \tag{2.95}$$

$$k_{wd}^{sd} = D_{sd}/\delta_{dw} \tag{2.96}$$

This interface is very important not only to the chemical transfer but also it serves as a reservoir of food for many aquatic biota. The fugacity mass transfer coefficients needed for the model calculations are the water column sediment layer diffusion, D_y, the settling of suspended particles, D_{dx}, the re-suspension from the sediment layer, D_{rx} and the burial or thickening of the sediment layer, D_{bx}.

The resulting fugacity MTC has mole/Pa.h units. The overall air to water transfer D_{A_W} and water to air transfer D_{W_A} are summarized below.

$$D_y = A_{water}\left(\frac{1}{k_{wd}^{w}Z_{water}}+\frac{1}{k_{wd}^{sd}Z_{4\_3}}\right)^{-1} \tag{2.97}$$

$$D_{dx} = A_{water}k_{dep}Z_{2\_3}\phi_{wx}) \tag{2.98}$$

$$D_{rx} = A_{water}k_{rssp}Z_{4\_3} \tag{2.99}$$

$$D_{bx} = A_{water}k_{bur}Z_{4\_3} \tag{2.100}$$

where k_{dep} represents the deposition rate of suspended particles, ϕ_x the volume fraction of bulk water that is suspended particles, k_{rssp} the re-suspension rate of water particles and k_{bur} the burial rate of sediment. The overall process between bulk compartment is as follows:

$$D_{W\_SD} = D_y + D_{dx} \tag{2.101}$$

$$D_{SD\_W} = D_y + D_{rx} \tag{2.102}$$

2.4.5 Plant Air MTC

The uptake by foliage vegetation is an important removal process of certain organic contaminant from the lower atmosphere (Hauk, H et al., 1994). The physical mechanism of this exchange includes the dry deposition of air particles on the leaf surface resulting in the formation of a thin layer of soil. The thickness of this layer, δ_{slyr} is equivalent to the diffusive path length discussed in the air surface soil exchange and is estimated to be 5E-6 m. The air-side of the air plant leaves boundary layer thickness is estimated to be 0.05 m (CEPA, 1993). The cuticle part of the leaf surface presents zero resistance to chemical transfer from air to the plants (Mansour, 1993), thus the thin layer over the leaf is the only resistance to gaseous transfer. Unlike the transfer through the cuticle, the stomata part of the leaf presents some resistance r_{stom}. This MTC has been estimated to be 180 m/h for certain pesticides (Thompson, 1983) and for the combined stomata and cuticle in the range from 0.0045 to 9 m/h for Citrus plant (Riederer, 1990).

In the present research, the overall plant air MTC is calculated as two parallel transfers (stomata k_{stom} and cuticle k_{cut}) and the cuticle transfer is assumed as a series of air side diffusion and diffusion through the thin layer of soil.

$$k_{ap}^{a} = D_{air} / \delta_{ap} \tag{2.103}$$

$$k_{ap}^{p} = D_{ss} / \delta_{slyr} \tag{2.104}$$

$$k_{stom} = 1 / r_{stom} \tag{2.105}$$

where r_{stom} is the stomata resistance to diffusion and is estimated using the water vapor mass transfer resistance.

$$r_{stom} = D_{wv-air} \, r_{wv-stom} / D_{air} \tag{2.106}$$

with D_{wv-air} the water vapor air diffusivity in the order of 2.1 m^2/d, $r_{wv-stom}$ the stomata resistance to water vapor estimated as 0.0027m/d (CEPA, 1993). The fugacity MTCs for this interface accounts for the diffusion occurring at the leaf surface D_{paa}, the aerosols deposition to the leaf surface D_{paq} and D_{pwash} the washout by rain and wind which balance the deposition.

$$D_{paa} = A_{veg} La \left(\frac{1}{k_{ap}^{a} Z_{air}} + \frac{1}{k_{ap}^{p} Z_{1\_3}} \right)^{-1} + k_{stom} Z_{air} \tag{2.107}$$

$$D_{paq} = A_{veg} La \phi_x v_{dep} Z_{1\_3} \tag{2.108}$$

$$D_{pwash} = A_{veg} La \phi_x v_{dep} Z_{1\_3} \tag{2.109}$$

where La is the total leaf area per m^2 of vegetative cover and is in the order of 30. The overall fugacity MTCs between bulk compartments are D_{A_P} and D_{P_A} for the air to plant and plant to air compartment respectively.

$$D_{A\_P} = D_{paa} + D_{paq} \tag{2.110}$$

$$D_{P\_A} = D_{paa} + D_{pwash} \tag{2.111}$$

2.4.6 Surface Soil(1) Root Zone Soil(2) MTC

The surface soil is sufficiently small in thickness to allow diffusive fluxes with both the air compartment and the underlying root zone soil. Furthermore, the infiltrating water passes through this interface and thus contributes to a positive downward flux of contaminant to the root soil. The mass transfer coefficient for the root zone soil is calculated in a similar manner to that of the surface soil, k_{ss} accounting for the diffusivity in the soil, D_{rz} and the diffusive path length, δ_{rz}. Additionally, the fugacity mass transfers, includes the diffusion between soil1 and soil2, D_{ssa} and the leaching from soil1 to soil2, D_{ssi} as described above. The parameter k_{vz} represents the MTC in the vadose zone and is included for the sake of completion and is not used in any transfer.

$$k_{rz} = {}^{D_{rz}}\!/\!_{\delta_{rz}} \tag{2.112}$$

$$k_{vz} = D_{vz} / \delta_{vz} \tag{2.113}$$

$$D_{ssa} = A_{soil}\left(\frac{1}{k_{ss}Z_{ss}} + \frac{1}{k_{rz}Z_{rz}}\right)^{-1} \tag{2.114}$$

$$D_{ssi} = A_{soil} v_{sep} Z_w \tag{2.115}$$

The parameter v_{sep} is the infiltration or seepage rate in m/h. The corresponding fugacity MTCs between these compartments are D_{SS_RZ} for soil1 to soil2 transfer and D_{RZ_SS} for soil2 to soil1 transfer.

$$D_{SS\_RZ} = D_{ssa} + D_{ssi} \tag{2.116}$$

$$D_{RZ\_SS} = D_{ssa} \tag{2.117}$$

2.4.7 Degradation Rates MTC

The degradation of organic contaminants represents a major part in their reduction from the environment. This degradation appears in a number of forms including photodegradation, oxidation, hydrolysis and microbial degradation. Furthermore, this process occurs in each of the seven bulk compartments used in the present model. The approach used here is to combine the different rates that occur in one compartment and use a unique degradation rate (Mackay, 1992). The fugacity mass transfer coefficients are then estimated as follow:

$$DR[i] = Z[i] * VOL[i] * RK[i] \tag{2.118}$$

where *i* represents a given compartment, VOL the total volume of that compartment in m^3 and RK the reaction kinetic rate in the compartment. This latter rate is estimated from the half life degradation rate HL of the contaminant in that compartment.

$$RK[i] = \frac{0.683}{HL[i]} \tag{2.119}$$

2.5 Mass Balance Calculations

The dynamic level IV fugacity model is set up using a mass balance relationship of contaminant mass in each compartment. The setup of the mass balance equation parameters is the same for both level III and level IV, with the level IV having time dependant parameters. The additional complexity has the cost of more input data as initial conditions will be required to perform the simulation. Level IV can be very advantageous, especially when long-term scenarios are being considered. Furthermore, it provides an estimation of the required time for an environment to return to acceptable level of contamination to decision-makers. The dynamic representation of the different processes controlling the fate of a contaminant also provides further insight for the relative importance of each process and the change in their effectiveness in the future.

From the previous sections, the estimated mass transfer coefficients are now used in Equation 2.120 below. With all the processes defined in term of fugacity mass transfers between adjacent compartments and mass transfers due to advection, degradation and inter-media transfers, a mass balance equation can be set up and solved. The change in total mass of a contaminant in a given compartment, *i*, is a simple difference between the gains and the losses.

$$V_i Z_i \frac{df_i}{dt} = I_i + \sum_{j=1}^{j=n} D_{ji} f_j - \sum_{j=1}^{j=n} D_{ij} f_i - D_{out} f_i^{t+1} \tag{2.120}$$

where V_i represents the volume, Z_i the bulk fugacity capacity, D_{ij} the inter-media input transfers from adjacent compartments, j, D_{ij} the inter-media output transfers from compartment, *i*, to the adjacent compartments, j, and I_i the direct input in the compartment *i*. The subscript j represents the other compartments contributing to the mass input into the compartment of interest *i*, and vary between n=1 to n=6.

The left-hand term is the total change in mass inside a given compartment and is taken as zero for the steady state level III. The variable m represents the number of advective vectors such as air, aerosols, water and suspended water particles out of the compartment. With seven bulk compartments and 11 different sub-watershed, a total number of 77 such equations are written. The computational task used to solve for the unknown fugacity f in the above equations is presented in the analysis section.

2.6 Computer Program Development

A computer program is written in object oriented C++ to represent and solve the above equations. The object-oriented paradigm is used in this study because of the need to represent the sub-watersheds as different entities and still be able to link them through the advective inflows and outflows. Using C++ programming tools yields two objectives, first it is a vehicle to perform calculations as any other programming language, and second it is modular in representing the different data from different sources. The modularity of the C++ language also allows independent development of the code and makes it fully portable.

The basic unit of an object-oriented model is the 'class', a separate entity which can be of any data type and which can be used in any number of ways with the use of 'objects'. An object is an instance of a class, thus a given class can have multiple objects and each object can be acted on differently. The watershed model developed herein, is composed of 11 environmental units, sub-watersheds, with each unit being comprised of 5 different classes. These classes are; the watershed characteristic class, watshd_char, the environmental transport vectors class, watshd_transp, the contaminant emission module, chem_ems, the chemical contaminant property class, chem_prop, and the model output module, Display_Results. The flow diagram describing the modular representation of this model is presented below in Figure 2.5.

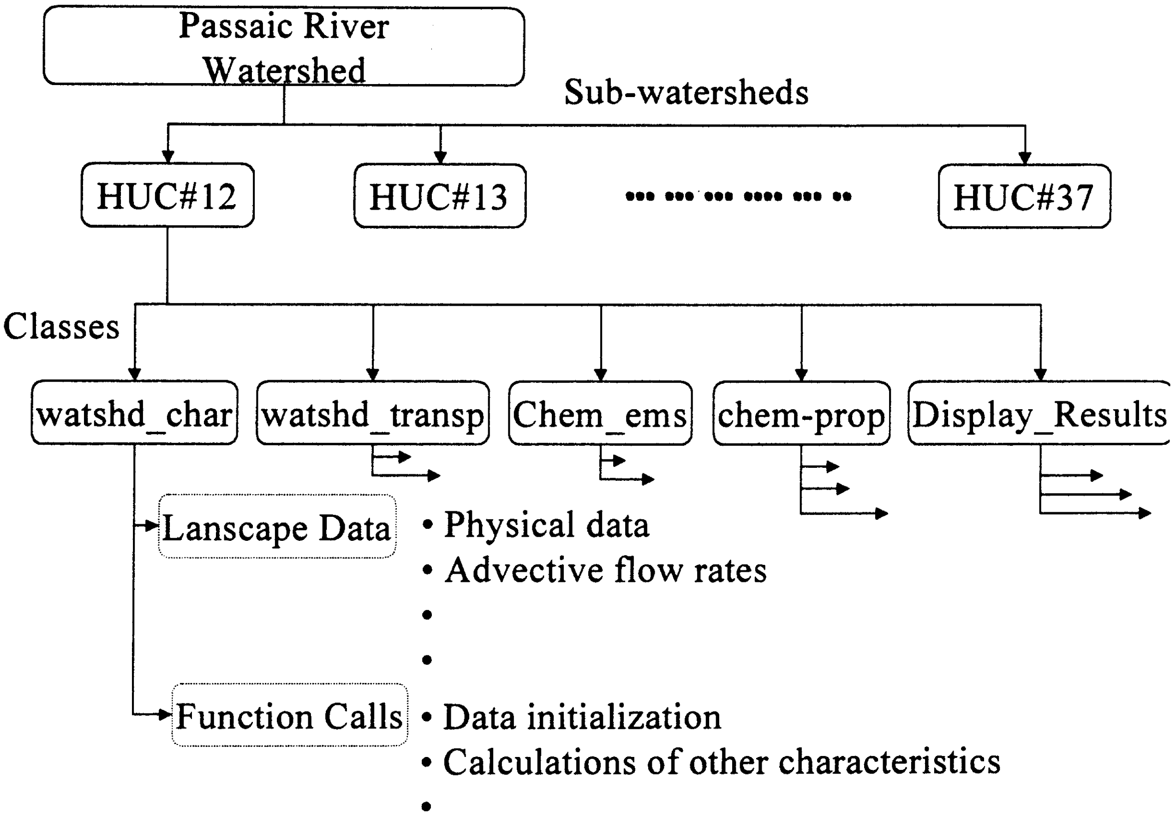


Figure 2.5 Flow Diagram of Multimedia Model Design

The object, which is an instance of the class, is used to perform computation on the landscape and chemical property data. As shown in Figure 2.6, each class contains its own set of data, which can only be manipulated inside the scope of the class. The functions, also called methods of the class are used to perform calculations on the class data. Additionally, since the data in the class can not be changed outside its scope, only an implementation of an object can use this data but cannot change its basic values. Therefore, for each class, there can be a number of objects, each performing a specific task, and new objects can be added without any change to the program structure. A description of each class, along with its data and member functions, is provided in the following section.

2.6.1 The Watershed Characteristics Class – watshd_char

The purpose of this class is to manage all the landscape characteristic data. It is composed of landscape parameters representing the dimensions of each compartment, the different volume fractions of the compartments (i.e. soil-air, soil water etc.) and the organic carbon content of the different phases and sub-phases. The definition of the watshd_char is shown in Figure 2.6.

The class method watshd_char, also known as the constructor, is used to initialize the data presented in this class and in the event where a variable is not known prior to the class implementation and needs to be estimated, this method will initialize it to zero. The class method watshd_calc is used to calculate the compartment volume, the sub-compartments volume fraction and each compartment density. Since there are 11 sub-watersheds, there must be 11 different objects or class instances, so that each sub-watershed will have a variable set as those in Figure 2.7. Finally, by declaring the other classes as friend of the watshd_char class, allows the use of this data by these classes. However, these other classes will not be able to change the content of the variables in the watshd_char class.

```
class watshd_char{
friend class watshd_transp;
friend class chem_ems;
friend class chem_prop;
friend class Display_Results;
public:
watshd_char(char id[7], double at, double aw, double av, double vw, double h[7], double
f23, double f33, double f43, double f63, double f73,.........);
        void watshd_calc(chem_prop &);
public:
        char huc_id[7];                 //Hydrologic Unit ID
        double area_ttl;                //Area of the entity (m2)
        double area_w;                  //Area of the entity covered by water (m2)
        double area_veg;                //Area of the entity covered by forest (m2)
        double Vw;                      //Wind speed in m/s
        double H[7];                    //Depth of the bulk compartment (m)
.....
.......
};
```

Figure 2.6 Representation of a Section of the 'watshd_char' Class

2.6.2 The Chemical Properties Class – chem_prop

This class is defined to handle the basic contaminant properties and to derive additionally chemical and physical properties needed for the multimedia application. As with the watershed characteristics, it is made friendly with the other classes and contains a constructor member function. In addition, two other methods were written, the chem_prop_calc and the chem_Z_calc. The first of these class methods is used to estimate among other things, the secondary chemical properties such as the fugacity ratio and all the partition coefficients. The second method, chem_Z_calc, is used to manage the fugacity calculations as shown in section 2.2.1. A section of the 'chem_prop' class is shown below in Figure 2.7.

```
class chem_prop{
        friend class watshd_transp;
        friend class chem_ems;
        friend class watsh_char;
        friend class Display_Results;
public:
chem_prop(char cn[15], double wm, double sg, double vpp, double vpa, double vphg,
double pkowl, double te, double tm, double fcm[3],......);
        void chem_prop_calc(watshd_char &);
        void chem_Z_calc(watshd_char &);
public:
        char chemN[15];                 //Name of the chemical
        double WM;                      //Molecular weight (g)
        double SG;                      //solubility (g/m3)
        double VPP;                     //Vapor pressure (Pa)
        double VPA;                     //Vapor pressure (atm)
.......
.......
};
```

Figure 2.7 Representation of a Section of the 'chem_prop' Class

2.6.3 The Contaminant Emission Class – chem_ems

This module of the multimedia model is used to input the contaminant discharges into the different compartments, the advective influx from adjacent watersheds, and the background concentration in each of the seven bulk compartments. The C++ code of a section of this class is shown in Figure 2.8.

The last 3 variables in this class, NE, NETK, NETT, are simply the sum of all the inputs of a contaminant into the watershed. Additionally, since there are 5 priority contaminant chemicals used in this model, 5 different instances of this class are needed. It should be noted that adding for chemicals will simply involve adding the required chemical parameters to the model input file.

```
// Emission rates, Background concentrations and Chemical characteristics
class chem_ems{
	friend class watshd_transp;
	friend class chem_prop;
	friend class watsh_char;
	friend class Display_Results;
public:
chem_ems(double cb[7], double e[7], double cax, double cwx, double cai, double cwi, double
ne[7], double netk, double nett);
	void chem_calc(chem_prop &);
public:
	double C_bckg[7];		//Background/Initial contaminant conc. (g/m3)
	double E[7];			//Direct emission into the compartment (kg/y)
	double CAx, CWx, CAi, CWi; //conc. air and aerosol inflow from adjacent
// watersheds (kg/m3)
	double NE[7];			//direct discharge into a compartment (mole/h)
	double NETK;			//total contaminant input in the watershed (kg/y)
	double NETT;			//total contaminant input in the watershed (mole/h)
};
```

Figure 2.8 Representation of a Section of the 'chem_ems' Class

2.6.4 The Watershed Transport Vectors or MTCs Class – watshd_transp

The fate and transport vectors are written in terms of fugacity mass transfer coefficients or D values, as shown in Section 2.4. The objectives of this class are to initialize the different variable and to calculate the D values. This class also borrows data members from each of the previous classes and thus must be made friend with them. The variables used in this class are for the most part derived from the landscape characteristics, such as the rain rates. However, the rain rate is not uniform between sub-watersheds, thus an array of objects representing the different sub-watersheds is needed. The listing of this class is shown below in Figure 2.9.

```
class watshd_transp {
        friend class chem_ems;
        friend class chem_prop;
        friend class watsh_char;
        friend class Display_Results;
public:
watshd_transp(double u1, double u2, double u3, double u4, double u5, double u6, double
u7, double u8, double u9, double u10, ……………);
        void Dvalue_calc(watshd_char &, chem_ems &, chem_prop &);
public:
        double U1;                              //Air side of air-water
        double U2;                              //Water side of air-water MTC
        double U3;                              //Rain rate
        double U4;                              //Aerosols deposition velocity (dry)
        …………
        …………
};
```

Figure 2.9 Section of C++ Code for the 'watshd_transp' Class

Several variables in this class, such as the dry deposition velocity must be estimated after the creation of the objects. Other variables needing further analysis include the boundary layer thickness at the different interfaces, air-soil, air-water, water sediment, etc. The class method also estimates the residence time of a contaminant based on the half-life residence of each transport vector. Finally, the D values are aggregated together on a compartment basis. The latter being the coefficients of Equation 2.120. The last class, Display_Results, is simply a management tool to handle all the outputs from the simulation. It includes such class methods as the display of fugacity, concentration, mass percentage, inter-media fluxes, gain and losses from each compartment, etc.

2.6.5 Numerical Computation

Recalling that Equation 2.120 is written for the 7 bulk compartments in each of the 11 sub-watersheds, the above analysis yields a total of 77 equations with 77 unknown fugacity parameters. Each of these equations is re-written in the implicit form as:

$$\frac{V_i Z_i}{dt}(f_i^{t+1} - f_i^t) = I_i + \sum_{j=1}^{j=n} D_{ji} f_j^{t+1} - \sum_{j=1}^{j=n} D_{ij} f_i^{t+1} - D_{out} f_i^{t+1} \tag{2.121}$$

Equation 2.121 can further be simplified by aggregating the 3rd and 4th coefficients of the right hand side in a new term S_2. Thus the above equation becomes:

$$(1 + S_o) f_i^{t+1} - S_i f_j^{t+1} = CI_i + f_i^t \tag{2.122}$$

where;

$C = dt/V_i Z_i$

$S_o = C(\Sigma D_{ij} + D_{out})$

$S_i = C\Sigma D_{ji}$

The total chemical input, I_i is simply the sum of the direct discharges and background concentration inside the compartment *i*. The above equation being fully implicit, any time step dt can be used without compromising the stability of the numerical scheme. The terms $1+S_o$ and S_i become the coefficients of the matrix, A, with the input term and the current fugacity the right hand side vector, B, as follows:

$$A * f = B \tag{2.123}$$

$$\begin{bmatrix} 1+S_0^1 & -S_1^1 & . & . & . & -S_{76}^1 \\ -S_0^2 & 1+S_1^2 & -S_2^2 & . & . & -S_{76}^2 \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ -S_0^{77} & . & . & -S_{74}^{77} & -S_{75}^{77} & 1+S_{76}^{77} \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \\ . \\ . \\ f_{77} \end{bmatrix} = \begin{bmatrix} CI_1 + f_1 \\ CI_2 + f_2 \\ \\ \\ CI_{77} + f_{771} \end{bmatrix} \tag{2.124}$$

Here the solution vector is simply substituted for the B vector for each time step. The vector B is further decomposed to extract the different compartment fugacity, i.e., f_1 represents the fugacity of the contaminant in the air compartment of the 1st sub-watershed, HUC12, and f_{77} the vadose soil in the last sub-watershed, HUC37.

In the above matrix, most of the coefficients are zero in value since each compartment can exchange with a maximum of 5 other sub-compartments, thus there is a maximum of 4 coefficients in each row. The latter case is visualized in Figure 2.2 with the air compartment having exchange vectors with the surface soil, terrestrial vegetation, surface water and the adjacent sub-watershed air compartments. The resultant matrix is banded around the diagonal line. Numerous numerical solution methods have been developed for such matrices depending on their size, how spare the matrix appears and level of accuracy required. Furthermore, a number of these numerical methods have been designed specifically for object oriented C++ programming. These include the popular LAPACK++ an OOP version of the LINPACK library (Pozo, 1996), the Templates for the Solution of Linear Systems (Barrett, 1994), the TNT or the Template Numerical Toolkit and the SparseLib++ library (Pozo, 1996) and the classical Matlab package. However, these very sophisticated routines were very cumbersome to use or required purchasing new software; it would not be justifiable going through such an effort to solve a simple 77 by 77 matrix.

The solution envisaged was to use the newly developed "Visual MATCOM" library for visual C++ (MathTools, 1999), the software used to develop the present model, from the makers of MATLAB. This new library is fully functional within a visual C++ environment and can run as a stand-alone application. It is best described as a portable MATLAB package, and is ideal for use in the present model since its code can be directly embedded into the present model. The resultant solution vector is assigned to the different sub-watersheds' compartments. The last class used in the present model, Display_Results, is used to manage the model's output. One section of the output is sent directly to the GIS for viewing and querying purposes. The complete computer model is composed of three original files; a header file, 'thesis.h', containing all the classes definitions, the implementation of the class methods file, 'thesis.cpp', and the main file, 'driver_thesis.cpp', use to implement the class instances.

CHAPTER 3

LANDSCAPE CHARACTERIZATION AND CHEMICAL RELEASES IN THE PASSAIC RIVER WATERSHED

The application of a multimedia model requires the achievement of certain tasks. These include the characterization of contaminant sources, the description of the landscape in which these sources are present and the application of the fate and transport model. The latter part, discussed in Chapter 2, requires the use of both landscape data as in the advective flows in surface water and the accounting of all the releases of a given contaminant in the watershed, as in the yearly amount. A complete description of the watershed environment landscape parameters follows in this section. The Passaic River Watershed is first described as one environmental unit and second as a collection of individual HUC11 sub-watersheds, each representing a unit environment. This exercise is to introduce a logical level of spatial resolution as stated in the objective section of this research.

Additionally, the contaminant input into the environment is defined using the toxic release inventory database (TRI). The methodology used to incorporate this database into the multimedia model, and the assumptions made are discussed in detail in the current chapter. In this chapter, geographical information system (GIS) is extensively used, both for data acquisition and for displaying the results of the model. The GIS representation is the format under which this data is distributed through NJDEP and U.S. EPA. A conceptual definition of the watershed as a unit environment is shown, followed by the division of the watershed into smaller units and a detailed description of each compartment. This chapter is concluded with the description of the TRI database used.

3.1 Conceptual Description of the Unit Environment

The Passaic River Watershed is represented as an environmental unit implying that only one compartment is used to describe each of the water phase, air phase, sediment layer, surface soil, root soil and vadose soil. Examples of using the unit environment include: USES (RIVM, 1994) and fugacity model for prioritizing air sources in the State of Minnesota (MPCA, 1992), all of which are significantly larger than Passaic River Watershed in spatial extent. Figure 2.2 illustrates this unit environmental description.

The unit world (as shown in Figure 2.2) consists of 7 compartments (air, water, surface soil, sediment, terrestrial vegetation, root zone soil and vadose zone soil). Each compartment in turn includes different phases; e.g. the bulk air phase is composed of pure air and aerosol particles. In total there are 18 sub-compartments used in the present models, including:

1. Bulk Air – Gaseous air, aerosol particles.
2. Bulk Water – Pure liquid water, suspended particles and aquatic biota such as fish.
3. Surface Soil – Soil air, soil water and soil solid particles. This compartment is commonly known as topsoil or 'A horizon' by soil scientists.
4. Bulk Sediment Layer – Sediment pore water and sediment solid particles.
5. Terrestrial Vegetation – Foliage part of the plant and plant roots.
6. Root Zone Soil – Soil air, soil water and soil solids. This is taken as the summation of the soil layers from the 'A' horizon to the depth of arable soils.
7. Vadose Zone Soil – Soil air, soil water and soil solids.

3.2 Description of the Watershed as Sub-watershed Unit Compartments

In the present study, the Passaic River Watershed is divided into 11 Hydrological Unit Codes (HUC) or drainage basins as defined by the USGS. This provides a higher spatial resolution of the watershed, as shown on Figure 3.2. Each sub-watershed (HUC) is now considered as a separate entity or unit environment. The introduction of this resolution will determine whether any advantage can be gained through the smaller division of the environmental compartments. The watershed is believed to be a more natural unit of the environment. Furthermore, the watershed division is chosen in the current model to better capture the flow of streams inside a compartment as shown in Figures 3.1 and 3.2.

Since only a limited state division is available in published data, the watershed division was chosen as the next most appropriate, since other divisions (small stream watersheds, topographic regions, counties, or municipalities) were either too small or too large to adequately represent the distribution of the published landscape data. The New Jersey Department of Environmental Protection has build an extensive monitoring program based on the county division of the New Jersey State. However, the boundaries of the counties and watersheds do not match as seen in Figure 3.3, and no such characterization for the watershed exists in the current literature. In the latter figure, it will be nearly impossible to accurately quantify all the inflow water into the county landscape because of the large number of inflow points and the lack of gauge reading on these small streams. Thus a redefinition of the databases published by NJDEP is necessary and was performed as part of this research; this constitutes a substantial effort in this study. This was accomplished using the Arc View GIS software and the databases available from the NJDEP, and the Soil Conservation Services (SCS). A detailed description of this procedure is provided in the description of the sub-watershed compartments.

A list of these input parameters is presented in Table 3.1. Other important properties included in this table are; the organic carbon content, void ratio of surface soils, hydraulic conductivity of both unsaturated and saturated sub-soils. These landscape data are derived from the released GIS Resources data from the New Jersey Department of Environmental Protection. This database is essential to multimedia application since most of the relevant landscape parameters can be generated from it. Furthermore, additional databases obtained from the USDA (United States Department of Agriculture) state geographical data are used to fill any data gap. The landscaped data for the remaining sub-watersheds and the Passaic Watershed as one unit are presented in Appendix A.

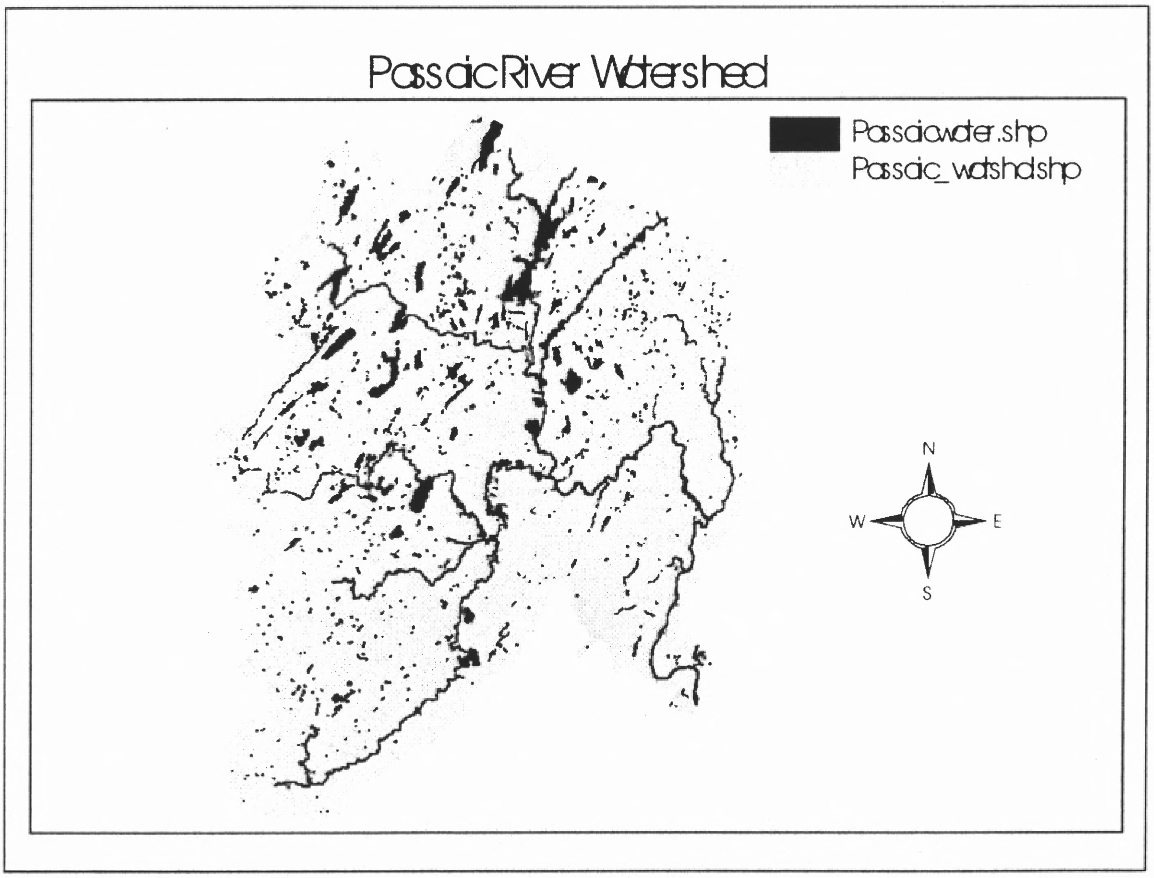


Figure 3.1 Surface Hydrology of the Complete Passaic River Watershed

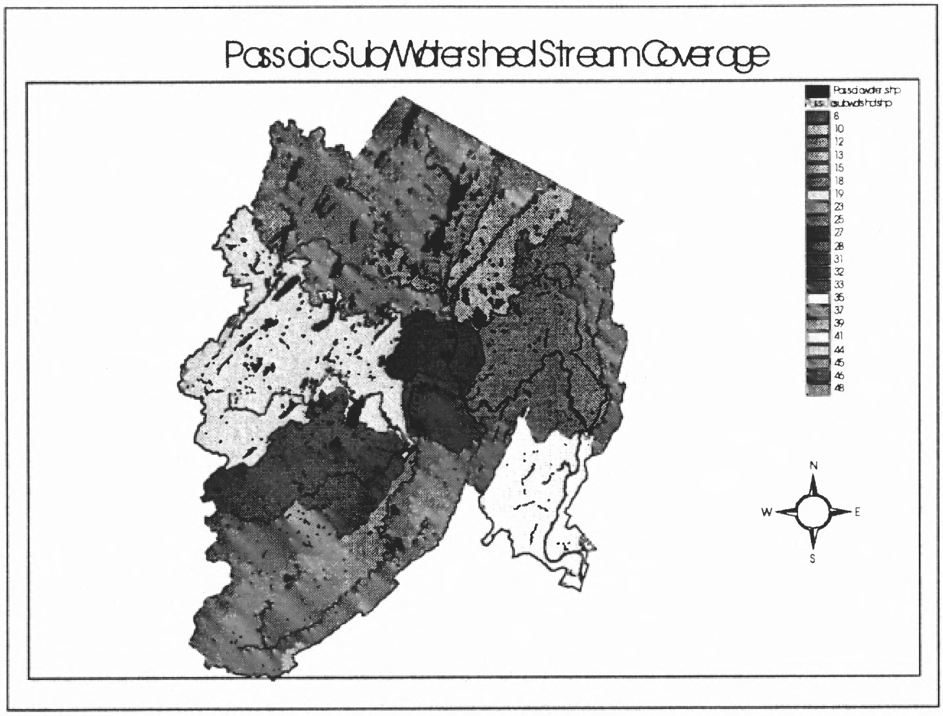


Figure 3.2 Surface Water Hydrology: A View of the Sub-watershed Representation

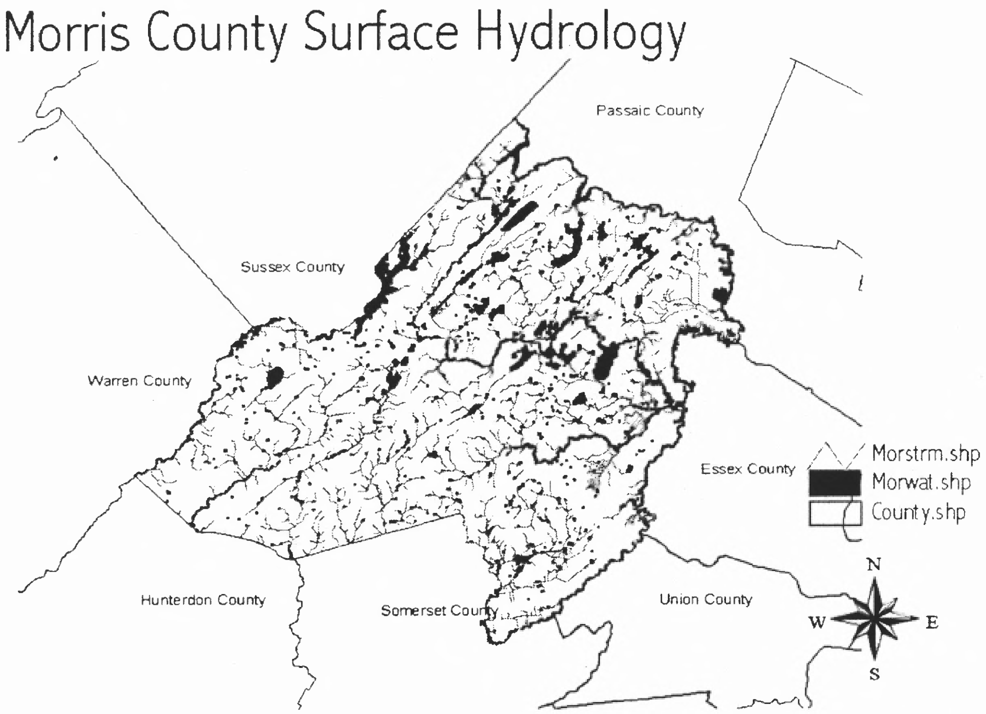


Figure 3.3 Surface Water Coverage on a County

Table 3.1 List of Landscape Parameters Used by the Multimedia Model

Landscape Parameters	Variable	Value – HUC#12
Total Area – m^2	Area_T	2.05E8
Air Column Height - m	H1	1000
Aerosol Volume Fraction	$\phi_{1,3}$	6.67E-12
Aerosol particle Density – kg/m^3	$\rho_{1,3}$	2400
Yearly Wind Speed m/h	V_w	15607.3
Rain Rate – m/h	Rain	1.46E-4
Dry Deposition Velocity – m/h	v_d	28.75
% Land Area in Surface water	Warea%	10.05
Depth of Surface Water – m	H2	3.5
Fraction Suspended Particle in Surface Water	$\phi_{2,3}$	6.7E-6
Runoff rate – m/h	U_{run}	9.87E-5
Surface Water Current – m/h	Current	806.4
Active Sediment Layer Depth - m	H4	0.05
Sediment Pore Water Content	$\phi_{4,2}$	0.9
Surface Water Particle Deposition Velocity – m/h	v_{sd}	60.0
Re-suspension Rate of Particles in Water – m/h	v_{ss}	4.5E-8
Fraction Organic Carbon Content of Water particles	Foc_2	0.20
Fraction Organic Carbon Content of Sediment	Foc_4	0.0209
Aquatic Biota Content	$\phi_{2,4}$	1.0E-6
Aquatic Biota Density – kg/m^3	$\rho_{2,4}$	1000
Flow In – m^3/h	QW_i	0
Flow Out – m^3/h	QW_o	5811
% Land in Vegetation	Varea%	67.5
Thickness of Foliage Vegeation - m	H5	0.50
Water Content of Surface Soil (SS)	$\phi_{3,2}$	0.239
Air Content of SS	$\phi_{3,1}$	0.289
Thickness of SS - m	H3	0.20
Fraction Organic Carbon Content of SS	Foc_3	0.029
Erosion Rate of SS – m/h	Eros	3.3E-9
Density of SS particles – kg/m^3	$\rho_{3,3}$	2650
Water Content of Root Soil (RS)	$\phi_{6,2}$	0.20
Air Content of RS	$\phi_{6,1}$	0.22
Thickness of RS - m	H6	0.56
Infiltration Rate in RS – m/h	V_{inf}	4.8E-5
Fraction Organic Carbon Content of RS	Foc_6	0.002
Density of Particles in RS – kg/m^3	$\rho_{6,3}$	2650
Water Content of Vadose Soil (VS)	$\phi_{2,4}$	0.28
Air Content of VS	$\phi_{2,4}$	0.17
Thickness of VS - m	H7	9.13
Infiltration Rate in VS – m/h	V_{infV}	4.8E-5
Fraction Organic Carbon Content of VS	Foc_7	0.002
Density of Particles in VS – kg/m^3	$\rho_{7,3}$	2650

The remaining parameters used in the present model are derived from the data set presented in Table 3.1. Each of the sub-watersheds is divided according to the environmental unit. The sub-watersheds are connected using advective flows of water and air. The environmental processes occurring in the environmental unit are partly described in Chapter 2, the remaining processes are described in the following sections. Along with the environmental processes, a detailed description of the methodology used to collect landscape data is also provided. Each compartment and sub-compartment is described, i.e., their physical characteristics along with the advective processes in the compartment.

3.3 The Atmosphere Compartment Characterization

3.3.1 Air Compartment

The mixing atmospheric layer is the height from the ground surface to the troposphere. A contaminant present in this layer is assumed to be available for vertical transport to the ground surface or to advective loss from the compartment. At continental scale, this height is usually as high as 6 km. However, for a regional and smaller scale modeling, a good approximation of 1 km was suggested (Mackay, 1991). The volume of this box is important in determining the total residence time of the contaminant and the dilution of such contaminant. The area extent of the Passaic River Watershed is estimated from the NJDEP GIS resources to be 2.04E9 m^2. The total areas of each of the 11 sub-watersheds are also estimated and are presented in Appendix A.

The movement of air that carries the contaminant in and out of a given sub-watershed is not a steady process and thus must be represented in the model. Meteorological data have shown that the yearly wind speed is around 9.7 mph (USCOE, 1972) with a predominant direction from the Northwest. This directional movement changes in the summer months when the winds originate from the Southwest ; this is about 5 months per year. The effect of wind is included in the present model by using the same annually averaged wind speed and allowing two directions, i.e., from the Northwest during the first 7 months and from the Southwest for the remaining of a given year. The advective air flows are estimated using the following relationship (CEPA, 1993).

$$FlowRate = \frac{0.0096 * v_w * H1 * Area\_T}{\sqrt{Area\_T}} \tag{3.1}$$

with v_w representing the predominant wind speed in m/d, H1 de depth of the active air layer in m and Area_T the total area of the unit in m^2.

3.3.2 Aerosol Particles

Aerosols particles constitute an important role in the deposition of chemicals from air. The deposition is in turn strongly related to the aerosol particles size which has been classified into 3 main modes according to their diameter: the nucleation mode (< 0.1 μm), accumulation mode (0.1 < d < 1 μm) and sedimentation mode (d > 1 μm) (Trapp, 1998). The nucleation mode particles are believed to aggregate to form the accumulation mode particles and tend to stay in the atmosphere for very long period. The first two aerosol modes (accumulation and nucleation) are responsible for long-range transport of a chemical to virgin areas such as Antarctic. On the other hand, local deposition is largely attributed to the coarser sedimentation mode. The latter is generally a product of industrial combustion processes and fossil fuel burning activities, and thus is related to the land coverage. Additionally, USEPA in 1987 has changed the National Ambient Air Quality Standards (NAAQS) measuring requirements for air particles from total suspended particles (TSP) to the inhalable particles with sizes less than 10μm (PM-10). The reasons advanced for this change involves the difficulties in reaching compliance with the old standard which was based on the transport of fugitive dust (PM-30). This implied that the role of the emitted particles (smaller in size) was largely underestimated (Cowherd, 1993).

The Passaic River Watershed includes different land covers, including forested areas, agricultural lands, barren lands and urban areas; all are used in the present model. These land cover areas are extracted from the NJDEP 1986 county delineation. From these land cover areas, the aerosol load in the air compartment is calculated using the monitoring data as follows. The measurement data were not available in all sub-watersheds, thus loading rates were assumed for some of them (HUC11# 13, 15, 18, 19, 27, 31, 33 and 37*)*. In making the above assumptions, a number of factors were considered, including; equaling aerosol loading for areas with similar land cover and using area weighed average of actual measurements just upwind of the area of interest. These data are collected from NJDEP 1997 Air Quality Report (NJDEP, 1997) and are considered to be an accurate representation of environmental conditions. The overall area weighed average aerosol load is calculated as 22.59 $\mu g/m^3$ or an air volume fraction of 9.41E-12 for the entire Passaic River Watershed. The aerosol load for the HUC11 sub-watersheds is provided in Table 3.2.

3.3.3 Deposition Processes

The contaminant present in the air compartment can take the form of gaseous form or sorbed to the aerosol particles. The diffusive transfer of the gaseous chemical is discussed in detail in Section 2.4 and its value is chemical dependent. On the other hand, the dry and wet deposition velocity of the aerosol can be represented in terms of landscape properties. Dry deposition of particles depends on the thickness of the boundary layer at the air-water surface, air-soil surface and air-leaf surface. The value of this parameter varies greatly in the literature from a low of 3.6 m/h (Van de Meet, 1993) to 30 m/h (Trapp, 1998).

Table 3.2 Aerosol Loading for the HUC11 Sub-Watersheds

Environmental Unit	Load, $\mu g/m^3$
12	16
13	16
15	28
18	24.25
19	19
25	28.9
27	27.25
31	28.9
33	27.25
35	36
37	19
Entire Watershed	22.59

In the present model, the dry deposition $v_{d,p}$ is estimated as 30 m/h. The overall dry deposition is thus a fractional sum of the gaseous and particle deposition, as follows (Trapp, 1998):

$$v_{dep} = (1 - f_p)v_{d,g} + f_p v_{d,p} \tag{3.2}$$

with f_p is the adsorbed fraction of the contaminant in air, $v_{d,g}$ and $v_{d,p}$ the dry deposition of the gaseous molecules and particles in m/s, respectively. The adsorbed fraction f_p is calculated as follows:

$$f_p = c_p /(c_g + c_p) = 1/(1 + K_{ax}) \tag{3.3}$$

The term K_{ax} is computed earlier as the air-aerosol particles partition coefficient, cp and cg are the chemical concentration in the air phase and particle phase, respectively. The deposition velocity $v_{d,g}$ is controlled by the laminar boundary layer and can be estimated from a reference chemical (Trapp, 1998).

$$v_{d,g} = v_{d,g(ref)}\sqrt{\frac{WM_{ref}}{WM}} \tag{3.4}$$

The reference chemical has a molecular weight WM_{ref} of 300 g and a corresponding deposition velocity of 18 m/h. The particle phase is divided into 3 main parts depending on its diameter size d, the nucleation mode ($d < 0.1\mu m$), the accumulation mode ($d > 0.1\mu m$ and $d < 1\mu m$) and the sedimentation mode ($d > 0.1\mu m$). Each of these modes will have a separate residence time and thus deposition velocity in the air compartment. The general rule given by Stoke's Law as the movement of large particles being controlled by gravitation forces while smaller particles movement is controlled by turbulence. Finally, a universal particle deposition velocity of 30 m/h is used in the present model.

The other mechanisms of movement of chemical is the wet depositional flux, including the dissolution of chemical into falling rain droplets and the sweeping of chemical-bound particles into the rain droplets. This sweeping of aerosol is represented in the model as a scavenging or washout ratio Q of 200,000 of particles in each rain droplet (Mackay, 1991). The dissolution into rain is calculated as the equilibrium fugacity between the air compartment and the rain-water. For each sub-watershed, the rainfall data is extracted from the NJDEP resources. The entire watershed had an annual rainfall rate of 1.253m.

3.4 The Water Compartment Characterization

The surface water compartment is characterized using the USGS stream network. This coverage is provided on a county basis and includes the lake coverage (major rivers and lakes) and the stream coverage (all the streams in the watersheds). The fact that these data are only provided on a county basis required a redefinition of the original data as provided by NJDEP and USGS. This was achieved by manually manipulating this data with ESRI's

Arcview functions for joining and clipping. Intersecting counties within the watershed area and joining the stream and the lake coverage is used to aggregate all the streams in a given watershed, this was saved into a mapjoint file. The next step is to clip the area of a given sub-watershed from the mapjoint file to provide us with the individual sub-watershed and the complete Passaic Watershed coverage for the lakes and major streams and the smaller stream network.

3.4.1 Liquid Water Phase

The water and air compartments are important compartments because this is where the releases of contaminant and the advective fluxes take place. The important processes controlling the contaminant fate in this sub-compartment include; dispersion, advection flows in and out of the compartment, absorption between the liquid phase and the suspended colloidal materials and with the underlying sediment layer and degradation. The physical parameters needed for this sub-compartment are the surface area, the depth, and advective inflow and outflow. Because the depth of the surface water is not reported in the literature or in the government databases, an average depth of 3.5 m is used for the entire watershed. This value is near those reported in the literature; 5m in CalTOX, 10m in Mackay models and 8m in the Minnesota model.

Other assumptions made include the calculation of the surface area of water bodies. The reason for this assumption lies in the fact that only lakes and major rivers with width of at least 18m are represented as polygons with surface area associated with them in the GIS databases. This type of representation saves disk space but also has an undesirable effect of omitting the majority of the stream network consisting primarily of smaller streams. For the sake of completion, an average width of 9m was used for the width of the smaller streams in obtaining a total surface water area. The latter is the sum of the area of the lakes and major streams coverage plus the total length of the minor streams times the assumed width of 9m.

The volumetric flow rate in and out of each sub-watershed is estimated from the USGS stream gage readings (USGS, 1996). With the exception of sub-watershed HUC11# 25, 27, 31 and 35, the total inflow is zero for all the sub-watersheds where the lower order streams starts. Where available, the stream gauge readings are used for the advective flow rates out of each sub-watershed; this was the case for HUC11# 12, 13, 15, 18, 19, 25, and 31. For the remaining unit the flow gage reading inside the unit is prorated to the entire sub-watershed to estimate its flow rate. This is made possible since the drainage area at any gage point of the USGS stations is provided. The inherent assumption made here is justifiable by taking the smaller sub-watershed flow characteristics to be uniform. In the model itself, an inflow rate of 1 m^3/h is assumed for the head water sub-watershed to avoid any division by zero during computations. These flow data are provided in Table 3.3.

Table 3.3 Volumetric Inflows and Outflows in the Passaic River Watershed

HUC11	Inflow - m^3/h	Outflow - m^3/h	HUC11	Inflow - m^3/h	Outflow - m^3/h
12	0	5811	27	63721	58409
13	0	15293	31	83296	86161
15	0	42617	33	0	18831
18	0	13662	35	166012	179674
19	0	33879	37	0	30684
25	144570	152350	Overall	0	180000

3.4.2 Suspended Particles in Water

The movement of contaminant via the sorbed phases in the water column has a great impact on the contamination of water bodies, sediment and aquatic biota. Additionally, the amount of suspended particles contribute to the degradation of the overall water quality by increasing the turbidity and reducing the amount of light reaching the bottom layers. Thus this parameter is of importance to regulatory bodies and thus has been extensively monitored. Suspended load strongly depends on the overland soil type and the flow characteristics, typical values reported include 5 to 10 mg/L (Mackay, 1991), 88 mg/L (CEPA, 1993) and 10 to 110 mg/L (Maidment, 1993). In forested areas, the suspended particle load is much lower than that of urban areas and thus a value of 10 mg/L is used for HUC11# 12, 13, 15 and 19 and 20 mg/L for the remaining sub-watersheds.

The fraction of organic carbon content f_{oc}, which dictates the chemical sorption to the particles, is assumed to be 0.20 everywhere in the watershed. In the present model, this default value is used due to lack of comprehensive watershed wide data on the physical characteristics of the sediment compartment. Similar values for this f_{oc} were used in Mackay's models (0.167), USES (0.10), ChemCan (0.20) and MPCA's MinnMod (0.59). Finally, the water volume fraction that is aquatic biota (fish) used here is 1 ppm; this is a typical value used in the literature (Mackay, 1996).

3.4.3 Processes in the Hydrosphere

The stream flow for the most part is generated from surface runoffs, i.e., from antecedent precipitation. The yearly averaged rainfall in the different sub-watersheds is extracted from the climate data of the NJDEP GIS Resources and vary between 1.19m for HUC#35 to 1.28m for HUC#12 and #13 on a yearly basis. This is presented graphically in Figure 3.4. The net movement of water from the land surface to the water bodies is estimated using classical Soil Conservation Services (SCS) runoff equations (US SCS, 1985 and 1986). The flow rate Q_f (in) from a given rainfall P (in) is estimated using the land cover characteristics runoff curve number CN which depends on the soil, land cover and hydrologic condition.

$$Q_f = \frac{(P-0.2S)^2}{P+0.8S} \tag{3.5}$$

where the variable S, in inches, is in turn obtained from:

$$CN = \frac{1000}{S+10} \tag{3.6}$$

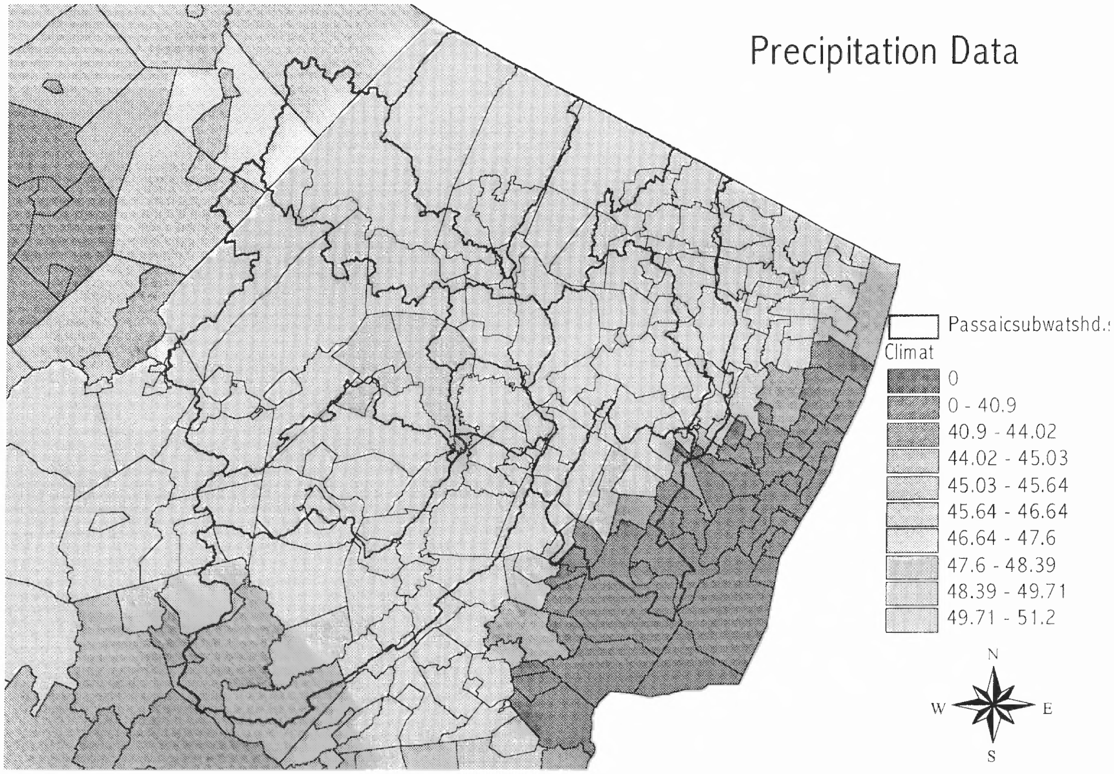


Figure 3.4 Distribution of Precipitation in the Passaic River Watershed.

For each land cover type (such as forest, urban etc.), i.e., a separate CN, the runoff Curve Number value is extracted using 1 of 4 hydrological soil groups or soil permeability (Maidment, 1993). The 4 groups are urban areas, cultivated agricultural areas, other agricultural areas and arid and semiarid range areas. Furthermore, each of these 4 land cover types has its own sub-division or grouping including: Group A for soil with high infiltration rate, greater than 76 cm/h, Group B for soil of moderate infiltration, between 0.38 and 0.76 cm/h, Group C for soil with low infiltration, between 0.13 and 0.38 cm/h and Group D for soil with high runoff potential. The land coverage of the Passaic River Watershed is extracted from the 'Land Unit Cover' GIS database from NJDEP and used here to derive the CN values. Examples of this coverage are presented in Figures 3.5 and 3.6 for the urban and forest areas, respectively. In Equation 3.5, the variable CN is related to the 'Land Use/Land Cover' described in the NJDEP database, which includes forest, urban, barren and wetland, only the first 4 of which are used in the present model. The CN values used for these 4 'Land Cover' terrain types are presented in Table 3.4.

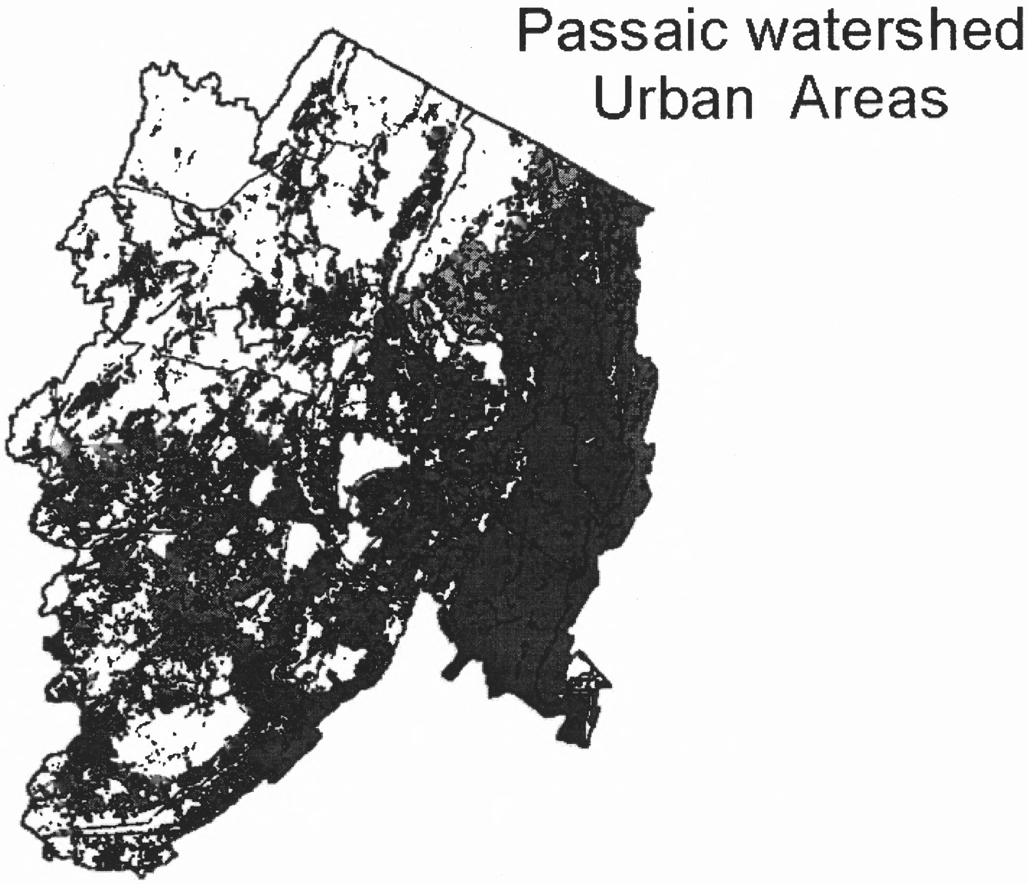


Figure 3.5 Urban Coverage of the Passaic River Watershed.

Table 3.4 Runoff Curve Number (CN) for the Passaic River Watershed Terrain Coverage

Hydrological Soil	Agricultural Cover	Urban Cover	Barren (Open)	Forest Cover
A	62	81	49	25
B	71	88	69	55
C	78	91	79	70
D	81	93	84	77

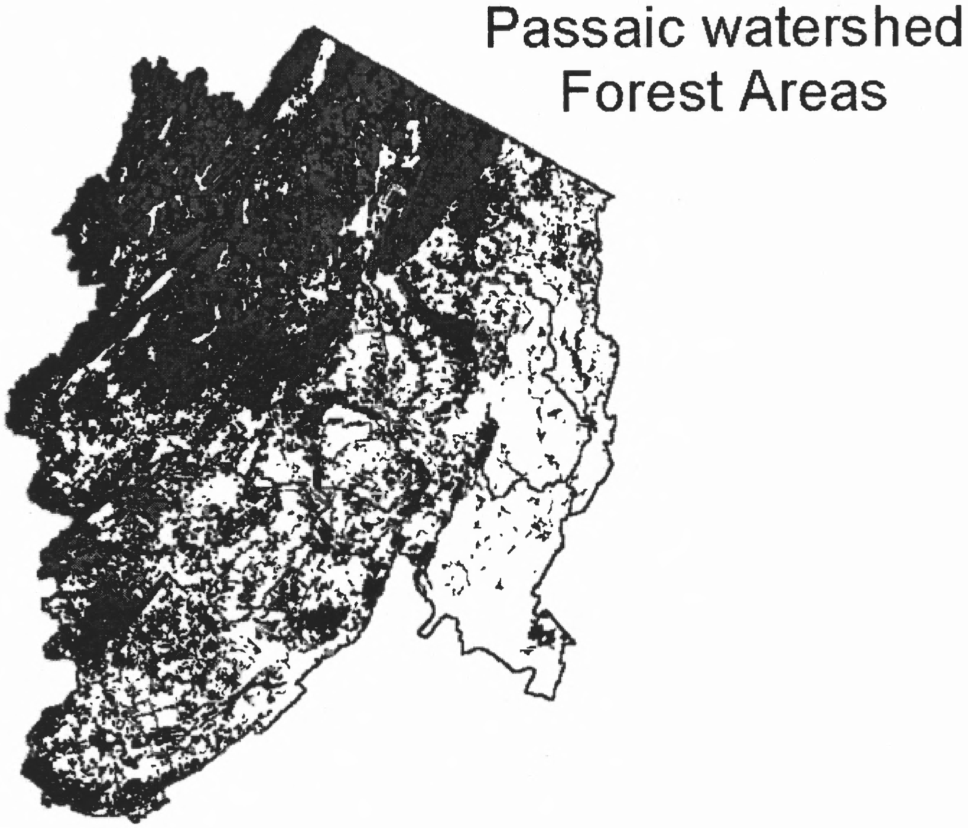


Figure 3.6 Forest Coverage of the Passaic River Watershed.

Using the depth weighed average of the soil permeability values given in the USDA SSURGO database, the overall average permeability of the soils exceeded the 0.76 cm/h for all the sub-watersheds. Consequently, only the soil 'Group A' was used for different land covers. The area weighed average of these CN values is estimated for each sub-watershed as per its land coverage to obtain the sub-watershed CN value. The parameter S is computed, and then the flow rate Q_f. The latter is also an estimation of the water exchange between the surface soil and the surface water bodies. Other process included in the surface water transport is the soil solid runoff to the water bodies after a period of rain, this is also known as soil erosion. In our model, an estimate of 2.89E-5 m/h is used for this process (MPCA, 1993).

3.4.4 Deposition Process in Surface Water

The sedimentation of the water column particles is an important route for the transfer of contaminant to the underlying sediment layer. In major harbors of the world, this sedimentation rate must be tackled with frequent dredging of the ship channels. The process of deposition itself is complicated and has extremely spatial and dynamic variability (Wesrich, 1988). It depends on numerous factors such as the river morphology (mature channel vs. active channel), the slope of the channel and the characteristics of the particles themselves. In some channels, the net sedimentation is positive with deposition greater than erosion while in other the opposite occurs. In the present model, the sedimentation process is over simplified to a unique sedimentation rate used throughout the watershed. A value of 2.5 m/day is used in the present model, as in USES (RIVM, 1994).

3.5 The Sediment Compartment Characterization

The sediment layer serves as a reservoir sink of the contaminant that is present in the water column. In the case of PCB and Dioxin in the New York Harbor, it was found that over 99% of these contaminants were distributed in the sediment layer, mainly because of their high affinity for the organic carbon of the sediment particles (Coulibaly, 1998). The above analysis was supported by experimental data as well (Thomann, 1989).

The characteristics of the sediment compartment include the depth of the active sediment layer d_{sd}, the sediment pore water fraction and fraction organic carbon content of the sediment solid. The first of these parameters, the depth of the active sediment layer, is the part of the sediment compartment that interacts with the water column via sorption, deposition of suspended particles and re-suspension of particles into the water column by the benthic population and flow dynamics. This depth is estimated from literature values as 0.05m and is similar to values of 0.03m in USES (RIVM, 1994; Van der Meent, 1993; Mackay, 1991), 0.02m in MinnMod (MPCA, 1992) and 0.05m in CalTOX (CEPA, 1993).

The pore water content of the sediment layer is also estimated from the values present in the literature as 0.9 or 90% with the remaining 10% being the sediment solid. Again the literature value varies from 0.8 in USES to 0.88 in MinnMod. Diamond (1994) suggested to use the 90 percentile after further review of the MinnMod. The same value is used in ChemCan. Finally, organic carbon fraction of the sediment layer solid particles is estimated as 0.03, which is close to the estimation in CalTOX (0.032), ChemCan (0.05) MinnMod (0.05) and USES (0.029). The organic carbon content of the sediment layer is assumed to be 0.029 (Heijna-Merkus & Hof, 1993).

3.5.1 Exchange at the Sediment-Water Interface

Sedimentation occurs with a re-suspension of the sediment particles where they may create a condition of net erosion, or net deposition or zero deposition. As with the sedimentation rate in Section 3.4.4, the re-suspension process is also simplified to a unique value applied to the entire watershed. This value is assumed to be 4E-4 m/year in the calculations (MPCA, 1993, Mackay, 1991). Additionally, the burial rate or the thickening of the sediment layer is estimated as 4E-4 m/year. It should be noted that the burial rate is not necessarily the difference between the depositional and re-suspension fluxes.

3.6 The Terrestrial Vegetation Compartment

Exchange between the air and land surface also occurs via vegetation uptake or release. For this purpose, the vegetation compartment is divided into 2 sub-compartments, the above ground (foliage) and the roots. This is a simplified version of the prevailing plant models currently available such as PLANT (Trapp, 1998)and PLANTIN (Grunhage, 1998). Other models present in the literature are Hauk (1994) and Paterson (1991). In the present research, the contaminant transport through the plant is simplified to a two-compartment model. The transport process is as follows: the leaf part of the plant exchange chemical with the air compartment via the cuticle and the uptake by the roots from the root zone soil water. The first process is diffusive while the second is one-directional transfer from the soil to the plant.

The above diffusion process is not trivial and should be examined in detail. For a gaseous chemical to get into the leaf, it must pass through a thin layer of soil deposited on the leaf surface. Thus a boundary layer that dictates this transfer exists in the air above the leaf surface and must be determined. This layer is estimated to be 0.005 mm (CEPA, 1993). Thus the diffusion is considered to be a series of resistance between the air-side and the plant side. Furthermore, the leaf's stomata offers a resistance to the transfer of gaseous molecules to the air, r_{stom}, it is considered a parallel resistance on the plant-side and it combined with the plant gas diffusion to give overall air and plant diffusion. The air side mass transfer is controlled by a boundary layer with a thickness of 5 mm. Finally, the net dry deposition on the leaf surface is balanced by the washout during wind agitation and rainfall events. The plant's roots and soil water transfer is one direction with a net transpiration rate or transpiration MTC v_{transp} of 5.0 m/h.

3.7 The Soil Compartment

3.7.1 Introduction

Of the bulk compartments used in the present model, the soil compartment is the least uniform and transport in this medium is both complex and may carry a great deal of uncertainty. The physical and chemical characteristics of the soil changes with time and space (thus contributing it to be the most stationary compartment). This spatial variability of the soil compartment is presented in Figure 3.7 for the HUC11#12 sub-watershed. Because of the inherent complexities of this compartment, our approach was to divide into three separate layers, the surface soil, the root zone soil and the vadose zone soil. The surface soil designation used in this research is also known as the 'A horizon' soil or the top soil by soil scientists and in agricultural practice. The root zone soil is taken as the combination of the B, C and D horizons, while the vadose zone soil is estimated from the bottom of the root soil to the top of the water table. Recently, other researchers recognized the need to differentiate among the different soil profiles, as was done in the CalTOX model. Similarly, in both USES and SimpleBox (RIVM, 1994), the soil is divided into 'natural soil', 'agricultural soil' and 'industrial soil'.

The justification for this distinct spatial soil representation is the fact that human activities determine to a great extent the loading of contaminant in soil and thus the variability in soil properties. For example, agricultural activities in an area systematically deplete the soil from its natural organic matter content and replace it with foreign compounds such as pesticides. The different soil layers significantly differ in soil characteristics and provide a much improved representation of the soil environment, as compared to the one soil compartment. Additionally, parameters such as the organic carbon content, which is a critical variable in fate and transport of contaminant, differ by as much as one order of magnitude between the different soil layers. Thus most hydrophobic contaminants will have a high adsorption to the layer of high f_{oc}. In Sections 3.7.2 through 3.7.4, the methodology used to divide the soil compartment is discussed in detail. The USGS soil reports provided in the NJDEP GIS resources and the USDA's NRCS (Natural Resource Conservation Service) SSURGO (Soil Survey Geographic Database) database are used as a basis for the following analysis. The SSURGO data are the most detailed soil mapping performed by NRCS so far.

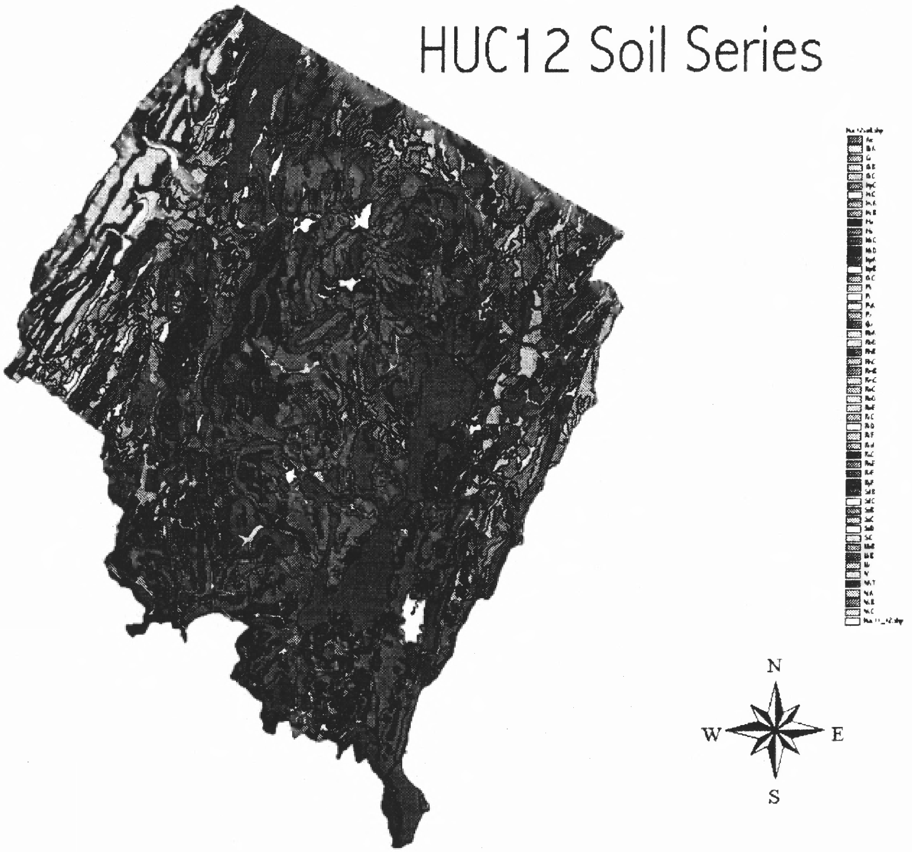


Figure 3.7 Soil Cover of the HUC11 #12 Sub-Watershed.

3.7.2 Soil Compartment Characterization

The NJDEP GIS database is the starting point of this analysis. It provides a spatial coverage of the different entity, which is coded either in latitude/longitude or state planar feet coordinate system. Thus it can be mapped using popular GIS software. Also, the attribute tables of each of these entities can be imported and queried into the above software as a database file. The spatial accuracy of these data is within 18m on the ground, at a scale of 1:24000. As with the water coverage, the soil cover is provided on a county basis only. Thus the methodology used earlier to join the enclosed counties and then clip the individual sub-watersheds was performed. The resulting attributes to be used from this exercise include the Soil_Label and their individual surface areas. For the extent of the Passaic Watershed, this resulted in over 17,840 separate soil polygons, although there are significantly less number of soil types. The reason for this large increase in the number of data is because each county performed its soil survey independently, and without any consistence in data labeling with other counties.

Also, no centralized procedure, based on a larger geographical unit such as a watershed or state, was used to unify the data collected by the different counties. Since each county in New Jersey established its own soil survey effort, the same soil in two different counties may have two different designations (Soil_Label). A schematic representation of the structure of the SSURGO and USGS Soil Survey is presented below:

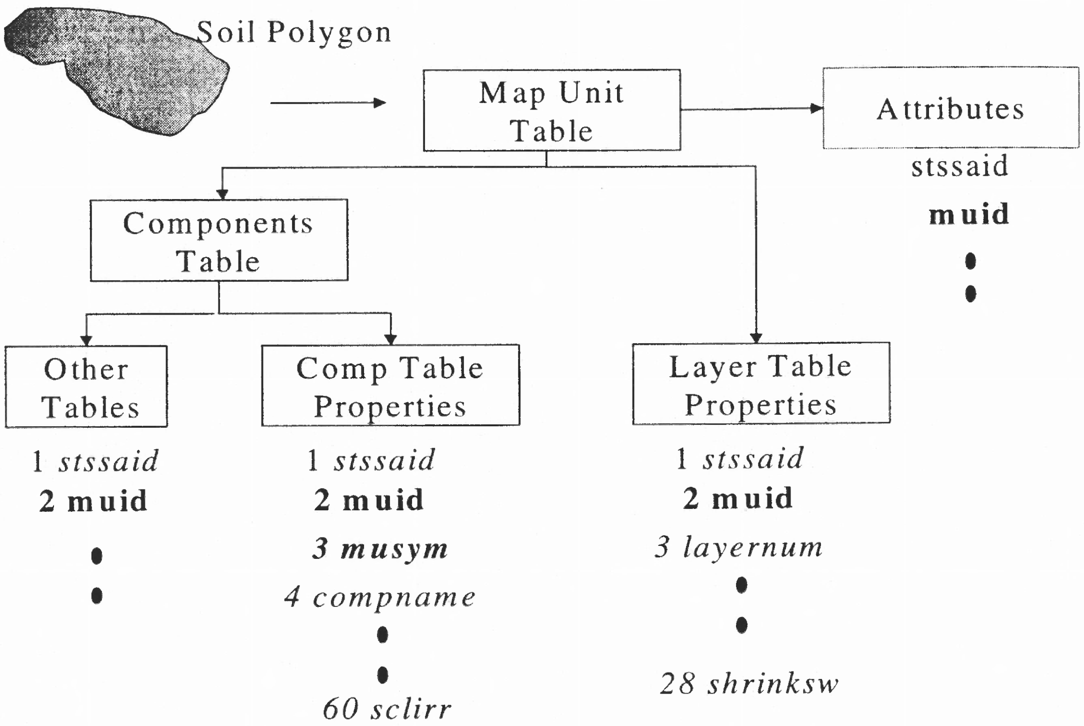


Figure 3.8 SSURGO Relational Data Representation

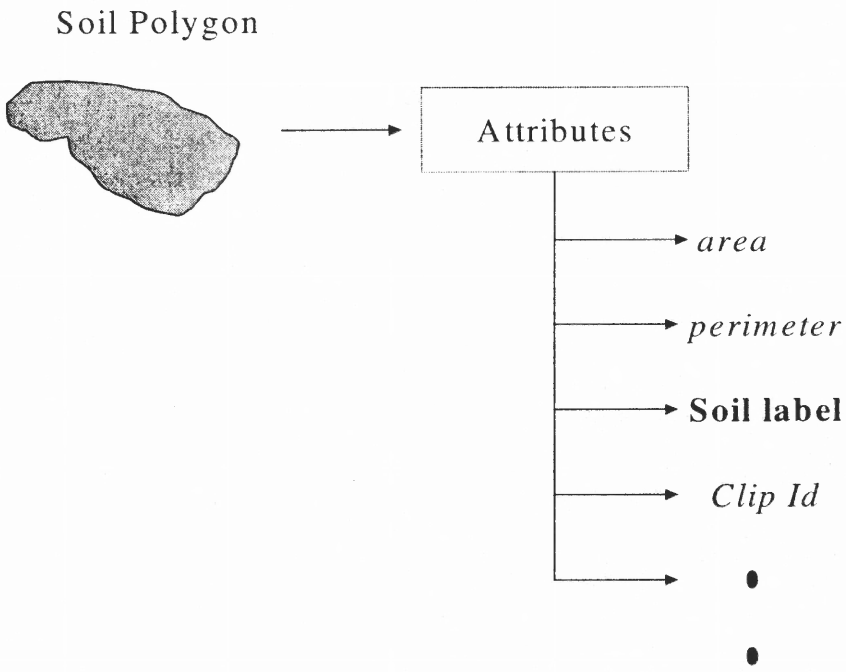


Figure 3.9 USGS Soil Survey Data Structure

As per Figure 3.8, the SSURGO database consists of 24 different data files defining the physical and chemical properties of soil, soil interpretation for engineering applications, water management, recreation, agronomy, woodland, range and wildlife uses (USDA, 1995). Of these, only the 'Comp' and 'Layer' attributes files are shown above. The Comp table (map unit component) represents all the soil component information in a total of 60 attributes, the most important includes the water table depth and bedrock depth. This data layer contains some 560 different soil designations. The Layer table (soil layer) stores the characteristics of soil layers for each soil component in 28 attributes including the particle size distribution, the bulk density, the available water capacity, the organic matter content and 1622 different soil entries.

The SSURGO Comp and Layer data for the Passaic Watershed were aggregated using a common attribute, the muid (map unit id) to form a new database table 'Layer-Comp'. This manipulation created a one-to-many relationship, since for each muid in the Layer table there are as many different entries as there are number of soil layers. Additional aggregation of this data is needed before the data needed to run the multimedia model are extracted. This consists of averaging the reported low and high values of the range of the numerous soil characteristics given in the layer file. The weighed average of these parameters is calculated using the depth of the soil layer as follows for the organic matter content, om:

$$omavg = (laydepH - laydepL)\frac{omH - omL}{2} \tag{3.7}$$

where laydepH and laydepL represent the beginning and ending depth of the soil layer from the soil surface, omH and omL the high and low organic matter content reported for the soil polygon and are exported to a new file 'Soil-Layer'.

Furthermore, a number of soil series in the 'Comp' table do not appear in the 'Soil-Layer' table due to their absence in the layer table. These could be attributed to inaccuracy in the database as these parameters were not measured during the survey. To avoid these data gaps from introducing any error in the analysis, the missing soil series were manually added to the 'Soil-Layer' table to yield the 'Soil-LayerNmod'. Thus bringing the number of entries in the original 'Layer-Comp' file from 1622 to 1647 in a new table 'Soil-LayerNmod'. Furthermore, to control the amount of computer time, all the data (attributes) in the latter table that were not used in the model were deleted. The procedure used for this adjustment was to find soil series that were similar to the missing series in S5id (Soil interpretation record number) and the compname attributes (soil component name used in taxonomic classification such as Haze, Hibernia or Carlisle). The latter's values are then assigned to the missing soil series. The results of this final correction of the SSURGO database is saved in a new table 'SoilLayerNmod'. The properties of each soil's layer are now available and can be joined to the landscape soil maps for use in the model.

The landscape soil maps provided in the USGS soil survey database is available by the NJDEP GIS Resources CDs. These maps (or soil polygons) are each associated with a data table including all its properties such as surface area, polygon perimeter and Soil_Label identifier. This soil label is the same as the musym identifier in the joined 'SoilLayerNmod' table. However, the Soil_Label used in this database is different from that used in the NDEP's UGSG database, thus making any joining of the two data prohibitive. This major hurdle was overcome with the assistance of the New Jersey State Soil Scientist in Trenton, NJ, Mr. Chris Smith. Based on the many personal communications with the USGS office in New Jersey, we have re-compiled and re-derived all the soil surveys for the counties intersecting the area of the Passaic Watershed. This resulted in a new SSURGO database with Soil_Label attributes matching with those of the USGS soil survey. The USGS data also needed to be aggregated to allow efficient computations and save disk space. For example the number of soil entities for sub-watershed HUC11 #37 was reduced from 2567 soil polygons to 141 polygons (wsm#sol). This was achieved by summing the areas of soil polygons having the same musym identifier.

Finally, the summarized soil polygons are joined together with the 'SoillayerNmod' to provide yet a newer table 'table#' for each sub-watershed with #1 representing HUC#12 and #11 representing HUC#37. This table is the basis of landscape parameters used in the Passaic watershed multimedia model. A sample representation of these tables is shown below for the bulk density (Bd).

Table 3.5 Soil layer Attributes

Stssaid	**Muid**	**S5id**	**Lay#**	**Layl**	**Layh**	**Bdl**	**Bdh**	**AvLay**	**AvBd**	**Cnt**	**SumArea**
NJ003	003Ad	MI0028	1	0	25	0.30	0.55	25.00	0.43	23	9070939.01
NJ003	003Ad	MI0028	2	25	66	1.40	1.75	41.00	1.58	23	9070939.01
NJ003	003BoB	NJ0049	1	0	6	1.30	1.45	6.00	1.38	9	5181988.28
NJ003	003BoB	NJ0049	2	6	23	1.55	1.65	17.00	1.60	9	5181988.28
NJ003	003BoB	NJ0049	3	23	41	1.65	1.80	18.00	1.73	9	5181988.28
.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.

Lay# represents the layering of the soil series, layl and layh the top and and bottom depth from the surface in inches, Bdl and Bdh the low and high values for the bulk density, cnt is the number of occurrence of the soil type in the sub-watershed and sum represents the total area of this soil series in ft^2. The remaining landscape parameters were derived from those in the 'Table' files.

The vadose zone soil compartment is defined from the bottom of the root soil to the top of the water table. This characterization is performed in the present research by delineating the water table throughout the different sub-watersheds using the USGS Water Resources Data (USGS, 1996). This data is compiled based on actual water level reading in wells and were reported for only 5 of the 11 sub-watersheds of the Passaic River Basin. From the USGS report, the yearly average water table depth was obtained for all the wells within a given sub-watershed and the overall average is used to obtain the depth of the vadose soils. Of these water table readings, the HUC11 #18 values needed a few adjustments; there, the average water table is above the surface soil (ponding conditions in the swamp areas). Therefore, in this sub-watershed, the lowest water table reading was used. The aggregate average of all the well data in or near the river basin is also used as the water table depth for those sub-watersheds where no well data was reported. The results of this analysis are presented in Table 3.6.

Table 3.6 Depth of the Water Table in the Passaic River Basin

Sub-Waterhed HUC	Depth to Water	Sub-Waterhed HUC	Depth to Water
13	1.58	33	3.57
18	0.24	37	17.16
19	3.79	12,15,25,27,31,35	9.89

3.7.3 Derived Soil Compartment Parameters

In addition to the 35 parameters extracted from the SSURGO databases, additional parameters such as the organic carbon content must be calculated. The derivation of these parameters is presented below.

3.7.3.1 The Organic Carbon Content of Soil: The soil organic carbon content OC is possibly the most important parameter in the fate and transport of organic contaminants in the soil compartment. However, this parameter is usually not measured during the surveys of soil, thus it must be estimated from other soil parameters such as the organic matter content (Om), the soil clay content and rock fragment. The Om attribute used above represents only the organic matter in soil particle size fraction less than 2 mm. A number of relationships have been developed for this purpose the simpler of which assumes the OC to be 50% of the Om per mass basis (Mackay, 1991) or 58% of the Om (Benzler, 1982 and SCS, 1993). A great number of values are also suggested in the literature primarily because the characteristics of the soil change drastically from one area to another and with depth from the surface. The suggested values vary from 0.02 (Mackay, 1991) to 0.03 (MPCA, 1993).

In the present SSURGO database, the Om value given reflects the soil particles less than 2 mm in size or soil passing through the No.10 sieve. Thus any organic carbon obtained from the Om value should be corrected to reflect the overall soil characteristics. Using the SCS relationship:

$$OC = \frac{Om}{1.724} \tag{3.8}$$

$$OC_{cor} = \frac{OC}{wt.\% < 2mm} \tag{3.9}$$

where wt.% < 2mm is simply the percent soil particles No.10, assuming the entire soil distribution has a uniform density. The OC_{cor} is the corrected soil organic carbon content.

3.7.3.2 Water Content of Soil: The water content of soil is important in the movement of chemicals through the soil layers either via diffusion or seepage. For surface soils, the water content of soil is comparable to the soil water content at field capacity. This parameter was calculated using the weighed average layer depth for each soil series in the Comp file. A relationship based on regression analysis by Bowers (1989) was used to estimate the field capacity using the soil clay content. It the SSURGO database, the clay content reported is that of the soil component less than 2 mm in size. Thus a correction for the rock fragments must be applied to reflect the water content of the entire soil.

$$FC = (0.4381 + 0.2788C - 0.005679C^2 + 0.00003889C^3) + 12 \qquad (3.10)$$

With FC representing the non-corrected field capacity and C the depth averaged clay content of soil in percent. Finally, the soil-water content SW is obtained by applying the correction for the rock fragment as follows:

$$SW = FC(1 - \frac{Bd * wt\% > 2mm}{265}) \qquad (3.11)$$

The term Bd here represents the depth averaged bulk density in g/cm^3 and the percent rock fragment is estimated as the soil component retained by the No.10 sieve.

3.7.3.3 Air-Filled Porosity of Soil: The air-filled porosity SA used herein is based on personal communication with the USDA-NRCS soil scientist in Lincoln, Nebraska, Mr. Robert Grossman. The method used is described in an internal USDA document. The SA at low suction can also be used to estimate the saturated conductivity. This SA value at 0.05 bar is based on the work of McKeague (1982) in estimating the amount of silt in soil.

$$SA = \left[(100 - \frac{100bBd}{\rho_s}) - W_{0.05}Bd \right] (1 - \frac{V_2}{100}) \qquad (3.12)$$

where ρ_s is the density of soil particles, $W_{0.05}$ the weight percent water at 0.05 bar (obtained from the soil water characteristics) and V_2 the volume of rock fragments. In the above equation, the term $W_{0.05}Bd$ is equivalent to the field capacity FC calculated earlier. The soil particle density is obtained from:

$$\rho_s = \frac{100}{\frac{1.6Fe}{4.2} + \frac{1.7OC}{1.4} + \frac{100 - (1.6Fe + 1.7OC)}{2.65}} \tag{3.13}$$

with Fe representing the percent extractable iron. However, since this value is not readily available in the SSURGO database, a generic value of 2.65g/cm^3 was used for the particle density. Furthermore, the volume of rock fragments is obtained from:

$$V_2 = V_{>250} + V_{2-250}\left(1 - \frac{V_{>250}}{100}\right) \tag{3.14}$$

where $V_{>250}$ is the volume fraction of soil particles greater than 250mm in size. This value is also not available in the databases used in this research, thus an alternative method was used. It is assumed that the rock fragments is simply the soil particles greater than 2mm in size. Thus the volume fraction is related to weight fraction mentioned earlier as follows:

$$V_2 = W_2 \frac{Pt}{P_2} \tag{3.15}$$

and

$$Pt = \frac{100}{\frac{W_2}{P_2} + \frac{1 - \frac{W_2}{100}}{P}} \tag{3.16}$$

.

where,

V_2 = Volume of soil > 2mm

W_2 = Weight of soil > 2mm

Pt = Bulk density inclusive of >2mm

P_2 = Particle density of > 2mm

P = Bulk density < 2mm

3.7.4 Soil Compartment Parameters Used

The remaining soil parameters calculated above were aggregated and averaged on a soil layer basis. The first layer of each soil component representing the surface soil compartment and the summation of the remaining layers for the root zone soil compartment. The database file was then sorted per layer, thus all the layer 1 soil of a given sub-watershed were shown and averaged out over the area extent of each soil component to provide the parameters needed for the multimedia model application. The same scenario was followed for the remaining layers to characterize the root soil. The values for vadose zone soil were estimated from the literature (RIVM, 1994; Mackay, 1996 and CEPA, 1993).

3.8 Chemical Input Summary

3.8.1 Description of Contaminant Sources

For the purpose of this research, all the air emission sources: direct discharges to water from POTW, non-point sources input and releases from contaminated sites will be aggregated on a compartment basis. This is permissible since the compartments of the multimedia model are assumed to be homogeneous and well mixed. As stated in Section 1.2, five of the priority organic compounds are to be modeled in the present study. These are chosen based on either their toxicity to receptors, persistence in the environment or the magnitude of their use in the state. For example, toluene is one of the chemicals released primarily through the air, and is the second most significant in total mass among all organic chemicals released. In 1994 alone, it is estimated that over 168,218,285 pounds of toluene were released into the air inside the United States (EPA-TRI, 1996).

The approach used to characterize the input of contaminants in the present model is described here. An inventory of the releases of a given chemical is made on the media basis. For example, the air sources in a given sub-watershed are summed up and are considered to constitute the air discharges in that compartment; the same methodology is applied to the water and soil media. Existing EPA databases provide the basis of this chemical release inventory. One example of such record is the "Toxic Release Inventory" made available by EPA as postulate by the public-right-to-know concept. This database is an ideal source for this research in the sense that the contaminant releases are given in mass instead of concentration. However, these releases are provided on a county or state basis rather than on watershed basis. Additionally, this data is not complete in coverage because only the sources (i.e. manufacturing processes) exceeding a certain threshold are required to report under the EPA rules. This threshold is available through EPA (EPA-TRI, 1996). An example of TRI data for Bergen County is shown in Table 3.7. Other points of discharge to the environment that are not included in Table 3.7 are land disposal, and underground injection. All these data are available from USEPA.

Table 3.7 Toxic Release Inventory (TRI) of Chemicals for Bergen County in Lbs/Year

Chemical Name	Fugitive	Off-site	POTW	Sack	Water
Formaldehyde	1	0	0	5	0
Aniline	104	0	6	10	0
Chloroform	48	8831	73	12	0
1,1,1-Tri-chloroethane	32392	21477	5	1180	0
Freon113	56	360	0	711	0
Ethyl ketone	15848	159266	0	23603	0
TCE	0	6044	0	396	0
1,2,4-Trimethylbenzene	950	9805	25000	450	0
Ethylbenzene	143	89287	66	1430	0
Toluene	24984	273917	655	37159	0
Phenol	0	0	0	0	0
Di(2-ethylhexyl)Phthalate	250	1931	0	250	0
Tetrachloroethylene	0	0	0	5	0
Xylene	9593	937232	0	18059	0

3.8.2 Incorporation of TRI in the Present Multimedia Model

As documented for the landscape data, a re-derivation of the TRI data is needed for use in the present multimedia model. The goal of this derivation is to summarize all the releases in any given sub-watershed and on per compartment basis. Additionally, the TRI (1999 NJ TRI) data is provided in the form of "facilities street address" instead of a geographical coordinate system. Thus, it could not be manipulated as was performed for the landscape data using Arcview. A necessary conversion from the address to a geographical format was needed. This was performed using the 'geocoding' technique in GIS which consists of matching the street address or zipcode to a nation wide database. The result is a new data set projected on a geographical coordinate system (i.e. longitude/latitude or state plan feet). It should be noted that the accurate method to perform geocoding is with the use of the street address. Because of the significant cost in using a private database such as the street database, a slightly less accurate method is to geocode the release facilities using their zipcode instead of street address. This is believed to be sufficient for the current multimedia model. A representation of this process is presented in Figure 3.10 below. It should be noted that although the TRI database does not provide a complete accounting of all the releases including; vehicle emission, it is still a valuable tool in characterizing environmental releases. Furthermore, the format that is used to disseminate this database is very useful and easily lend itself to multimedia modeling since it is given in term of mass estimate instead of environmental concentrations.

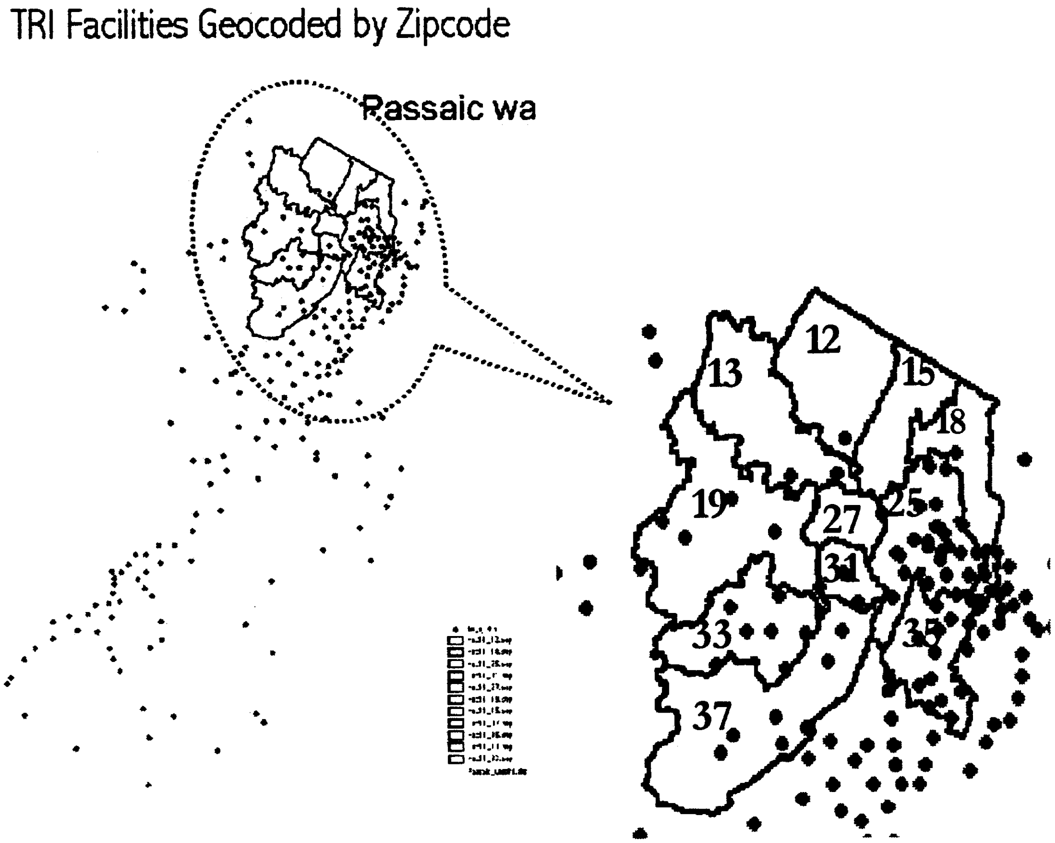


Figure 3.10 Geocoding of TRI Facilities in the Passaic River Watershed.

In the above figure, each point represents all the facilities associated with a given zip code. These geographical data points are clipped per the sub-watershed to obtain the total releases in each unit. In sub-watershed HUC11 #12, the release data is shown as one data point in Figure 3.10 and is summarized in Table 3.8 below. A summary table of the 5 contaminants release in the Passaic River Watershed is also presented in Appendix A. The TRI data is one of two methods for chemical input into the model. The second chemical input is via advective inflow of air and water.

Table 3.8 HUC11 #12 Sub-Watershed Chemical Releases

FACILITY	FACIL_ADD	CITY	CHEM_NAME	FUGITIVE	STACK_	WATER	INJECTION	LAND	POTW	OFF
ARROW GRO	3RD AVE.	HASKELL	N-BUTYL A	0	253	0	0	0	0	0
ARROW GRO	3RD AVE.	HASKELL	TOLUENE	0	312	0	0	0	0	41780
ARROW GRO	3RD AVE.	HASKELL	XYLENE (M	0	644	0	0	0	0	0
ARROW GRO	3RD AVE.	HASKELL	METHYL ET	0	260	0	0	0	0	0
ARROW GRO	3RD AVE.	HASKELL	NAPHTHALE	0	652	0	0	0	0	0
ARROW GRO	3RD AVE.	HASKELL	1,2,4-TRI	0	410	0	0	0	0	0
ARROW GRO	3RD AVE.	HASKELL	CERTAIN G	0	923	0	0	0	0	0
ARROW GRO	3RD AVE.	HASKELL	ZINC COMP	0	0	5	0	0	0	0
U.S. ALUM	86 4TH AV	HASKELL	ALUMINUM	3150	0	0	0	0	0	0

3.8.3 Background Concentration and Advective Inflows

The present model was developed with the idea to simulate releases of contaminant and to perform pollution reduction scenarios as outlined in Chapter 1. The simulation of a contaminant released in the Passaic River Watershed may be performed using some background (initial) concentrations and advective fluxes, or without any background. Consequently, using these background concentrations may have much greater impact than the actual releases. The background concentrations are divided into two categories: the local background levels and the concentration from off-site locations such as neighboring sub-watersheds. The above mentioned concentrations have a strong dependence on the land use cover of the environmental unit and the land use of the up-wind locations. In the present model, only the air and water background and advective inflows are included since these are the two media with extensive monitoring focus.

The surface water background concentrations are the most accurate of these parameters and are obtained from the Ambient Water National Contaminant Occurrence Database, or NCOD (EPA, 1999). This database is regularly updated and is available on a state and watershed basis, thus providing a reliable benchmark for background concentrations. The background air concentrations are derived from national monitoring programs of toxic organic compounds (EPA, 1996) and are included in the present model using the following assumptions:

1. The reported background concentrations are assumed to be appropriate for sub-watersheds with little or no urban coverage. These include HUC#12, 13, and 15 where the forest coverage from the NJDEP GIS resources dominates the landscape.

2. The low end values of the urban concentrations were used for those sub-watersheds with moderate urban and forest coverage. These include HUC#19, 33 and 37.

3. Finally, the maximum range of the reported urban concentrations was used for the highly developed areas such as HUC#18, 27, 31 and 35. These units are aggregated in the eastern part of the Passaic River Basin and enclose highly industrial areas such as Bergen County and Jersey City Areas.

The advective inflows are estimated using the terrain coverage just up-wind of the environmental unit of concern and concentration derived above for the appropriate land cover. For the water compartment, the advective inflows are estimated internally in the model using the upstream concentrations and the flow rates. Of the 11 sub-watersheds, HUC#25, 27, 31 and 35 received advective influx from upstream units. The background concentrations, when used, serve the role of the initial concentration in the simulation. Then based on the release, the resultant simulation will show an increase or a decrease in environmental media concentrations. These concentrations are summarized in Table 3.9 below. The advective inflows and background concentrations are the subjects of on-going research, as such they are not well defined with the exception of few contaminants such as NOx, SOx and Ozone for which there exist a national network of monitoring program.

Such a monitoring effort must be extended to organic contaminants if the determination of their fate and transport is to play an important role in environmental assessment.

Table 3.9 Background (Initial) Levels for the Chemicals Used in the Multimedia Model

Contaminant	Water ($\mu g/m^3$)	Air – Rural ($\mu g/m^3$)	Air – Moderate ($\mu g/m^3$)	Air – Urban ($\mu g/m^3$)	#Air – Watershed ($\mu g/m^3$)
Toluene	188.8	17	109	350	137
1-1-1 Trichloro-ethane	5.4E3	3E-2	0.33	16	4.66
TCE	341	8E-2	2.6	50	15.4
Xylenes	44.1	0.17	12	91	29.2
Naphthalene	121.9	0.17	0.45	1.2	122

Air concentration estimated using area weighed average of all the HUC11 sub-units

3.8.4 Chemical and Physical Properties of the Contaminants

The chemical and physical properties of each of the five priority contaminants are developed and made available for use in the present model. The fate of a chemical compound is largely dependent on its basic properties such as its partitioning among different media, its partial vapor pressure, molecular weight, etc. The literature of chemical-physical properties on organic contaminants is extensive and widely available. Some of the references that are used in this research are those compiled by Mackay et al. (1992). Also the USEPA has compiled very extensive data of certain classes of chemicals (based on their toxicity and wide use). Additionally, there are numerous commercial softwares available to obtain the different properties of chemical contaminants.

Since the behavior of chemical contaminants in the environment tends to be divided among specific classes, the current effort will focus only on organic compounds. The reasons for this selection include the effectiveness of the fugacity approach for chemical with appreciable vapor pressure and the fact that some of the most toxic chemicals are organic such as dioxin, etc. Also since organic compounds tend to have only one valence, the problem of speciation is avoided, thus simplifying the chemistry in the model. A listing of the most important chemical-physical properties needed to run the multimedia model is presented below:

- Physical properties of the contaminant including the molecular mass, solubility, vapor pressure, melting point, gas constant etc. These properties, for the most part, are related to the transport of the contaminant in a medium.

- Chemical properties of the contaminant including the fugacity capacity, organic-water and organic-carbon partition coefficients, the Henry's Law constant, etc. These properties drive the contaminant to move from one medium to another based on its relative affinity in the two media (i.e. PCB, which is hydrophobic will freely transfer from water to the organic sediment).

- Degradation rates such as half-lives of the compounds in water, air, sediment etc will determine the persistence of the contamination in a given medium and in the total environment.

- Other partition properties can be derived from the above air-water properties using the relationship between air phase fugacity capacity Z_a and water phase fugacity capacity Z_w. These include the sediment-air partition, fish-water partition, particle-water partition coefficient etc.

The basic physical and chemical properties of the 5 organic contaminants used in the present model are summarized in the Table 3.10. These properties are essential for multimedia applications, it is thus proposed that they should constitute the minimum properties that must be available for a contaminant to allow for a proper assessment in an environmental setting.

Table 3.10 Characteristics of Contaminants Used in the Multimedia Model

Chemical	MW (g)	TM (°C)	SG (mg/L)	PV (Pa)	PKWOL	HL1 (day)	HL2 (day)	HL3 (day)	HL4 (day)	HL6 (day)	HL7 (day)
Toluene	92.1	-95	515	3800	2.69	2.38	13	28.43	107	28.43	108.5
Xylene	106.2	13.2	185	1170	3.15	0.97	17.5	15.1	183.5	15.1	187
TCE	131.4	-73	1100	9870	2.29	3.46	121.5	923	217	930	757
Naphtalene	128.2	80.2	31.7	10.4	3.35	0.68	10.3	454.5	129.3	454.5	129.5
1-1-1 Trichlordane	133.4	-32	730	12800	2.47	1237	206.5	175	616	175	616

Where MW represents the molecular weight, TM the melting temperature, SG the aqueous solubility, PKOWL the log octanol-water partition coefficient and HLs the degradation half life in the 7 bulk compartments.

CHAPTER 4

RESULTS OF THE MULTIMEDIA MODELING OF THE PASSAIC RIVER WATERSHED

4.1 Introduction

The unsteady state multimedia model developed in this study is designed to produce several specific information. These include the resulting environmental concentration from discharges of a specific contaminant, the distribution of the contaminant in various media, an accurate estimation of the environmental processes that drive fate and transport and the impact of using different spatial scales on the results. These results must be subject to several processes of validation and accuracy determination. The accuracy here means that the model output is consistent with what is expected and that the mathematical and computational operations are performed accurately. The validation process is directed to comparing the model's results against field data, experimental measurements or results of other models. These requirements are addressed differently by researchers who contribute to make the 'accuracy and validation' issue very contentious (Oreskes, 1994).

The results of the model developed in this research provide a comprehensive picture of the contaminant in a watershed environment and thus can be used to make numerous inferences and draw multiple conclusions. An accuracy check was performed in the present model by simple mass balance calculations of the contaminant mass in the environment. Also, the results of the present model are validated using other established models such as ChemCAN, since validation using actual measurements in this case is nearly impossible because of a lack of comprehensive data on organic contaminants. For a complete and true validation to occur, precise knowledge of the amount of chemical emitted and advective fluxes across legislative boundaries must be available. The general scheme of the present model's results is shown in Figure 4.1. In the following sections, a detailed description of each of the elements represented in Figure 4.1 will be provided along with the output of one sub-watershed.

4.2 Validation of the Multimedia Model

4.2.1 Overview

A validation task was performed to determine the accuracy of the present model. Since true validation is nearly impossible, it was decided to check the results against those of established and well reviewed models. One such models is ChemCAN, developed to simulate the fate and transport of priority contaminant in Canada (Mackay, 1996). This model has enjoyed extensive use from the academic community and has been thoroughly reviewed by others (Devillers, 1995). It should be noted that the ChemCAN multimedia model is a steady state model; therefore, the current validation will be a comparison between a steady state model (Level III) versus the fully dynamic (Level IV) multimedia model developed in this study. The steady nature of the ChemCAN model and its lack of spatial resolution make this comparison with the multimedia model non-trivial, and thus, only a comparison at the watershed level will be possible. The accuracy and consistency of the present multimedia model are treated herein. The same environmental data set, contaminant chemical properties and emission rates are used in the two models. To appreciate the difference between the two models, the important characteristics of each model are given in Table 4.1.

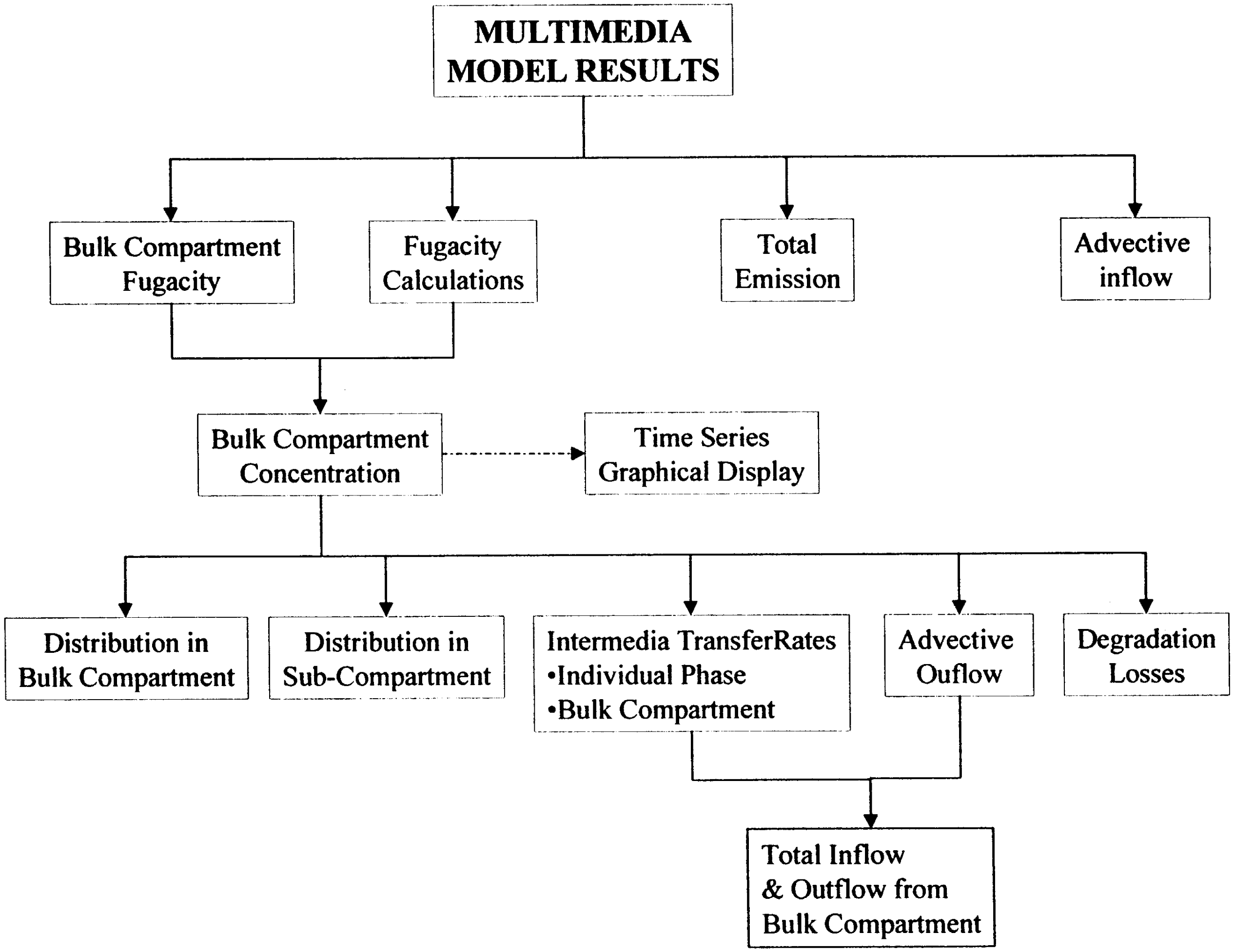


Figure 4.1 Schematic Representation of the Present Multimedia Model Results

Table 4.1 Characteristics of the Present Multimedia Model and the ChemCAN Model

	ChemCAN	Present Model
Time dependence	Steady State	Dynamic
Environmental Units	One	One or Many
Bulk Compartments	4	7
Sub-Compartments	10	18
Vegetation	Not Represented	Represented
Number of Soil Compartments	1	3
Variable Wind Direction/Advection	No	Yes
Environmental Processes	Constant	Varying
Cross boundary Exchanges	No	Yes
Background or Initial Concentration	Not Available	Included

4.2.2 Validation Methodology

Simulations of toluene release were performed using both models. Two separate simulations were performed in the present multimedia model using a total simulation period of 25 years for the first and 2000 years period for the second. The need for longer simulation period in our model arose from the fact that after 25 years, the environmental concentrations were still increasing -- see Figure 4.2. Furthermore, since the ChemCAN model uses a steady state approach, a much longer simulation period is necessary so that the changes in the current model concentrations become small, i.e. approaching steady state conditions. Thus a 2000 years simulation was used and is shown in Figure 4.3. It should be noted that zero background concentration level and zero advective fluxes in the watershed were assumed in this analysis; a summary of the results of the two models is presented in Table 4.2. The time series concentrations for both simulation periods are presented below for the entire Passaic River Watershed landscape (as one unit).

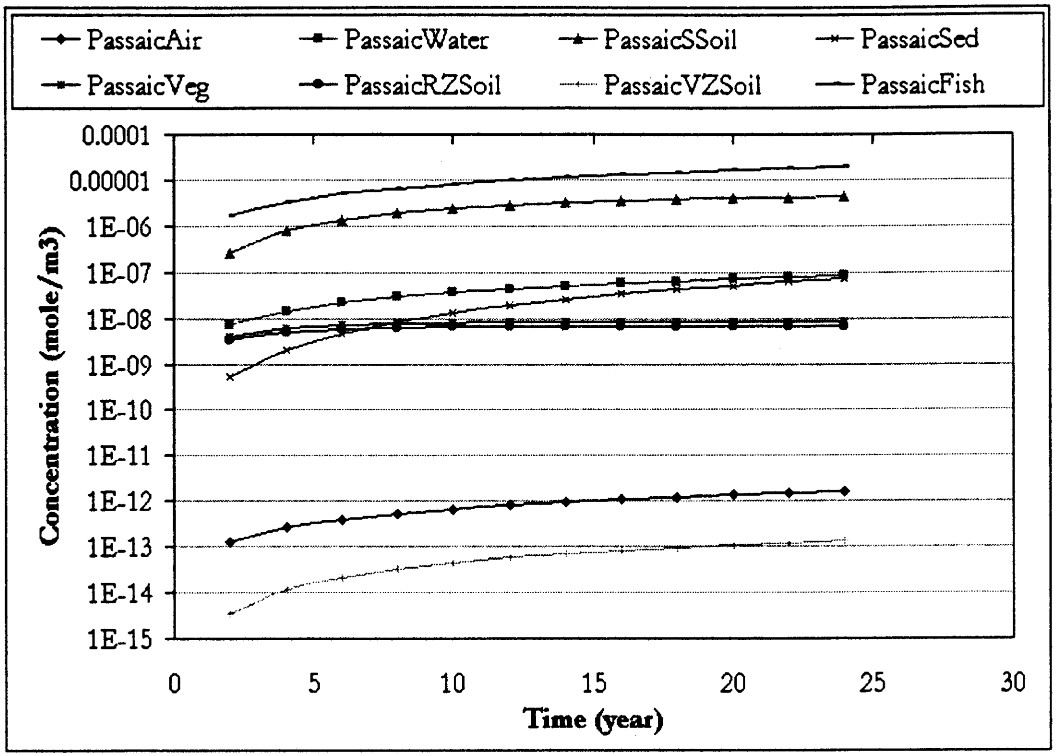


Figure 4.2 Time Series Concentrations of Toluene in the Passaic River Watershed Using the Present Multimedia Model and 25 Years of Simulation.

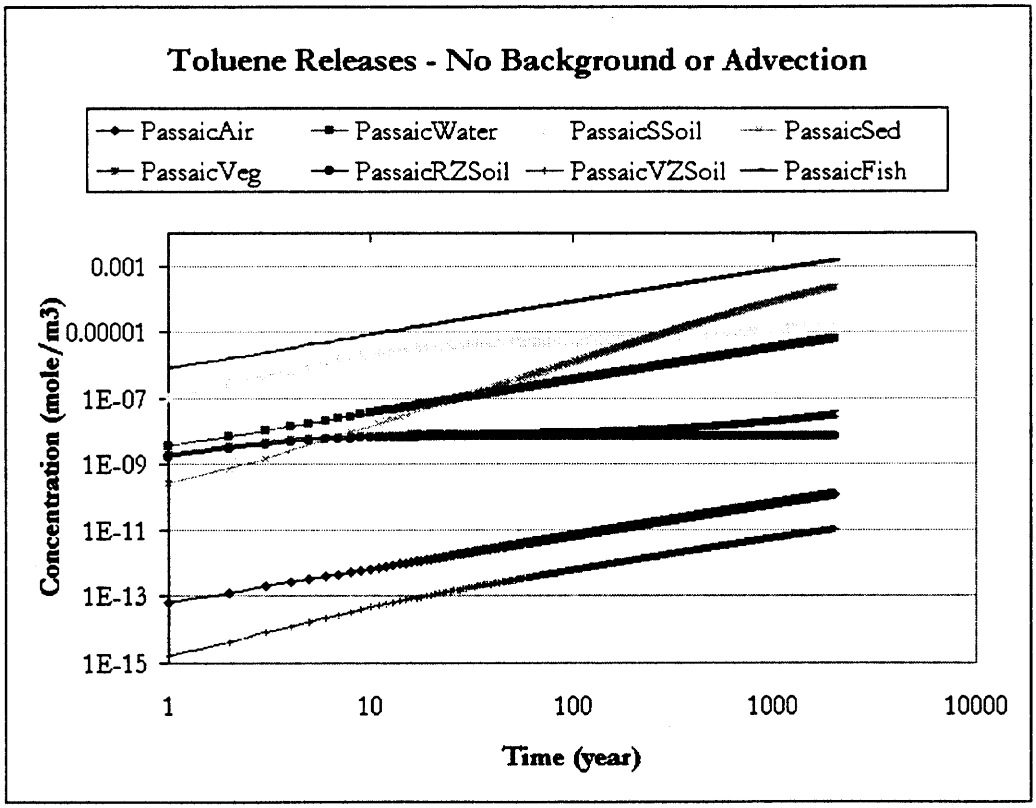


Figure 4.3 Time Series Concentrations of Toluene in the Passaic River Watershed Using the Present Multimedia Model and 2000 Years of Simulation.

Table 4.2 Bulk Compartment Concentration (mole/m3) of Toluene after 2000 years of Simulation

Bulk Compartment	Current Model	ChemCAN
Air	1.26E-10	4.42E-10
Water	6.31E-6	5.52E-6
Fish	1.44E-3	1.26E-3
Surface Soil	1.85E-5	2.08E-6
Sediment Layer	2.31E-4	2.15E-4
Terrestrial Vegetation	3.24E-8	3.90E-7
Root Zone Soil	6.94E-9	2.08E-6
Vadose Zone Soil	1.07E-11	2.08E-6

The concentration of toluene in Table 4.2 demonstrates the accuracy of the multimedia model developed in the present research. The only point of significant divergence between these two models appears in the soil compartment. The ChemCAN model, which uses only a single soil profile, concentration is still within the range of the predicted concentrations of the three soil profiles (surface, root and vadose) in the present model. The soil compartment is divided into three separate layers because of the change in the soil physical characteristics with depth. The variation is represented using different porosity, organic matter content, microorganism content etc. The terrestrial vegetation concentration is also slightly different. This compartment is represented explicitly in the present multimedia model and is included in the mass balance calculations, while it is only estimated from soil concentration in the ChemCAN model using the root concentration factor. It can be seen from Figure 4.3 that the time to reach equilibrium is indeed long for certain compartments (sediment, soil layers). Although the 2000 years is not sufficient to reach steady state levels, it allows certain compartments concentration to approach steady state. The duration of the simulation plays an important role in the final concentration since the ChemCAN model is steady state while ours is dynamic.

4.2.3 Effects of Background and Advective Inflows on the Models Results

In the following sections, the influence of the background concentration and advective inflows are discussed. In contrast with Figures 4.2 and 4.3, the time series concentration of the Passaic River Watershed is significantly different as shown in Figure 4.4, specifically when advective inflows are included. These inflows occur only in the mobile compartments; air and water. Here, the surface soil, instead of the sediment, has the highest concentration, primarily because of the large influence of the advective inflow on the mass balance. The increase in media concentration is consistent in both models, as ChemCAN simulation also resulted in significantly higher concentration in air, soil and vegetation. The results of using the advective inflows in the models are summarized in Table 4.3. The compartments exhibiting higher concentration due to advection inflows (in air and water) are in contact with the compartments where these inflows occur. It should be noted that while the present model can accurately incorporate inflows and outflows in an unit environment, no such adjustment is feasible in the ChemCAN model. The latter uses a default residence time to estimate inflows and outflows in both air and water compartments. However, in the case of a (sub) watershed, these inflows may not exist as was the case for 8 of the 11 sub-watersheds of the Passaic River Basin. Therefore, in ChemCAN, there is a fictitious inflow of contaminants in the watershed. This is remedied in the case of simulating the entire Passaic River Watershed as one unit by including the advective inflow of air and excluding equivalent transfers in water. However, this correction may not be extended to the sub-watershed level due to the active exchange between the different environmental units.

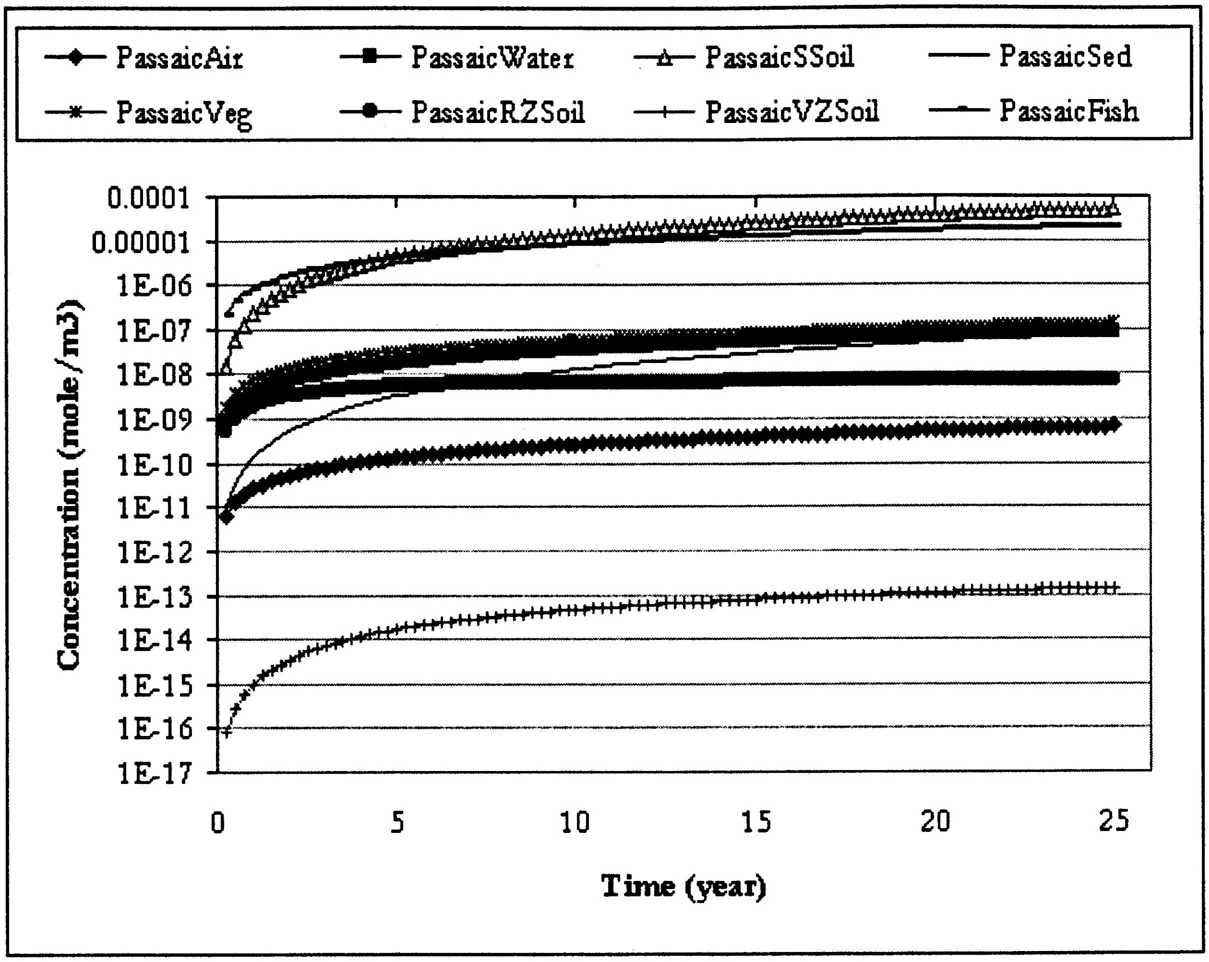


Figure 4.4 Time Series Concentrations of Toluene in the Passaic River Watershed Using only Advective Inflows.

Table 4.3 Bulk Compartment Concentration (mole/m3) of Toluene using Advective Inflows

Bulk Compartment	ChemCAN - Advection	Model – Advection	Model -Advection & Background
Air	1.65E-7	4.58E-8	1.16E-6
Water	6.04E-6	7.36E-6	6.71E-5
Fish	1.96E-3	1.67E-3	1.53E-2
Sediment Layer	2.35E-4	2.61E-4	2.68E-3
Terrestrial Vegetation	1.46E-4	8.81E-6	2.22E-4
Surface Soil	4.04E-6	5.04E-3	0.1277
Root Zone Soil	4.04E-6	1.69E-8	2.52E-7
Vadose Zone Soil	4.04E-6	1.93E-11	4.54E-10

The use of zero background or initial concentrations and advective influxes in the simulation of both models has a significant impact on the model results. For example, HUC#11 sub-watershed is essentially clean of any contaminant since there is no release of toluene and there is no cross boundary influx. For others sub-watersheds with continuous releases, the time to reach steady level is made very long since the simulation starts with essentially zero concentration. The ChemCAN and the present multimedia model are also different in their representation of the background concentration. While our model can account for both advective inflow and the local background or initial concentration, only advective inflows can be included in ChemCAN. The consequence of omitting the background concentrations in ChemCAN is significant, since these concentrations may be as high as the steady state concentrations. Also, in Table 4.3 are presented the results of the simulation of our model using just the advective inflow and the time series toluene concentrations are presented in Figure 4.5. In Table 4.3, the toluene concentrations in the soil layers are much different between the two models. The inclusion of the background concentration introduces a difference of up to 2 order of magnitudes in the air compartment and thus manifests some of the differences between the two models. In Figure 4.5, the concentrations are significantly higher than those of Figure 4.4 after the same simulation period. Furthermore, with these background concentrations, the steady state levels are reached within a much shorter time (approximately 10 years). However, after a long duration the concentration levels start to exhibit some changes with the water and sediment level increasing while the vegetation, surface and root soil show a small decrease. Although the objective of this chapter is not to contrast the two models, some of the advantages in using a dynamic fugacity model over a steady state model are revealed clearly.

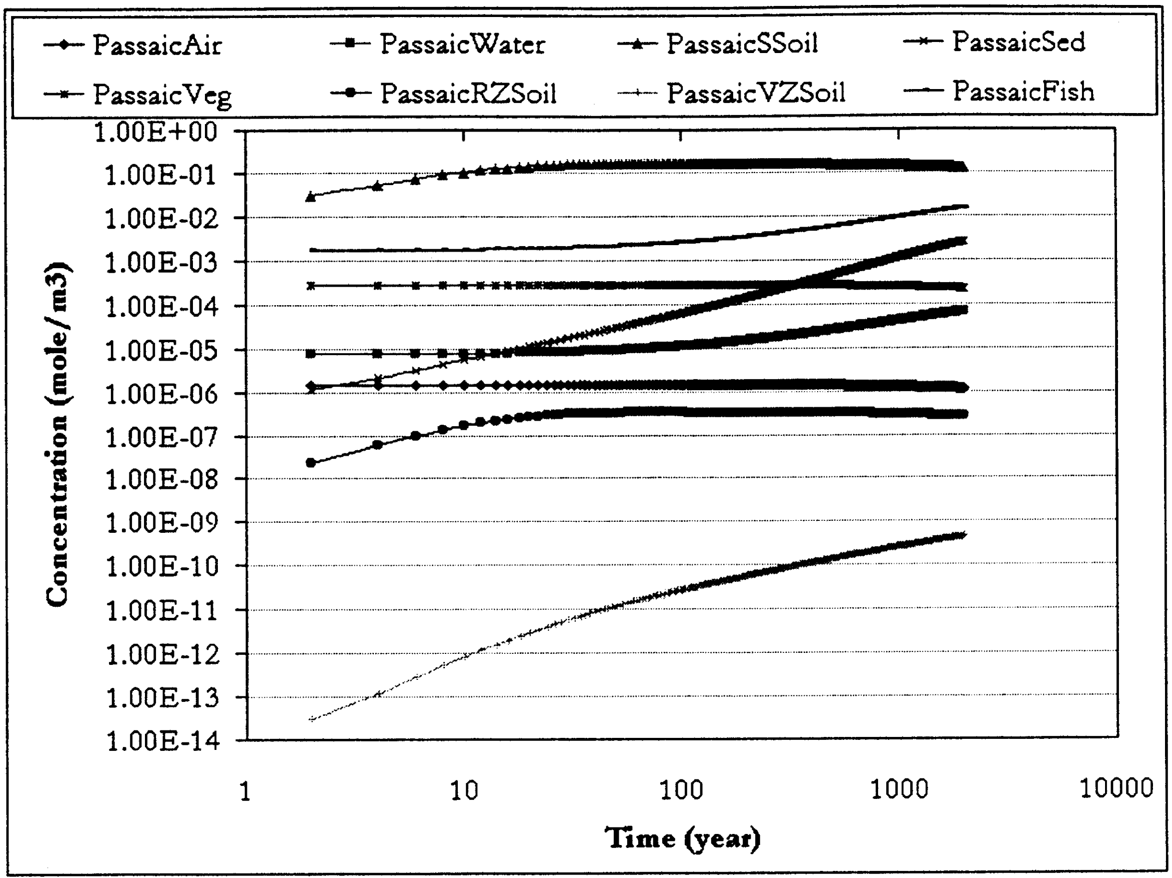


Figure 4.5 Time Series Concentrations of Toluene in the Passaic River Watershed Using Background Levels and Advective Inflows.

Although the concentrations from the two models are different, they do not provide a complete account of the difference between the two models. This is shown by observing that the media' concentrations do not reach steady state levels even after 2000 years of simulation (see Figure 4.3). The implication being that the steady state may not be reached except in the very mobile compartments such as air and water. The main sinks are the sediment layer and the soil compartments and are likely to remain so for most organic contaminants unless significant releases occur directly there. A better comparison will be between the environmental processes that drive the fate and transport of the contaminant in the environment. Although process rates change with time, the fugacity mass-transfer coefficients or D values, which are described in Chapter 2, are not time dependent.

Therefore, a comparison between the D values of both models will reveal their relative strength in representing the actual environmental processes. Table 4.4 summarizes the above comparison.

Table 4.4 Fugacity Mass Transfer Coefficient or D Values (mole/Pa.h) Between Bulk Compartments

Compartment	Air	Water	Surface Soil	Sediment	Vegetation	Root Soil	Vadose Soil
Air	-	2142, 2139	12177, 18230	-	-, 4.92E7	-	-
Water	2121, 2118	-	-	151, 130	-	-	-
Surface Soil	11764, 17820	34.8, 338.5	-	-	-	-, 135.2	-
Sediment	-	26.7, 5.68	-	-	-	-	-
Vegetation	-, 4.92E7	-	-, 2.81E7	-	-	-	-
Root Soil	-	-	-,61.8	-	-,5.75E6	-	-,138.4
Vadose Soil	-	-	-	-	-	-	-, 138.4

The first value in each cell of the above table represents the ChemCAN D value and the second presents multimedia D value. The two models appear to represent the environmental processes in a similar manner as per the D values with the exception of water sediment and water soil transfers. The difference in D values is attributed to the differences in the representation of environmental processes in the two models. Additionally, the physical and chemical characteristics of the soil layers being different between the two models, also contribute to the difference in results. Such characteristics include variation in soil porosity, organic matter content and sorption coefficient with depth; all of which strongly influence the movement of the contaminant. The vegetation compartment is not represented in ChemCAN, thus does not enter the mass balance calculations. This exclusion apparently has an impact on the ChemCAN model outcome, as a fraction of the contaminant mass that will otherwise partition in this compartment and is now made available to the soil, air and water compartments.

4.3 Environmental Concentrations

One of the advantages in using a dynamic (or Level IV) fugacity model is to obtain the non-equilibrium contaminant fugacity (or concentration) as well as its variation with time. The time dependent concentration of the contaminant is derived from the fugacity values obtained as a result of the numerical simulation described in Section 2.7 and by using Equation 2.1. These fugacity values are strongly dependent on the initial or background concentrations as shown in Section 4.2. For this reason, two separate simulations are devised, one using a clean background and one using the reported monitoring values as initial conditions. The background concentrations are only available for the air medium (EPA, 1996) and for the water medium (EPA, 1999). Of the 5 chemicals used in the present model of the Passaic River Watershed, toluene, xylene and naphthalene are emitted in both air and water, and only in selected sub-watersheds. Therefore at least one of these sub-watershed concentration levels will be a good indicator of background concentration influence on the model results. Toluene released in HUC11 #25 is used for this purpose due to the significance of its releases and availability of background concentration in both air and water.

In addition, the present model allows the simulation of different scenarios of cross boundary inflows and allows for observation in decrease of concentrations by curtailing current releases. The first of these situations appeared during this study, where inflow air concentrations for selected sub-watersheds were varied to reflect the upwind land use (urban versus rural or forest). In the Passaic River Basin, background levels in sub-watersheds HUC#12, 13, 15 and 19 were chosen to reflect areas with little or no industrial activities, while those of HUC#33 and 37 reflected typical national urban concentrations. Finally, HUC#18, 25, 27, 31 and 35 background levels mirrored those of urban areas with industrial activities.

4.3.1 Simulation Using Reported Background Concentrations and Advection

The time series concentrations of toluene in the 7 bulk compartments of sub-watershed HUC#25 are presented in Figure 4.6. In this figure, the air, vegetation and surface water compartments do not show much variation with time, even though, the air and water compartments are very active in advective exchange with adjacent compartments and sub-watersheds. This apparent lack of variation is attributed to the high magnitude of the initial or background concentration used in these compartments.

In contrast with the air and water compartments, noticeable changes in the sediment and soil (surface, roots and vadose) compartments are observed in Figure 4.6. These compartments represent major sinks of contaminant mass and their concentration will undoubtedly increase until an equilibrium point is reached between them and the air and water sources. Finally, the vegetation compartment shows little variation in contaminant concentration during the simulation period. An interpretation of this monotonous behavior is that the plant foliage reaches equilibrium with the air compartment rapidly, thus reproduces its exact behavior. Also, the contaminant concentration in the root zone soil and the plant roots uptake are small compared to that of the air compartment to allow the air single dominance on the fate of the contaminant in the vegetation.

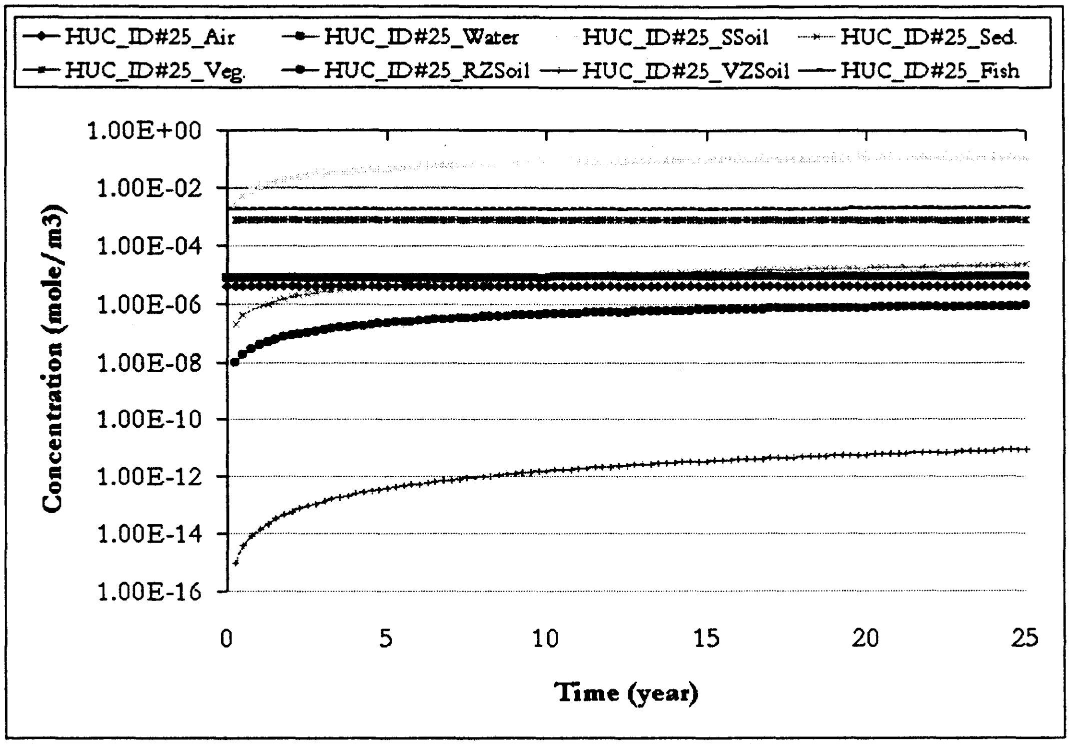


Figure 4.6 Time Series Toluene Concentration in HUC11 #25 Using Advective Inflows.

Other observations made included a change in air and vegetation concentrations due to the change in wind direction. This change is very small compared to the high background concentration, approximately 3% increase for the non-urban areas and less than 2% decrease for the urban areas. The time series toluene concentrations for the sub-watersheds are shown in Figures 4.7 and 4.8. This variation illustrates another advantage of the present model and displays the impact of seasonal and spatial (upwind land use) variation on environmental contamination.

A second watershed view of the toluene concentration is provided in Figure 4.9. It is observed that the water and vegetation compartments show minimal change with time as was the case with the air compartment shown in Figures 4.6 and 4.7. It can therefore be concluded that the current releases have a limited impact on the present and future level of toluene contaminant in the Passaic River Watershed's air, water and vegetation

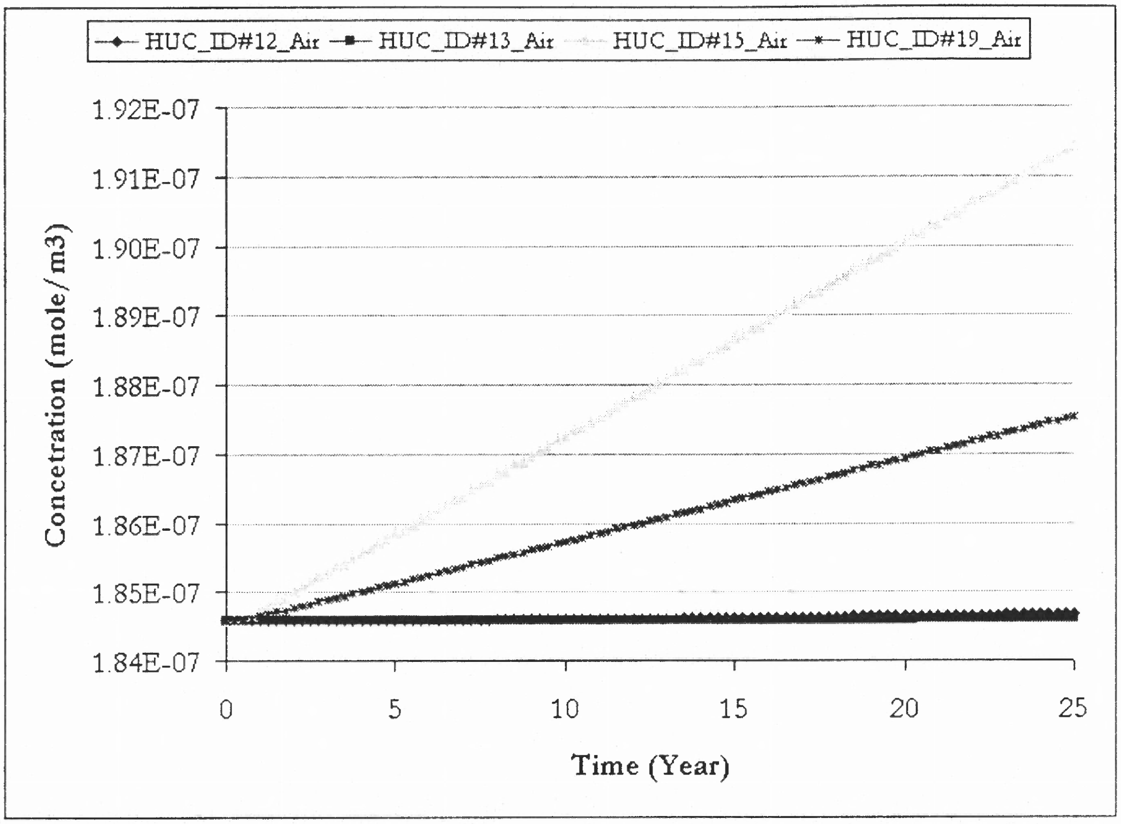


Figure 4.7 Variation of Non-Urban Watershed(s) Air Compartment Concentration.

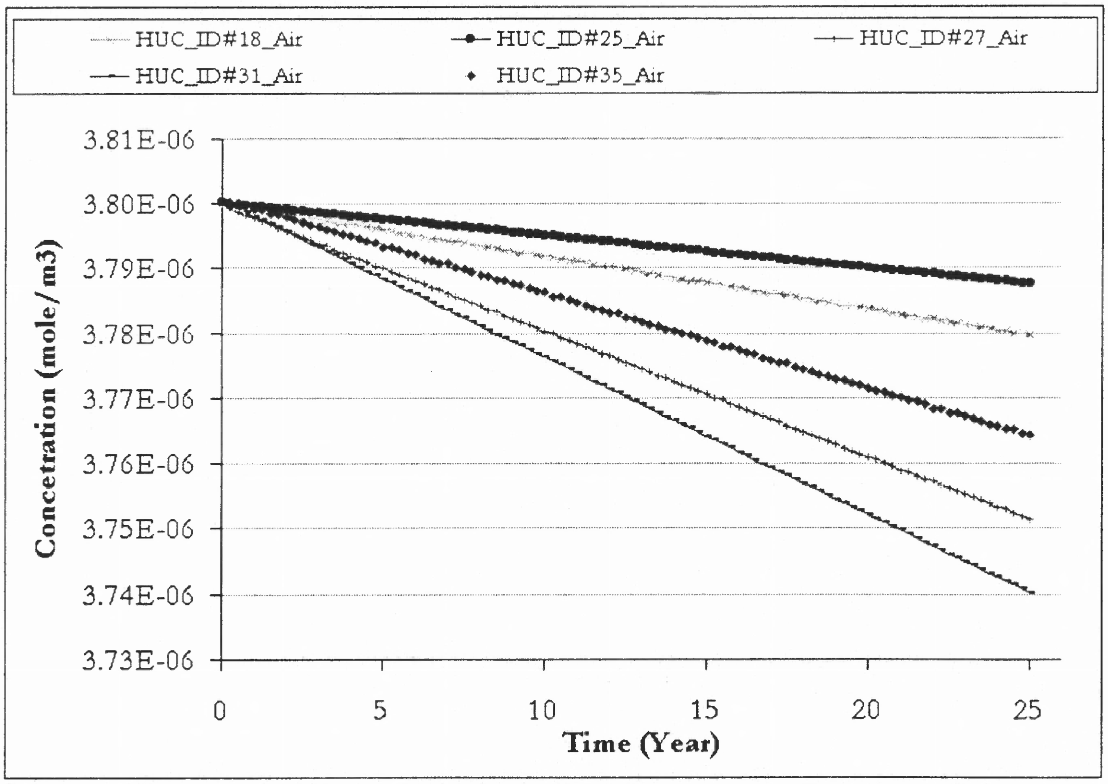


Figure 4.8 Variation of Urban Watershed(s) Air Compartment Concentration.

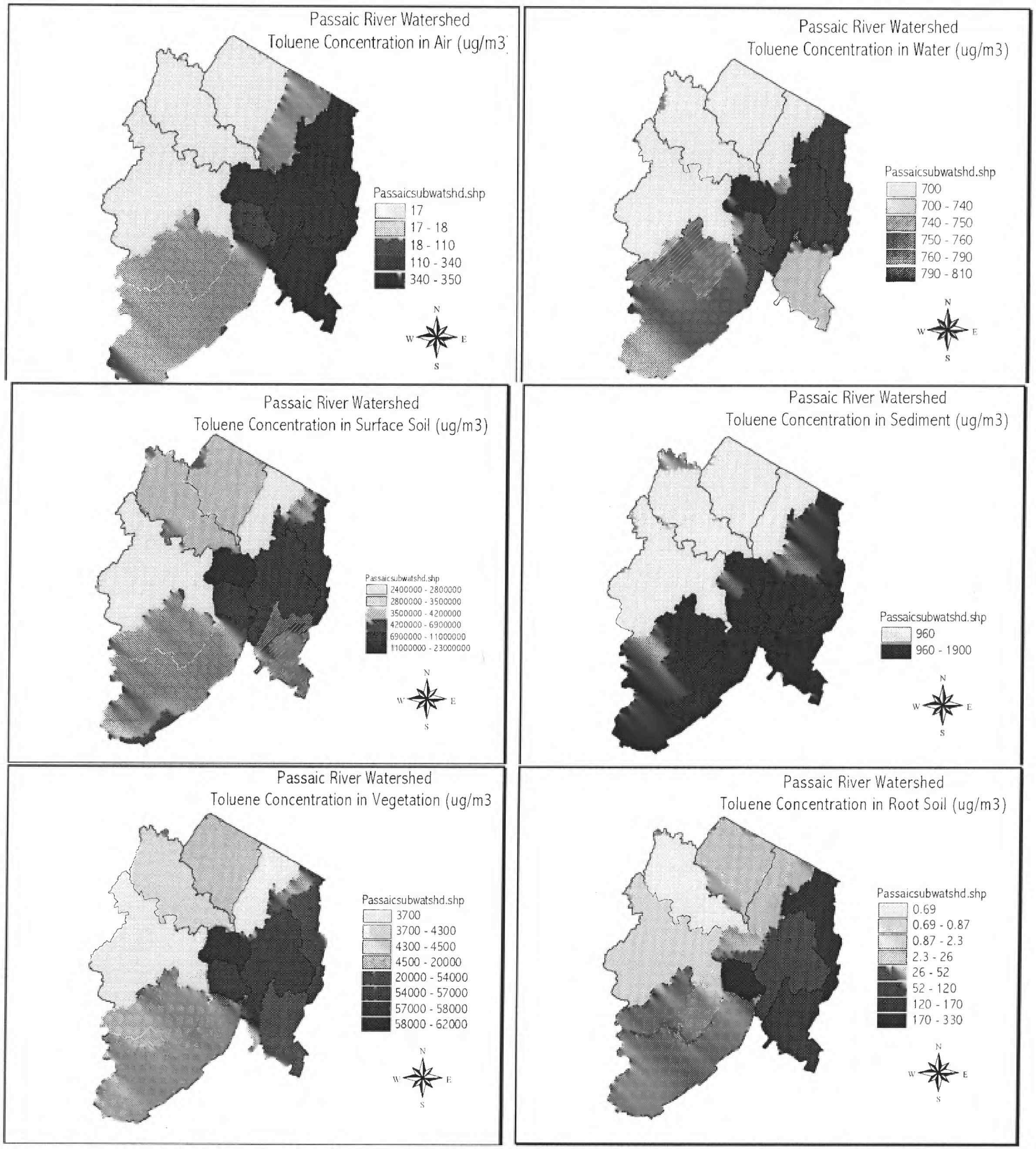


Figure 4.9 Toluene Concentration in the Passaic River Watershed using Advective Fluxes and Reported background Concentrations.

compartments. For the remaining compartments, this conclusion is not applicable since their initial level is zero background and thus a noticeable increase is observed.

Figure 4.10 displays an appreciable change in the surface soil concentration, this is attributed to the strong exchange between the surface soil and air, and between the surface soil and vegetation (foliage loss during winter).

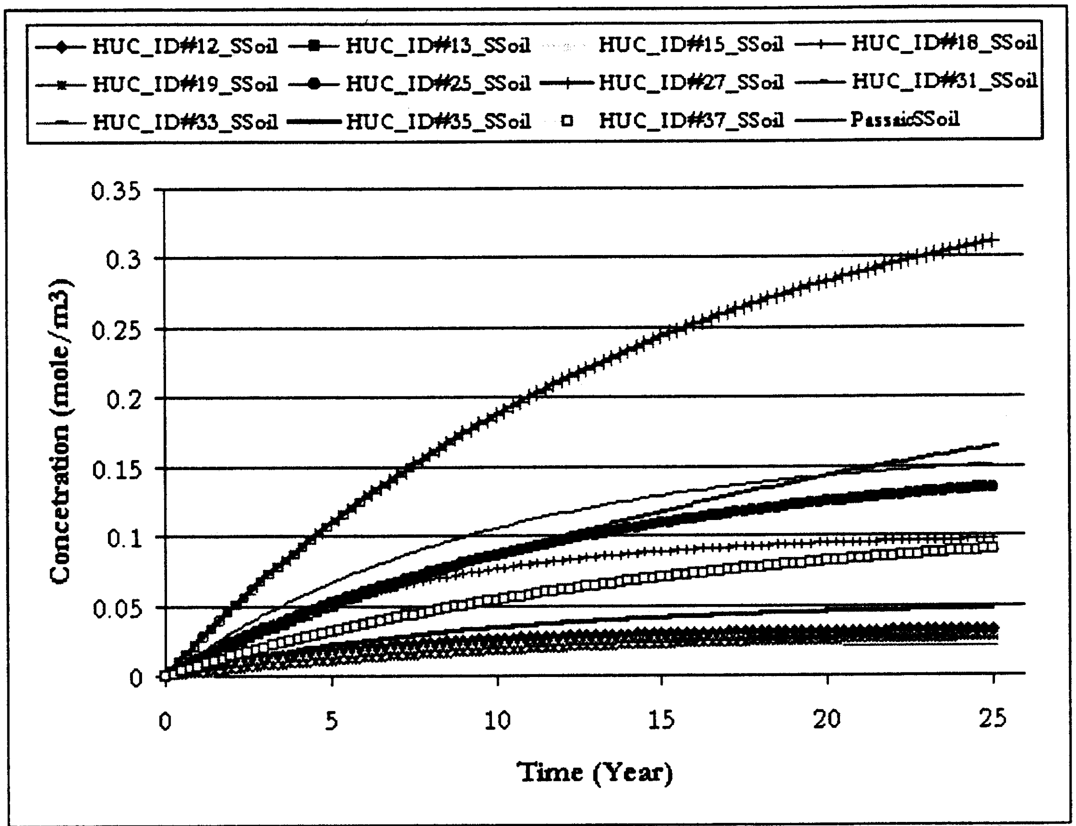


Figure 4.10 Watershed-Wide Concentrations of Toluene in Surface Soil (ug/m^3).

4.3.2 Simulation of Toluene Releases Using Only Advective Inflows.

The monotonous behavior of the contaminant shown in Section 4.3.1 is addressed by performing simulation of the same chemical with zero background contamination. The result is presented in Figure 4.11. The use of a zero background level dictates that steady media concentrations are not achievable in 25 years of simulation. During this time period, the environmental concentrations increase steadily with the vegetation, surface and root soil compartments having the highest initial increase; they behave as a "sink". However, the vegetation and root soil compartments, followed by the surface soil, approach steady state level shortly after 15 years of continuous release. From its slope, the sediment compartment is major sink and will continuously accumulate the toluene contaminant until its sorption capacity is reached. The remaining compartments also show continuous increase well after the 25 years of simulation in each of the 11 sub-watersheds.

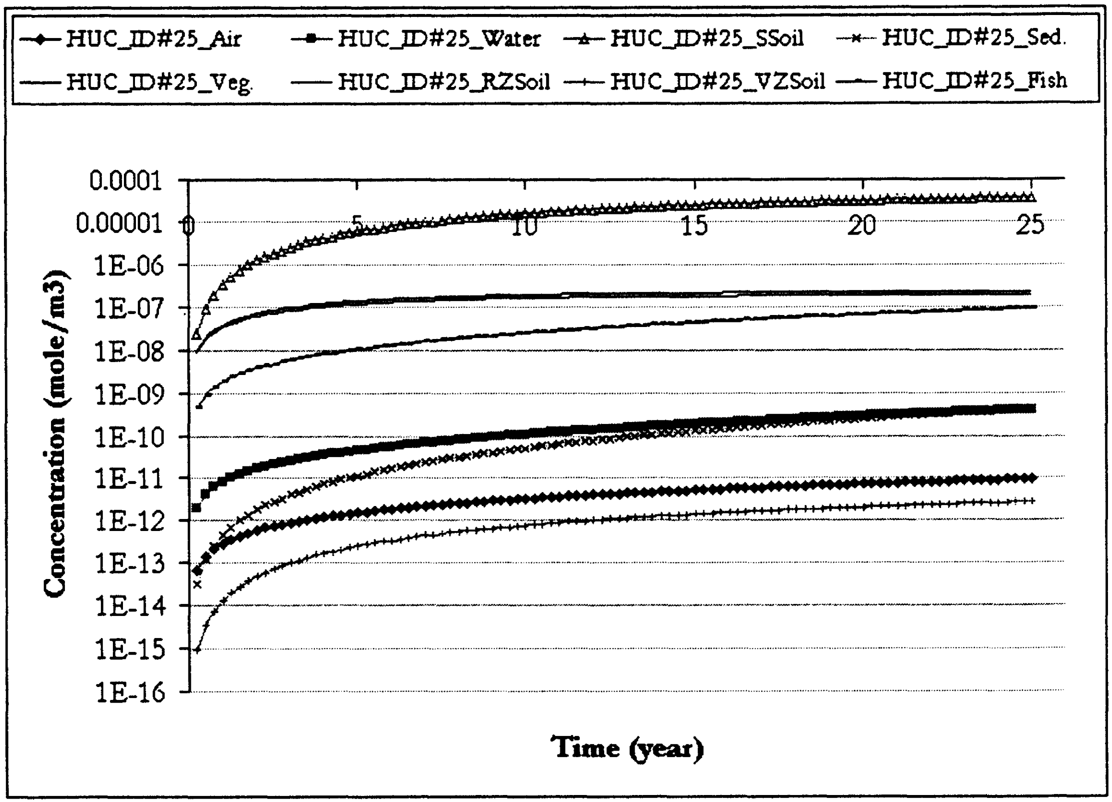


Figure 4.11 Time Series Toluene Concentration in HUC11 #25 with only Advective Influx.

The spatial distribution of the contaminant concentration is a function of both its physical and chemical properties and its point of release. This release is primarily in air, water and root soil compartments, mainly inside the landscape of sub-watersheds #25 and 35. Based on these emissions, the advective inflows and the fugacity model developed in the present study, the sub-watershed toluene concentration is mapped in Figure 4.12.

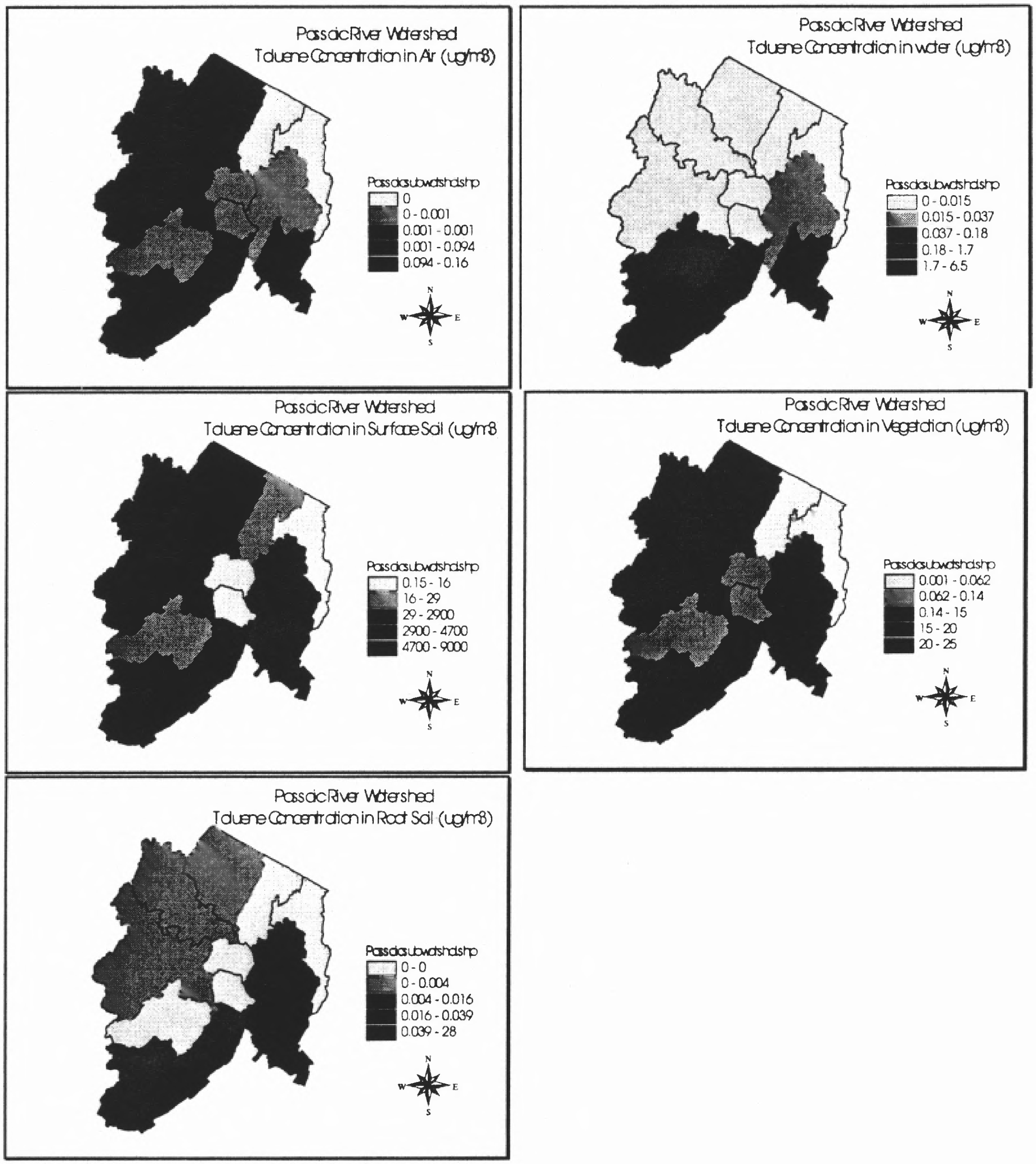


Figure 4.12 Passaic River Watershed Toluene Concentration using only Advective Inflows.

The toluene concentration in the vadose soil compartment is similar to that of the roots soil shown above. The aquatic biota spatial distributions are similar to that of the water compartment. From the above results, it can be concluded that current releases of toluene in the Passaic River Watershed do not appear to have any significant adverse effect. Although the concentration in all but the air and water compartments do increase for a period, primarily because of the absence of contaminants initially, the final levels are not too high. Of these compartments, the sediment compartment seems to be a significant sink as per its time series slope.

The dynamic nature of the environmental processes as represented in the present model make the analysis of contaminant concentration a not so trivial exercise. One should not look for only the final concentrations, as is done in the fugacity level II or level III models, but on how the contaminant concentration has changed to arrive at the present level. Only a dynamic level IV fugacity can provide us with such an insight as is shown in Figure 4.13.

Implicit in Figure 4.9 and 4.12 is a comparison between the sub-watershed concentration versus the entire Passaic River Watershed as one environmental unit. The inclusion of spatial resolution is observed to improve the accuracy of the model results by as much as 9 order of magnitude as in the case of the root zone soil. It is further shown in the above figure that the overall watershed concentrations lie within the range of concentrations estimated for the sub-watershed units. It is thus concluded that the inclusion of a spatial resolution to the present model is significant and is necessary in order to obtain accurate results of environmental concentrations.

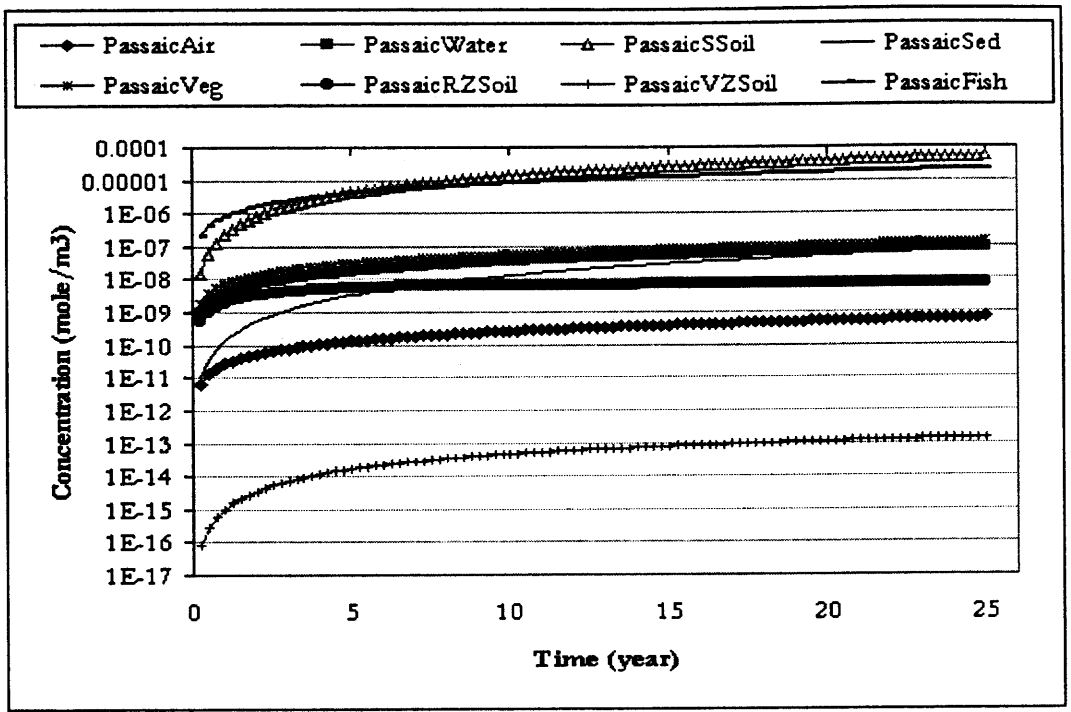


Figure 4.13 Environmental Concentration of Toluene Contaminant in the Total Watershed

4.4 Distribution of Contaminants between Environmental Compartments

The characteristics of the landscape and the compartments in which the contaminants are released significantly impact their final distribution. The following results are for a simulation period of 20 years and using a zero initial concentration. Although the toluene is primarily emitted in the air and water compartments, the resulting simulation shows that the contaminant accumulates in the air, sediment and root zone soil. For HUC11 #12, 13, 15, 18, 19, 27 and 31 the air compartment is the media of residence for this contaminant. Figure 4.15 shows that the air releases are not significant in these sub-watersheds, thus the concentration gradient between the air and other compartments is negligible. This would explain the lack of toluene movement into the other compartments. Additionally, in the following sections, the advective and background concentrations are not included. Therefore, a better assessment of the multimedia model capabilities will be available. For the chemical toluene in the Passaic River Watershed, the releases (in mole/h) are summarized in Figure 4.14. The releases are primarily in air, water and root soil compartments, with the sub-watersheds #25 and 35 having the major fraction of these releases in air and water.

In HUC11 #25, the distribution is highly skewed towards the root zone soil, despite the fact that the emission in the air compartment is nearly 2 order of magnitude higher than that of the root soil. Also, the advective processes have a limited impact on the immobile root soil compartments. In HUC11 #33, 35 and 37, the sediment compartment is the main sink of contaminant fate followed by the air compartment. In these cases, the toluene emission in water is significant, although lower than in the air. Based on the results of the model, the trend on the contaminant distribution in the environment is as follows: when toluene is released in small amount, it tends to remain in the medium where it is released; when appreciable amounts are emitted in the air compartment, it will distribute between the air and vegetation. When released in the water column, toluene has a preferential movement to the sediment compartment and when released in an immobile medium such as the root soil layer, it persists in that medium. The overall mass distribution in the different sub-watersheds is provided in Figure 4.15.

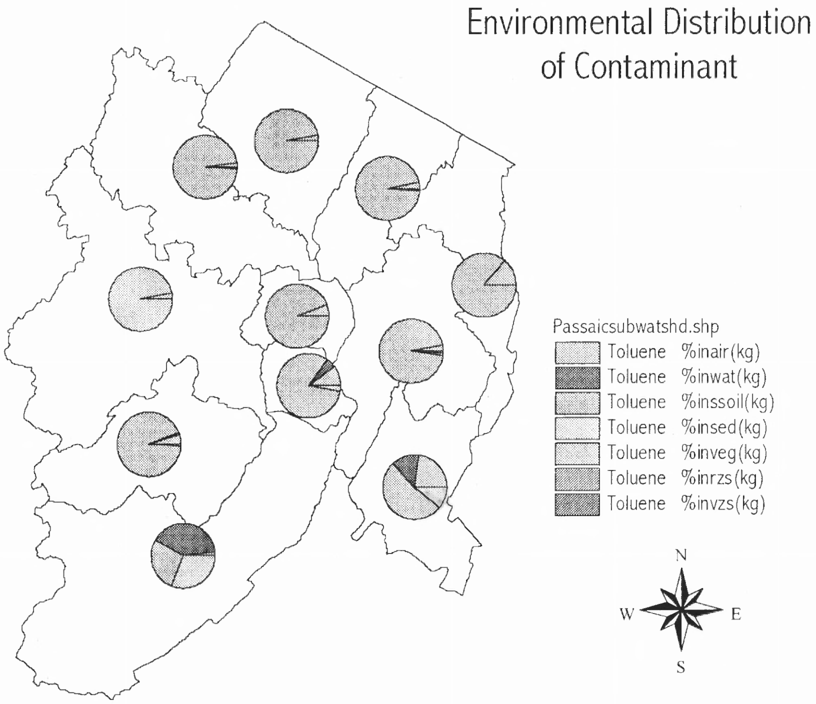


Figure 4.14 Distribution of Toluene among Bulk Compartments in the Sub-Watersheds.

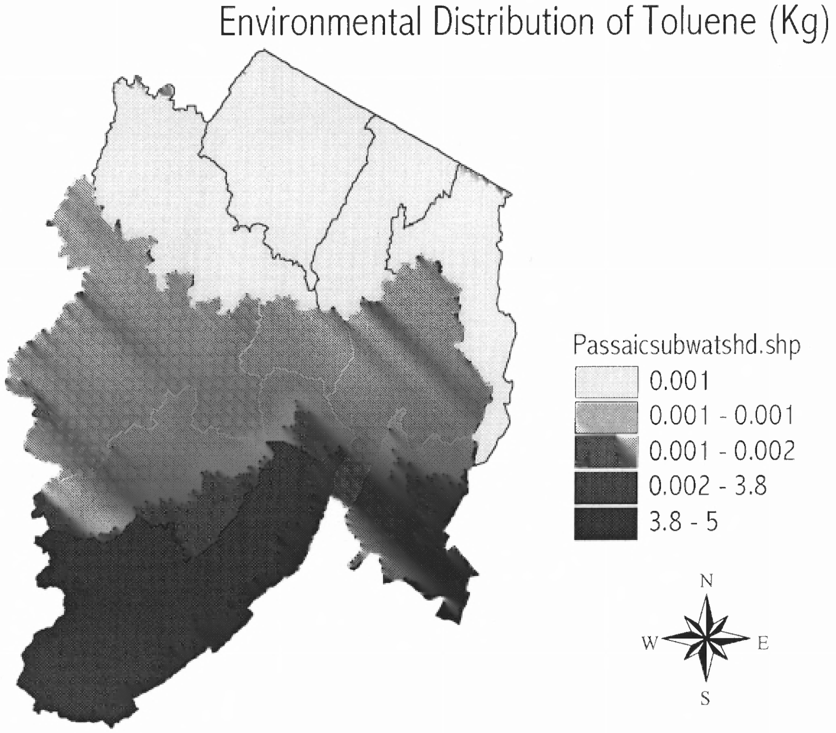


Figure 4.15 Mass Distribution of Toluene in the Passaic River Watershed.

4.5 Environmental Processes in the Multimedia Model

The main advantage of using a multimedia model over conventional models, is the amount of information it provides to the user. Such information includes the individual transfers to and from an environmental compartment or a box, and the exchange rates between adjacent compartments, landscapes and regions. In the present model, these processes are dynamic since they depend on the contaminant fugacity in the different compartments. The processes used in the model are divided into 4 main parts; compartment total gains and total losses, individual process rates or fluxes, intermedia transfer rates between bulk compartments, and total transfer in and out of each compartment. Each of these processes is described in detail in the following subsections with the example of a given sub-watershed (HUC#25). These results are generated from the simulation of toluene using a zero background concentration in each medium.

4.5.1 Compartment Total Gains

The gain in each compartment includes the amount of contaminant being continuously emitted and contribution of advective influx from the neighboring sub-watersheds. The emissions are not time dependent and are derived from the TRI data for each compartment with the soil disposal taken to occur in the root soil. The advective influx depends on time as the concentrations from the upwind or upstream of a sub-watersheds vary with time as seen in Section 4.2.2. A representative output of these processes is shown in the Table 4.5.

4.5.2 Individual Process Rates

While the Level III fugacity model results in a single equilibrium concentration, it does not directly estimate the time to reach this equilibrium. This time varies between compartments as can be inferred from the above figures in Section 4.3. Furthermore, the steady state contamination level provides us with only a snap shot of the contaminant fate. A qualitative analysis of these results also indicates that the environmental processes that drive the fate of the contaminant are not constant processes. For example, sorption of the contaminant from

Table 4.5 Gain and Loss Process in Environmental Compartments for HUC#25

Emissions			
Compartment	**mole/h**	**kg/h**	**kg/year**
1. Air	38.44	3.54	3.101e+004
2. Water	0.02986	0.00275	24.09
3. Soil	0	0	0
4. Sediment	0	0	0
5. Vegetation	0	0	0
6. Root Soil	5.233	0.482	4222
7. Vadose Soil	0	0	0
Total	43.7	4.025	3.526e+004
Advection	mole/h	kg/h	kg/year
1. AIR	0	0	0
2. WATER	0	0	0
LOSSES: Degradation/Reaction & Advection			
Degradation	mole/h	kg/h	kg/year
1. Air	0.01849	0.001703	14.92
2. Water	1.793e-005	1.651e-006	0.01446
3. Soil	1.483	0.1366	1197
4. Sediment	3.409e-008	3.14e-009	2.75e-005
5. Vegetation	0.002756	0.0002538	2.224
6. Root Soil	0.009502	0.0008751	7.666
7. Vadose Soil	1.261e-006	1.161e-007	0.001017
Total	1.514	0.1395	1222
Advection	mole/h	kg/h	kg/year
1. AIR	0.4908	0.0452	396
2. WATER	6.099e-005	5.617e-006	0.0492

the water column to the sediment layer strongly depends on both the water column and sediment fugacity. Thus any change in these fugacity values will translate into changes in the adsorption process between these two compartments. For this reason, the environmental processes calculated in the present model are shown for a single time (the end of the simulation period). Therefore, the rates shown are indicative of only the time at which they are calculated. These environmental processes are presented in Table 4.6 for the sub-watershed HUC#25. The process rates describe the strength of each environmental process on the fate of the contaminant. Additionally, since they are outputted in the same unit, these processes are comparable to each other and decide the dominant factors for the distribution of the contaminant. Furthermore, they are presented using the different environmental interfaces such as the water sediment exchange or the leaching of the contaminant through a given soil layer. The processes are presented in Table 4.6.

Of the many processes on the fate of contaminant toluene in Sub-Watershed HUC#25, the uptake by vegetation foliage and roots and the volatilization from surface soils are the most significant process, while the leaching to the groundwater represents the least significant process. Additionally, the surface runoff is fairly significant and transports most of the pollutant from urban areas to the water bodies. The yearly loading of this runoff to surface waters is estimated as 122 kg per year.

4.5.3 Intermedia Transfer Rates Between Bulk Compartments

This section is simply the summation of the contaminant exchange between adjacent compartments. The following table as such provides us with an insight of the relative importance of the sinks and sources in the environment and the persistence of the contaminant in each compartment. This persistence is displayed in the form of contaminant half-life. Finally, the strength of each source and sink is also provided regardless of the compartment of release, this is in the form of fugacity mass transfer coefficient or D values.

Table 4.6 Environmental Fluxes of Toluene in Sub-Watershed HUC#25

INDIVIDUAL PROCESS RATES OR FLUX	mole/h	kg/year
AIR WATER INTERFACE		
Adsorption from Air	2.386e-006	0.01898
Volatilization from Water	3.309e-005	0.2633
Aerolols Dry Deposition	3.072e-011	2.444e-007
Wet Deposition - Rain Dissolution	2.334e-008	0.0001857
AIR SOIL INTERFACE		
Adsorption from Air	3.605e-005	0.2868
Volatilization from Soil	0.7797	6204
Aerolols Dry Deposition	3.072e-011	2.444e-007
Wet Deposition - Rain Dissolution	7.728e-007	0.00615
AIR PLANT INTERFACE		
Adsorption by Foliar Plant	0.0345	274.6
Volatilization from Plants	5.205	4.141e+004
Net Deposition onto Plants	5.55e-020	4.416e-016
WATER SEDIMENT INTERFACE		
Adsorption to Sediment Layer	7.516e-008	0.0005981
Desorption from Sediment	5.728e-009	4.558e-005
Sediment Deposition	2.906e-006	0.02312
Sediment Re-suspension	1.067e-009	8.488e-006
Sediment Burial	1.067e-009	8.606e-007
SURFACE SOIL(1) SURFACE WATER INTERFACE		
Surface Water Runoff	0.01529	121.7
Soil Erosion	3.834e-005	0.3051
SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE		
Difusion(Air+Water) into Soil2	0.003937	31.33
Difusion(Air+Water) into Soil1	0.0002362	1.879
Infiltration/Leaching to Soil2	0.001411	11.23
PLANT ROOT ZONE SOIL(2) INTERFACE		
Net Plant Uptake	5.173	4.116e+004
ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE		
Leaching/Infiltration	0.0003386	2.694
VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE		
Leaching	4.17e-009	3.318e-005

4.5.4 Total Transfers (Gains and Losses) in Compartments

The total transfer is defined here as the summation of all the environmental processes occurring in a given compartment, including advection, degradation, emission and intermedia transfers. The total transfer determines, in the overall scheme, the compartment in which the contaminant will accumulate by taking the difference between the input and the output (Table 4.8).

Table 4.7 Intermedia Transfers Rate of Toluene between Bulk Compartments in HUC#25

Compartment	Rates(mole/h)	Rates(kg/y)	Dvalues(mol/Pa.h)	Half-Life(h)
1 TO 2	2.409e-006	0.001944	125.4	168.9
1 TO 3	3.682e-005	0.02971	1917	1242
1 TO 5	0.0345	27.84	1.796e+006	0.002166
2 TO 1	3.309e-005	0.0267	124.2	168.9
2 TO 4	2.981e-006	0.002405	11.19	1307
3 TO 1	0.7797	629.1	1876	1242
3 TO 2	0.01533	12.37	36.88	6.604e+004
3 TO 6	0.005349	4.315	12.87	6.744e+004
4 TO 2	6.794e-009	5.482e-006	0.3345	1638
5 TO 1	5.205	4199	1.796e+006	0.002166
5 TO 3	2.946	2376	1.016e+006	0
6 TO 3	0.0002362	0.1905	9.475	6.744e+004
6 TO 5	5.173	4174	2.075e+005	4.338e+013
6 TO 7	0.0003386	0.2732	13.58	7.308e+004
7 TO 2	4.17e-009	3.365e-006	13.58	7.874e+005

Table 4.8 Individual Transfer Rates in Compartments

TRANSFER RATES INTO INDIVIDUAL COMPARTMENT			
Compartment	Rates(mole/h)	Rates(kg/h)	Rates(kg/y)
1. Air	5.984	0.5512	4828
2. Water	0.01533	0.001412	12.37
3. Soil	2.946	0.2713	2377
4. Sediment	2.981e-006	2.746e-007	0.002405
5. Vegetation	5.207	0.4796	4201
6. Root Soil	0.005349	0.0004926	4.315
7. Vadose Soil	0.0003386	3.118e-005	0.2732
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT			
Rates(mole/h)	Rates(mole/h)	Rates(kg/h)	Rates(kg/y)
1. Air	0.03454	0.003181	27.87
2. Water	3.607e-005	3.322e-006	0.0291
3. Soil	0.8004	0.07372	645.7
4. Sediment	6.794e-009	6.257e-010	5.482e-006
5. Vegetation	8.15	0.7506	6575
6. Root Soil	5.174	0.4765	4174
7. Vadose Soil	4.17e-009	3.841e-010	3.365e-006

CHAPTER 5

GENERAL MODEL APPLICATIONS AND DISCUSSIONS

The application of the present multimedia model to assess the fate and transport of the remaining 4 chemicals is discussed in the following sections. These contaminants; TCE, 1-1-1 trichloroethane, xylene and naphthalene, are very different in physical and chemical properties, persistence in the environment and points of release. Their distribution in the environment and the different compartments is investigated and the important environmental processes that drive the fate of these contaminants are identified. Finally, a long-term analysis of a contaminant is performed using EPA Region III Risk-Based Concentrations.

5.1 Watershed-Wide Distribution of Contaminants

The fate and transport of toluene, discussed in Chapter 4, is different from those of other chemicals used in this research, more specifically, the naphthalene contaminant. The latter differ from toluene in its physical and chemical properties; it has a higher molecular weight (128 g/mole), it has a relatively low solubility (31.5 mg/L), a low vapor pressure (10.4 Pa) and a low persistence in the environment as per its degradation rates. The 5 chemicals used in this study can be classified into 3 categories based on their vapor pressure and molecular weight. TCE and 1-1-1 trichloroethane are very similar in physical characteristics, while toluene and xylene are similar in physical characteristics. An analysis of naphthalene as well as the other 3 chemicals; TCE, 1-1-1 trichloroethane and xylene, are presented in the following sections. Because the background concentration and advective inflows are taken from national and state-wide monitoring databases, respectively, they may not necessarily reflect the background levels in the Passaic River Basin, we decided to perform the simulation based solely on the TRI (Toxic Release Inventory) releases.

5.1.1 Fate and Transport of Naphthalene

The current model was used to simulate the releases of naphthalene contaminant in the Passaic River Watershed for a period of 1000 years. The 1000 years duration is chosen here because advective inflows and background levels are not used, therefore, it is needed in order to allow the environmental concentrations to reach steady levels. The resultant environmental concentrations and distribution in the watershed are presented below in Figures 5.1 and 5.2. The dominant process in this analysis is the air-foliage exchange followed by the leaf transfer to the surface soil. The environmental processes that drive the fate of naphthalene are presented in Appendix B.

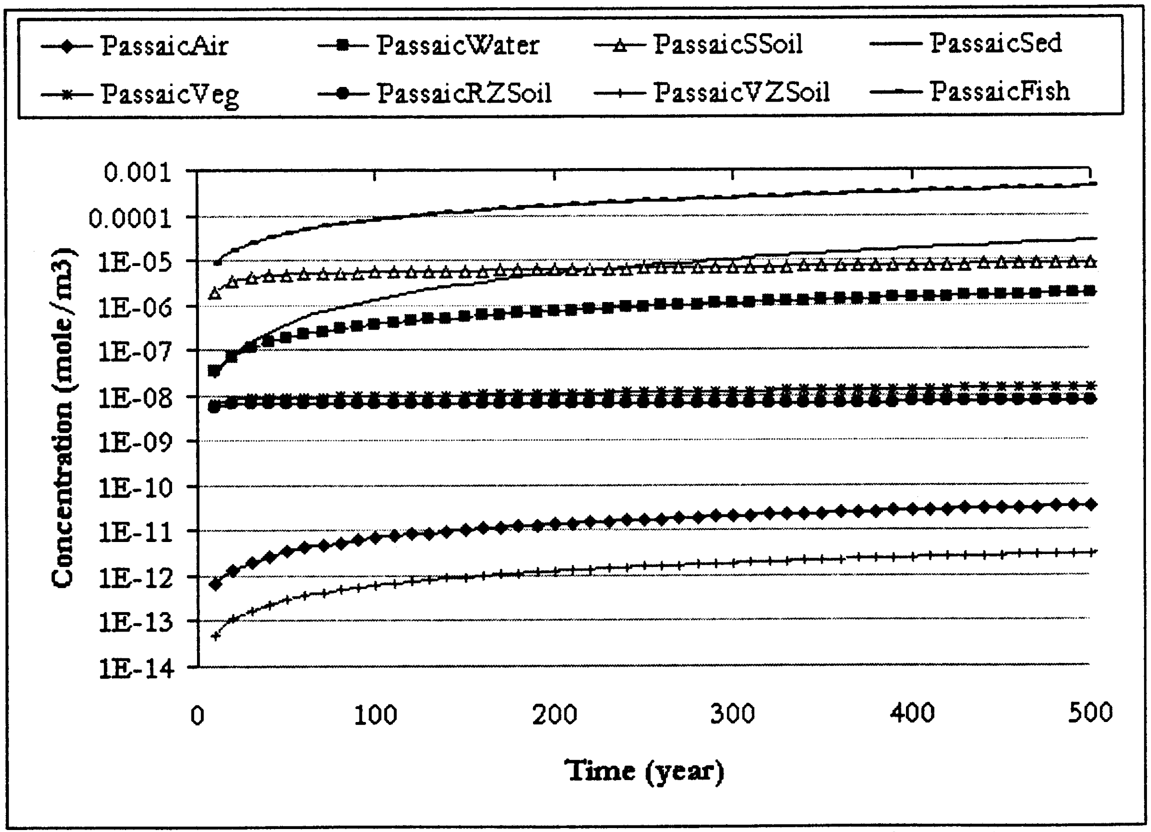


Figure 5.1 Time Series Concentration of Naphthalene in the Passaic River Basin

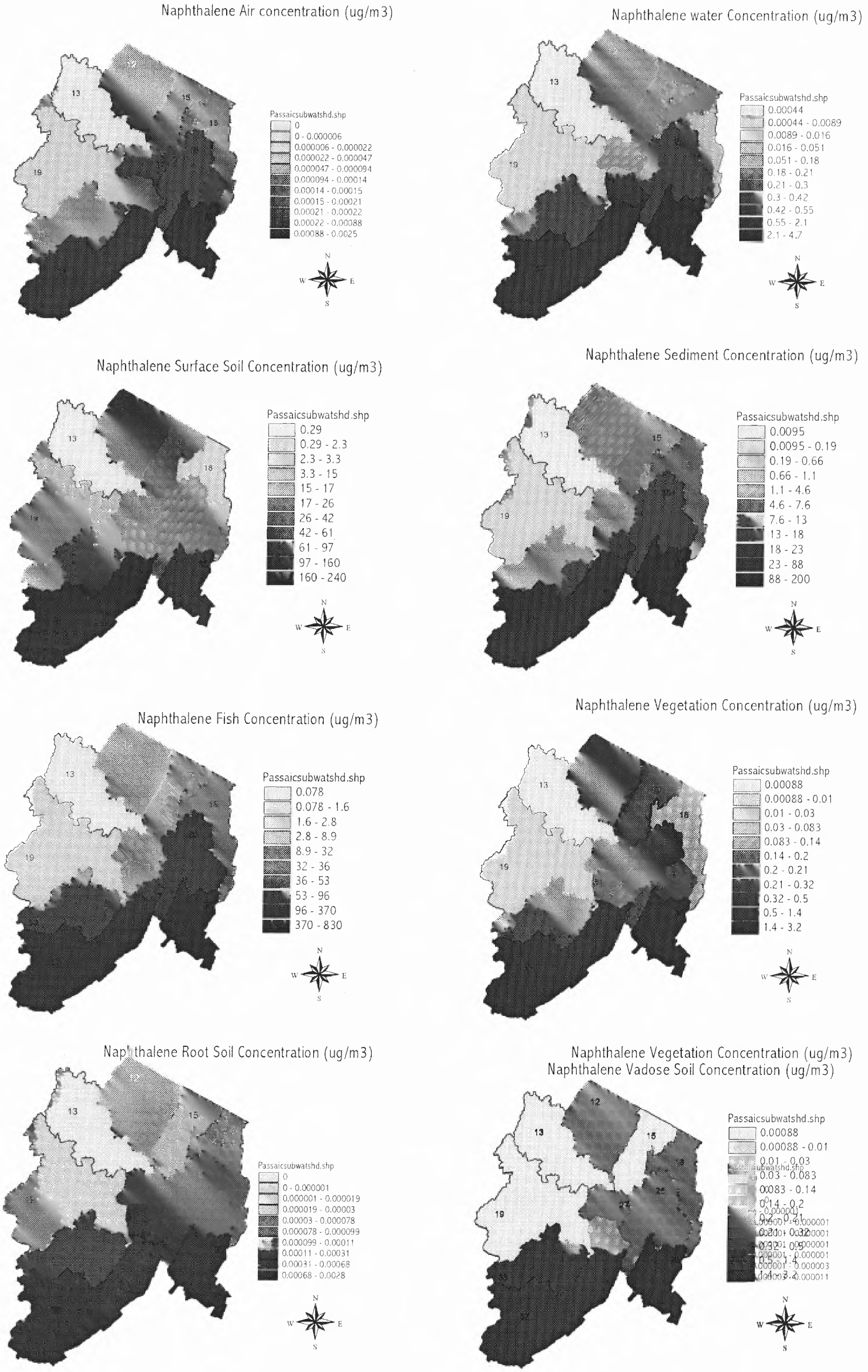


Figure 5.2 Watershed-Wide Concentration of Naphthalene in the Passaic Watershed.

The distribution of naphthalene shows that the bulk of the contaminant is present in the surface soil with the air compartment, a distant second. A first look at this result and the emission table of naphthalene, in Section 3.8, raises some questions since it is only released in the air and water compartments. Understanding this affinity for the soil compartment is possible by analyzing the contaminant physical and chemical properties. Since it has a much higher sorption coefficient to organic phases, log KOW of 3.35 and a relatively less biodegradation potential in soil, half life greater that 454 days, the soil compartment will thus serve as a strong sink. In the sub-watershed HUC#35, a good portion of the contaminant mass is found in the air compartment. This is explained by the fact that air releases in this unit are significant and account for over 41% of the total releases in the entire watershed.

The HUC#17 sub-watershed air compartment is void of any contaminant since the releases here amount to zero and the advective inflow from HUC#19 is negligible, also due to lack of air releases. HUC#15, 18 and 19 show small level of air contamination, this is attributed solely to advective inflows from HUC#12 and 27, HUC#15 and 25, and HUC# 33, respectively. The pattern of terrestrial vegetation is identical to that of the air compartment since all the exchange is at the air-leaf interface in the absence of naphthalene release in the root soil compartment. Similarly, the sediment and surface water compartment expectedly mirror each other, while the root and vadose zone soils show significant divergence. The latter is attributed to the variable soil layers between the different sub-watersheds. For example, while the depth root and vadose soil in HUC#18 is almost nil, they are very deep for HUC#12, thus presenting a strong barrier to contaminant vertical movement. Finally, the air and surface water and the air surface soil form pairs that are strongly linked by intermedia transfer. For example, while the releases are not significant in the water compartment, it still receives contaminant via deposition, surface runoff and adsorption. This analysis is not exhaustive since such an exercise will be beyond the scope of this research and should be performed as a follow up research. It has been shown in the above section that the importance of using multimedia models for environmental assessment and the wealth of information generated from such model can be used to perform countless analysis in making environmental decisions. The final concentrations after 1000 years of simulation along with the time series concentration in the entire watershed are presented below. The overall distributions of naphthalene among the different phases and the summary of the releases in the different sub-watersheds are presented in Figure 5.3. It is observed that naphthalene tends to accumulate in the soil compartments, even though there are little or no releases in these compartments throughout the Passaic River Watershed.

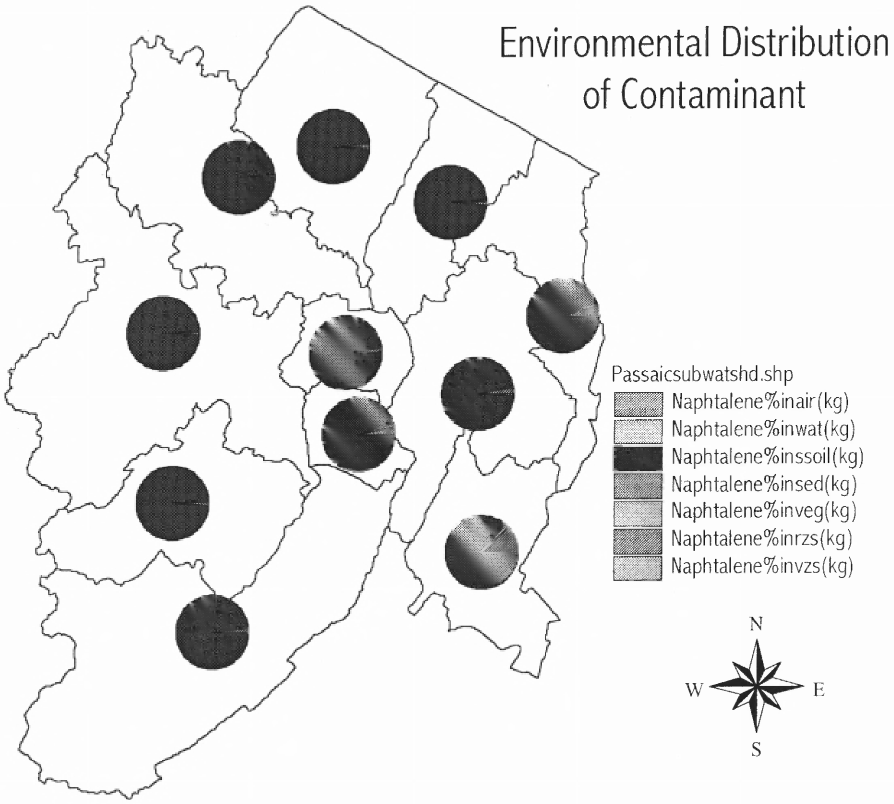


Figure 5.3 Environmental Distribution of Naphthalene in the Passaic River Watershed.

5.1.2 Fate and Transport of Contaminant Xylene

Although different from naphthalene in physical characteristics (volatility, solubility and molecular weight) and persistence, xylene also has a tendency to accumulate in the soil compartment. Like naphthalene, there is no release of xylene into the soil compartments but it has a high KOW coefficient. Thus, the xylene contaminant will readily move to the organic carbon rich surface soils. One important observation was made for HUC#35 where the releases in air and water are significant. There, only 45% of the contaminant mass is found in the soil while more than 53% remains in the air and water compartments. This distribution is different from that of naphthalene (see Section 4.6.1), since the xylene contaminant is more volatile and will actually volatilize from the soil at a significantly higher rate. The concentrations of xylene are shown in Figures 5.4, 5.5 and 5.6.

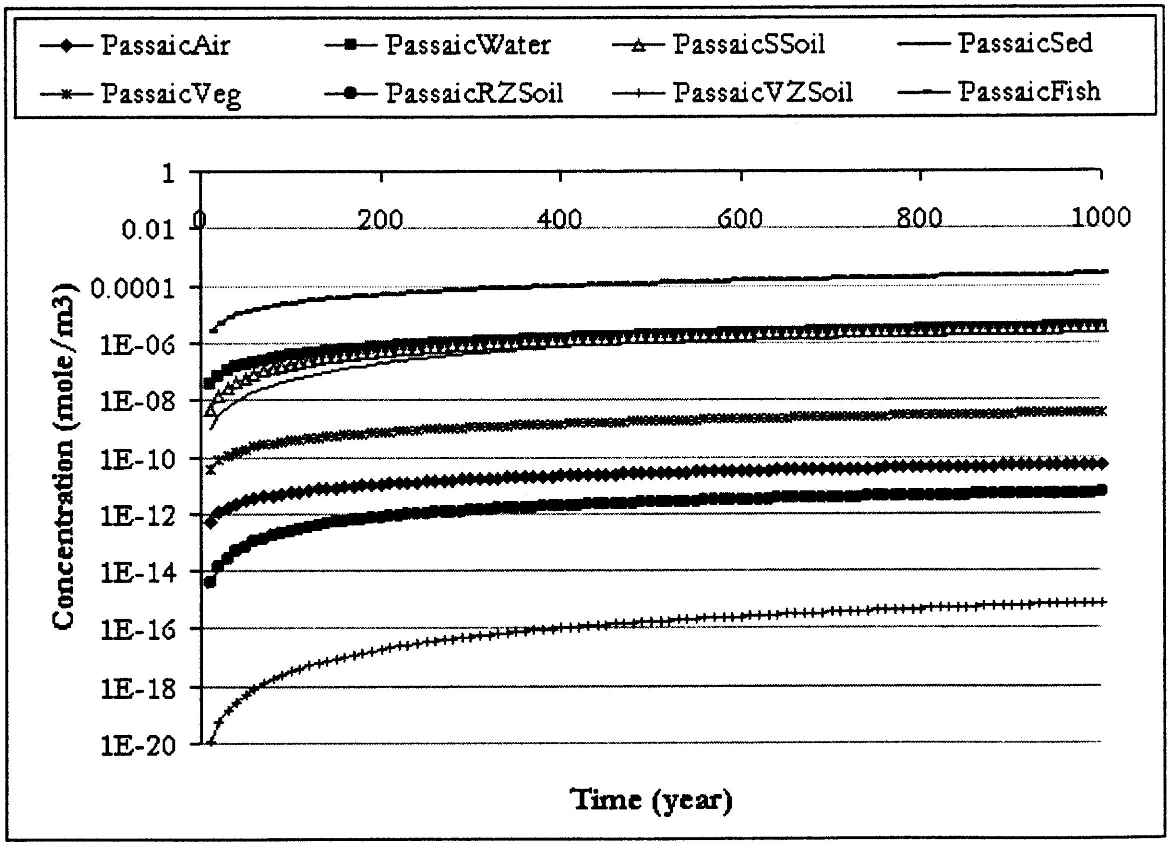


Figure 5.4 Time Series Concentration of Xylene in the Passaic River Basin.

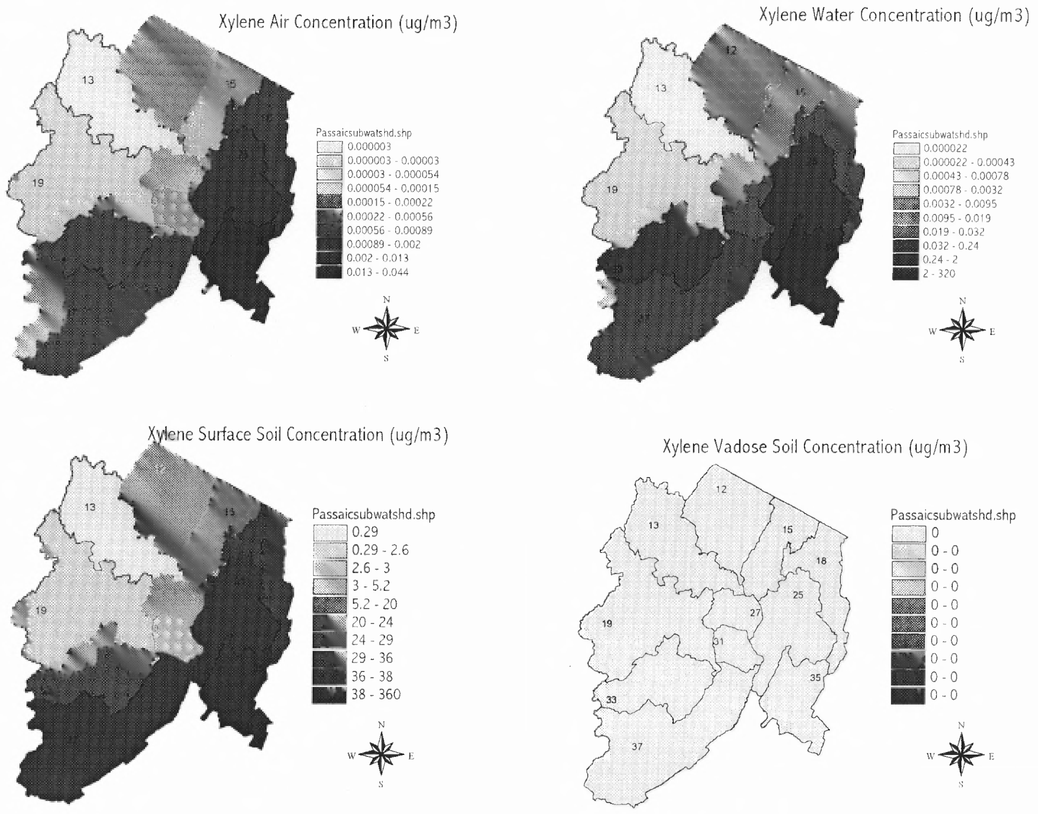


Figure 5.5 Watershed-Wide Concentration of Xylene.

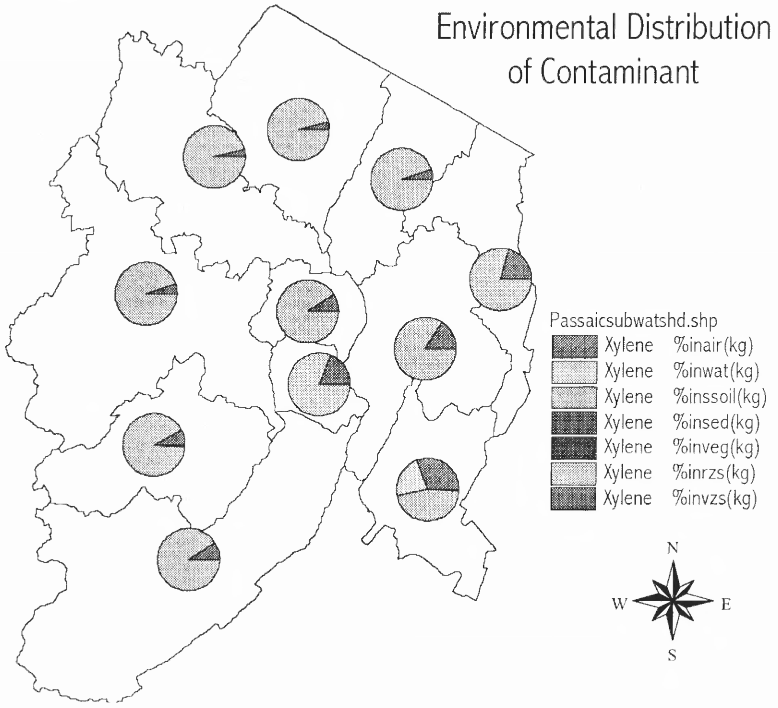


Figure 5.6 Environmental Distribution of Xylene in the Passaic River Watershed.

5.1.3 Fate and Transport of 1-1-1 Trichloroethane

In a major departure from the previous two cases, this chemical shows a preference for the air compartment. Of the 5 chemicals used in this research, it has the highest vapor pressure, 12800 Pa, and the greatest persistence in air, half-life of 1237 days. This combination of persistence and volatility drives the contaminant mainly into the air compartment for all the sub-watersheds except HUC# 13 and 31. In these two units, there is no release in any compartment, HUC#13 or the release in the soil is more than in the air, HUC#31. The HUC#12 has zero level of contamination since it receives no release and negligible advective inflow from HUC#13. An analysis of cross boundary transfer of this contaminant from the state of Pennsylvania would be possible in the present model, provided the information on that area background level is available. Such analysis will continue to be important for regulatory bodies as they seek to estimate the contribution of each source, local or long range.

The high volatility of this contaminant also plays a role in its absence from the water compartment and subsequently the sediment and aquatic biota. Additionally, at every environmental interface, including air-soil, air-vegetation, air-water, the volatilization dominates the adsorption and depositions. The time series plots of 1-1-1 Trichloroethane are presented in Figure 5.7; the environmental mass distribution is shown in Figure 5.8 and the watershed concentrations in Figure 5.9. In the time series plot, the concentration level using the watershed as one environmental unit is much different from the concentration using the sub-watershed division. However, the former has values well within the calculated values of the sub-watersheds. This analysis is valid for each of the 5 chemicals used and can be seen in the different time series plot throughout this dissertation.

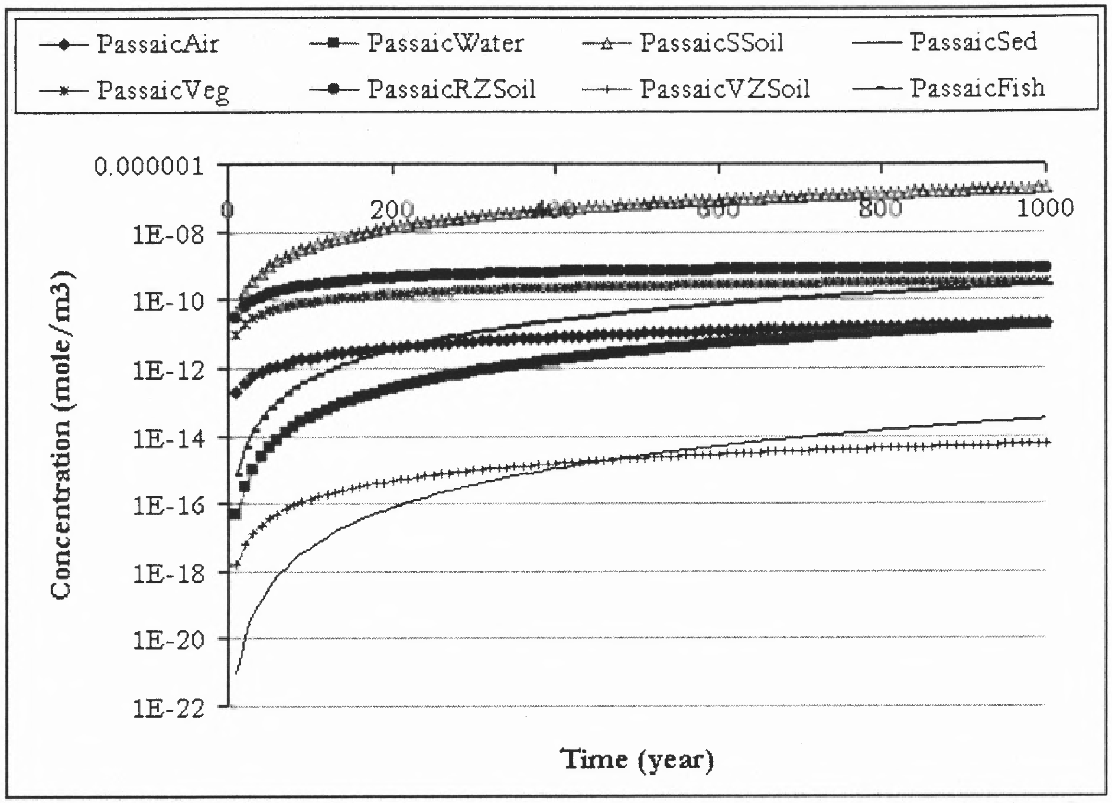


Figure 5.7 Time Series Concentrations of 1-1-1Trichloroethane in the Passaic River Basin.

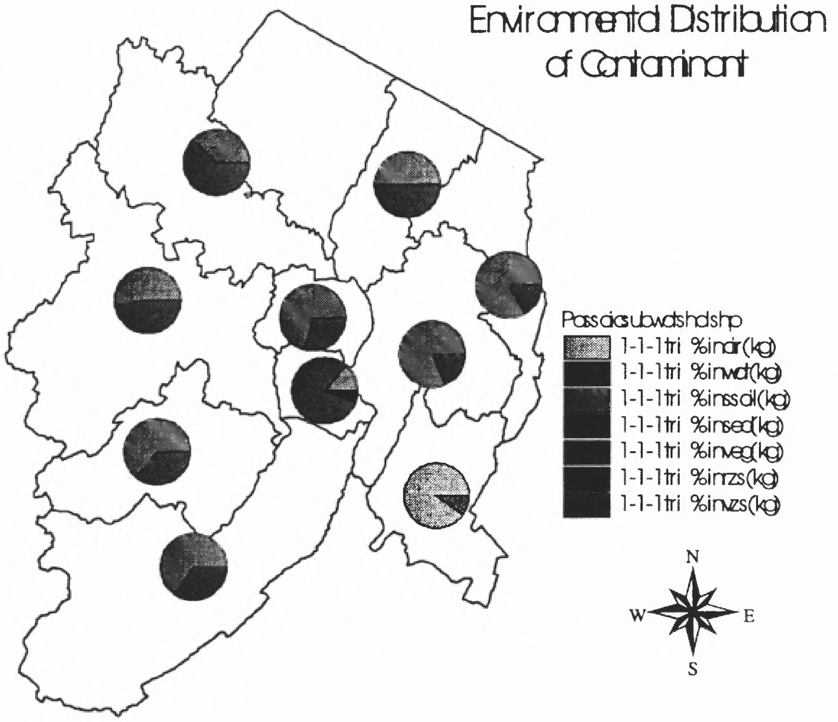


Figure 5.8 Environmental Distribution of 1-1-1Trichloroethane in the Passaic River Basin.

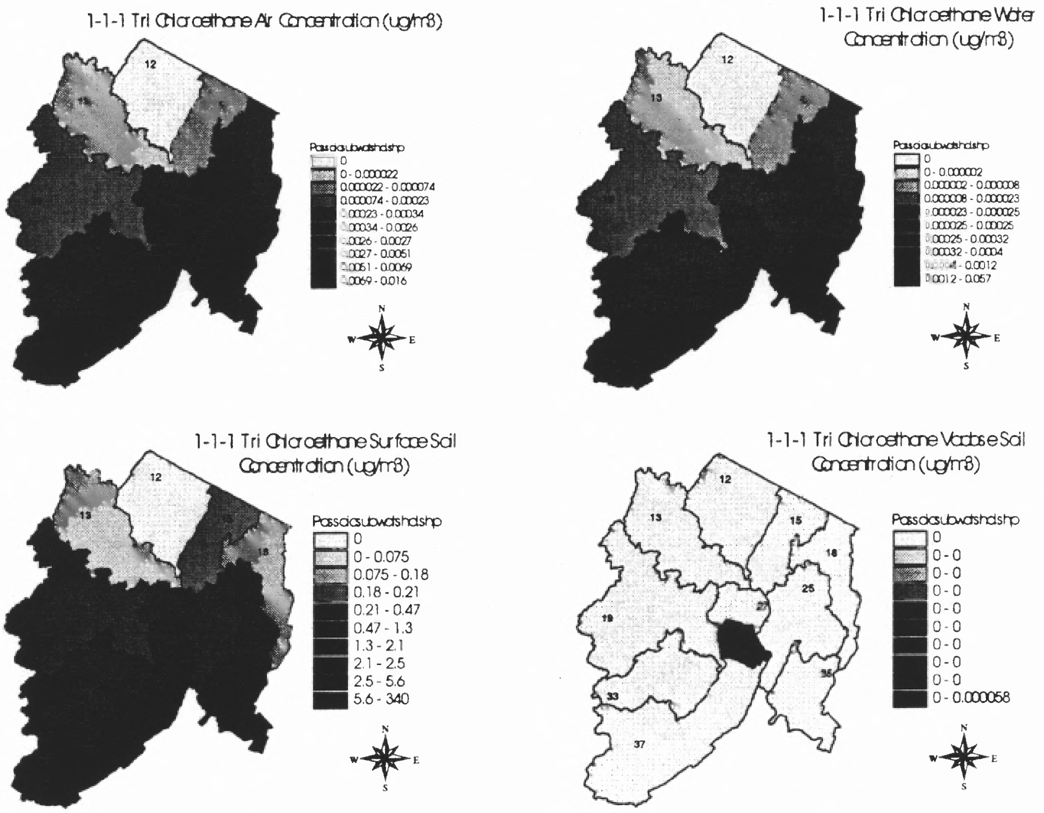


Figure 5.9 Water-Wide Concentrations of 1-1-1Trichloroethane.

5.1.4 Fate and Transport of Trichloethylene (TCE)

TCE is very similar to 1-1-1Trichloroethane in physical and chemical characteristics and in its persistence in the environment. Thus, its fate in the environment nearly mimic that of 1-1-1Trichloroethane with similar environmental media distribution and interphase transfer rates. Additionally, since the releases of these two chemicals are somewhat similar, the concentrations calculated from the model are nearly identical. Thus it can be concluded that the present model is consistent in representing the environmental processes for contaminant with similar characteristics. The time series plots and distribution of TCE are provided in Figures 5.10 and 5.11. The watershed concentrations are also presented in Figure 5.12.

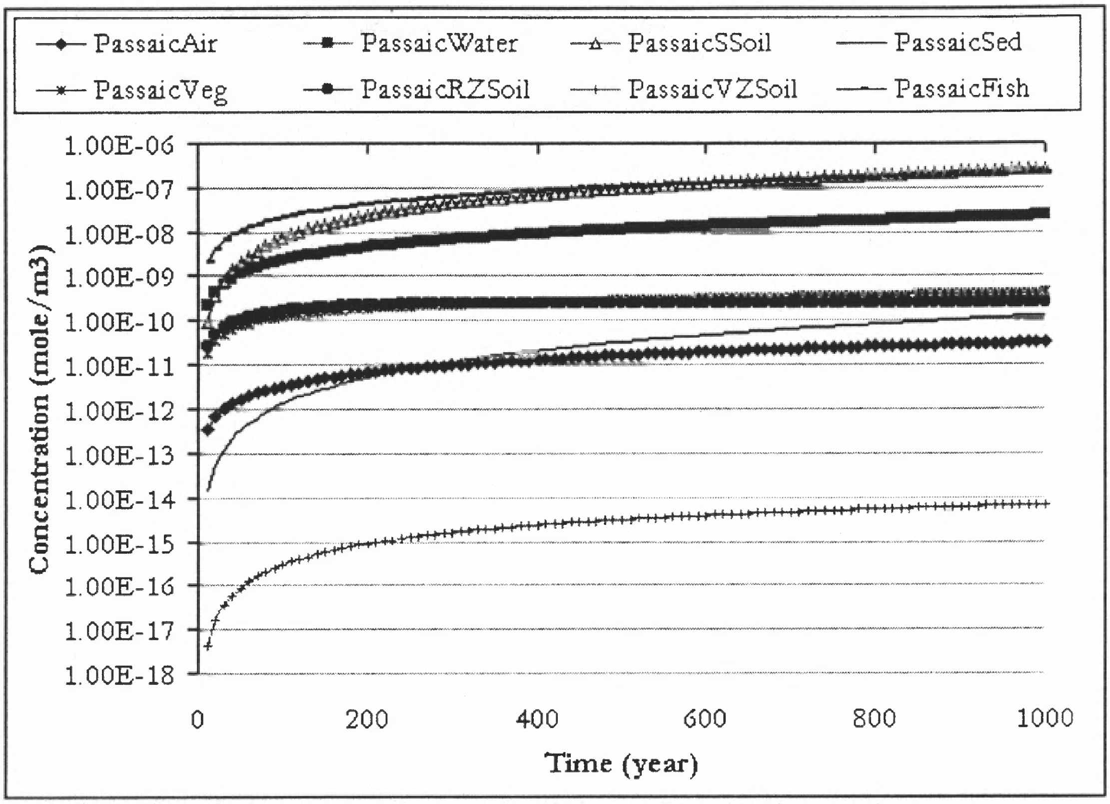


Figure 5.10 Time Series Concentration of TCE in the Passaic River Basin

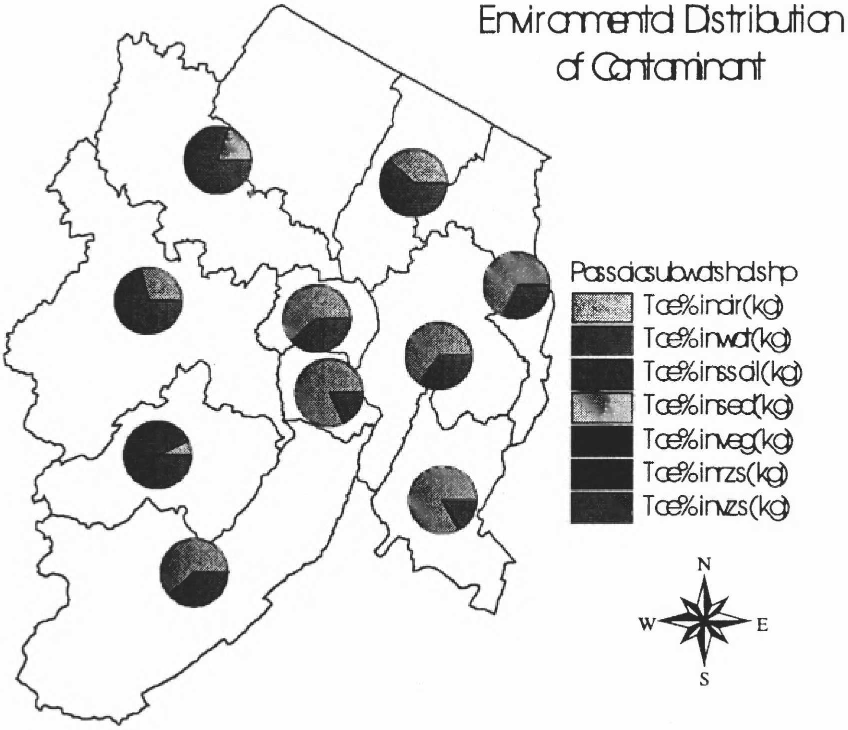
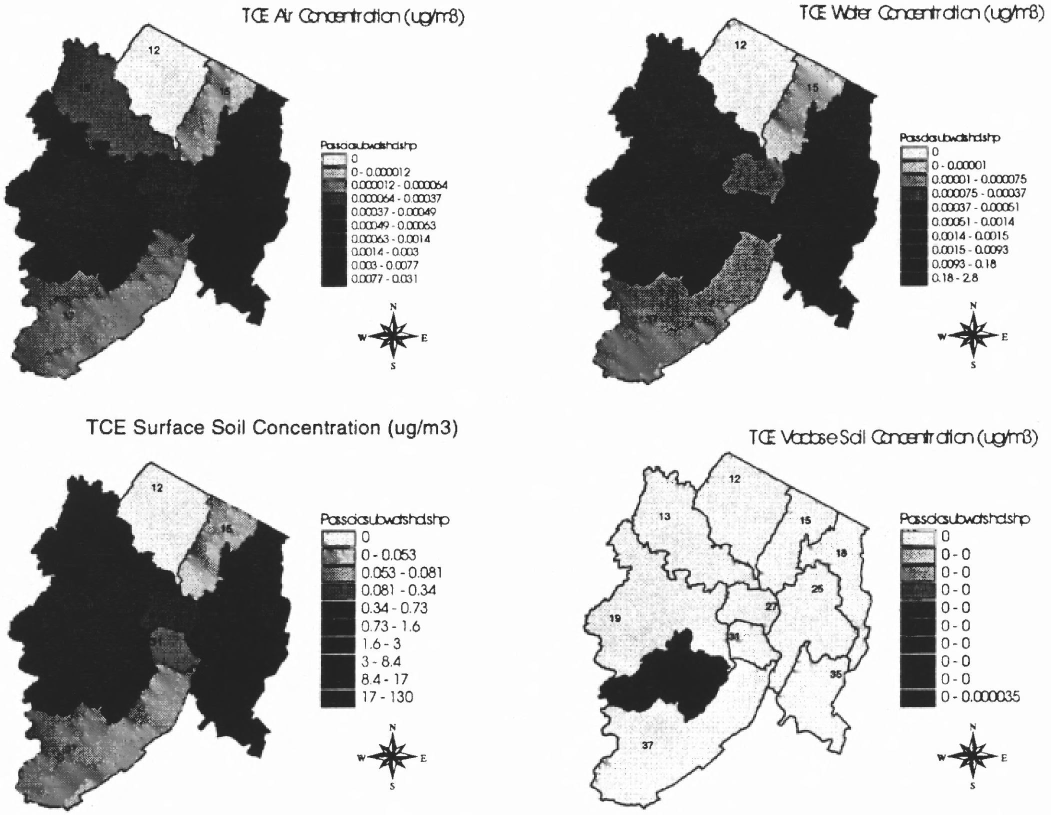


Figure 5.11 Environmental Distribution of TCE in the Watershed


TCE Air Concentration (ug/m3)

TCE Water Concentration (ug/m3)

TCE Surface Soil Concentration (ug/m3)

TCE Vadose Soil Concentration (ug/m3)

Figure 5.12 Watershed-Wide Concentrations of TCE.

5.1.5 Media Specific Distribution

In analyzing the fate of the 5 chemicals in the different sub-watersheds, certain issues such as the reduction of releases may be finally addressed. If the fish concentration levels are higher than allowable limits in certain sub-watersheds, a decision may be taken to reduce the releases in only those sub-watersheds to bring the fish concentration within allowable limits. Since the releases are provided in term of mass, such regulatory control will be easy to implement as the total mass from the emitters can be set per annum.

In cases where there is a need to differentiate between the contribution of local emissions versus cross boundaries sources, the multimedia model developed in this research can be used to address such ambiguity. By allowing the background level inputs in the model as was done in Section 4.3.1, the total contribution of these cross boundary sources can be assessed and their impact be determined with certain level of confidence. If very accurate analysis is needed, the current model can still be applied with the addition of the necessary input to obtain higher resolution to represent the fluctuation of environmental parameters such as wind speed, wind direction, high rainfall events, etc.

In the above analysis, the surface soils do not receive any release and the diffusion from the root soils is very small. Additionally, the adsorption and deposition is usually balanced by the volatilization from the soil for all the 5 chemicals used. This compartment acts as a major sink and is essentially caused by the transfer from the terrestrial vegetation to the surface soil through leaf loss during the cold season. It is assumed in the present research that the vegetative leaf-loss occurs each year thus the total amount of contaminant in the plant foliage is lost to the surface soil each year.

5.2 Watershed Long Term Planning

As mentioned in the objectives of this research (Section 1), the multimedia model can be used to make numerous scenario analysis, which are of interest to regulatory bodies such as the State Department of Environmental Protection. One such analysis is to determine the time period it would take for current concentrations to decrease to acceptable levels, as defined by the regulations, using different reduction strategies for the releases. In the current section, we will approach this problem by reducing the environmental releases to zero and using the highest reported monitoring data as the initial concentration in air and water compartments. The risk based concentration (RBC) values will be used as the endpoint of the simulation. The brief description of these RBCs derivation is provided below.

5.2.1 Derivation of RBC Values

The risk-based concentrations of a given contaminant are derived from the risk assessment procedure, which consists of multiplying the exposure concentration to the chemical toxicity value as shown in Equation 5.1 for carcinogenic contaminants and Equation 5.2 for non-carcinogenic contaminants (USEPA, 1989).

$$\text{Risk} = \text{CDI} \times \text{SF} \tag{5.1}$$

where:

Risk = a unitless probability (e.g., 2 x 10) of an individual developing cancer;

CDI = chronic daily intake averaged over 70 years (mg/kg-day); and

SF = slope factor, expressed in (mg/kg-day).

$$\text{Noncancer Hazard Quotient (HQ)} = \text{E}/\text{RfD} \tag{5.2}$$

where:

E = exposure level (or intake);

RfD = reference dose; and E and RfD are expressed in the same units.

For multiple chemicals or for a chemical intake via multiple pathways, the total risk for an individual is the summation of the above equations for each pathway and for each chemical. This total risk should not exceed 1E-6 for carcinogens and 1 for non-carcinogens. Furthermore, the uncertainty in the exposure assessment and the toxicity studies should be accounted for using an uncertainty factor (e.g. 10 if the exposure concentration estimated can vary by as much as 10) which is then multiplied by the above risk. The RBCs are obtained by performing risk assessments in reverse. For a single contaminant in a single medium under standard default exposure assumptions, the RBC corresponds to the target risk or hazard quotient. The RBCs are calculated using values of the Reference Doses (RfDs) and Cancer Slope Factors (CSFs) for over 400 chemicals and the 'standard' exposure scenarios and the chemical toxicity factors. The resultants chemical concentrations are for the promulgated levels of risk (i.e., a Hazard Quotient (HQ) of 1 or lifetime cancer risk of 1E-6, whichever occurs at a lower concentration) in water, air, fish tissue, and soil. These RBCs should be used for only chemical screening during baseline risk assessment according to the EPA's Risk Assessment Guidance for Superfund (RAGS), EPA (1989, 1991). The present model uses RBCs developed by Region III toxicologists (EPA, 1999).

The RBC derivation for inhalation of contaminated air of a carcinogen is shown in Equation 5.3 below using an adjusted inhalation rate for child and adult, IFAadj. This adjustment factor is shown in Equation 5.4. These risk-based concentrations are presented in Table 5.1.

$$RBC(\mu g/m^3) = \frac{TR * ATc * 1000\mu g/mg}{EFr * IFAadj * CPSi} \tag{5.3}$$

$$IFAadj(\frac{m^3.y}{kg.d}) = \frac{EDc * IRAc}{BWc} + \frac{(EDtot - EDc) * IRAa}{BWa} \tag{5.4}$$

where:

TR is the target cancer risk: 1E-6

Atc, the averaging time for carcinogens (d): 25550

Efr, the exposure frequency (d/y) for residential exposure: 350

IFAadj, the inhalation factor, age-adjusted (m3-y/kg-d): 11.66

CPSi, the carcinogenic potency slope inhaled (risk per mg/kg/d) or cancer slope factor SF

EDc, the exposure duration, age 1-6 (y): 6

IRAc, the inhalation, child (m^3/d): 12

EDtot, the exposure duration in a residential setting, total (y): 30

IRAa, the inhalation, adult (m^3/d): 20

BWc, the body weight of child, age 1-6 (kg): 15

BWa, the body weight of adult (kg): 70

Table 5.1 RBCs for the contaminants used in the present Multimedia Model

Contaminant	Tap water ($\mu g/m^3$)	Ambient Air ($\mu g/m^3$)	Edible Fish (mg/kg)	Soil Industrial (mg/kg)	Soil Residential (mg/kg)	*Soil – Migration to Groundwater (mg/kg)
^{N}Toluene	7.5E5	4.2E2	2.7E2	4.1E5	1.6E4	4.4E-1
^{N}1-1-1 Trichloroethane	5.4E5	1.0E3	2.7E1	4.1E4	1.6E3	5.1E-1
^{C}TCE	1.6E3	1.0E0	2.9E-1	5.2E2	5.8E1	7.7E-4
^{N}Xylenes	1.2E7	7.3E3	2.7E3	4.1E6	1.6E5	8.5E0
Naphthalene	-	-	-	-	-	-

* Vadose soil concentration assuming zero dilution
N Non-carcinogenic effects
C Carcinogenic effects

5.2.2 Scenario Analysis using RBC Values

Of the list of chemicals presented in Table 5.1, TCE is a good candidate for use in the scenario analysis when the releases are curtailed to zero. This is especially true for the air sources where the RBC is within the reported background concentrations, with HUC11# 12, 13 and 15 having lower values than the RBC. The background water concentration of 3.41E2 $\mu g/m^3$ is much smaller than the TCE tap water RCB value of 1.6E3 $\mu g/m^3$ and time required to reach this RBC is too great. Thus a value slightly less that the RBC is used, this background concentration is taken as 1.59 $\mu g/m^3$. Similarly, the background concentrations of 3.89E4 $\mu g/m^3$ and 4.43E2 $\mu g/m^3$ were used for the surface soil and vadose soil, respectively. The remaining compartments are simulated using zero release and background concentrations. The summary of the background levels is presented in Table 5.2.

Table 5.2 Initial (Background) Media TCE Concentrations in μg/m^3

Media	Air	*Water	*Surface Soil	Sediment	Plant	Root Soil	*Vadose Soil
HUC#12	0.08	1.59E3	3.89E4	0	0	0	4.43E2
HUC#13	0.08	1.59E3	3.89E4	0	0	0	4.43E2
HUC#15	0.08	1.59E3	3.89E4	0	0	0	4.43E2
HUC#18	50	1.59E3	3.89E4	0	0	0	4.43E2
HUC#19	2.60	1.59E3	3.89E4	0	0	0	4.43E2
HUC#25	50	1.59E3	3.89E4	0	0	0	4.43E2
HUC#27	50	1.59E3	3.89E4	0	0	0	4.43E2
HUC#31	50	1.59E3	3.89E4	0	0	0	4.43E2
HUC#33	2.60	1.59E3	3.89E4	0	0	0	4.43E2
HUC#35	50	1.59E3	3.89E4	0	0	0	4.43E2
HUC#37	2.60	1.59E3	3.89E4	0	0	0	4.43E2
Passaic	15.4	1.59E3	3.89E4	0	0	0	4.43E2

*Concentrations taken as slightly different from BRCs

Using the background concentrations shown in Table 5.2, a simulation of TCE release using the multimedia model was performed and the results are compared against the RBCs. The surface soil concentration is compared to the residential soil RBC for the soil ingestion pathway and the vadose soil concentrations are compared to the RBC soil for migration to groundwater and not with the other soil compartments. The reasoning for this choice is trivial since the vadose compartment is in direct contact with the groundwater and its concentration is significantly different from the other top-soil layers which are different in physical characteristics and contaminant fate calculations. The comparison between the media specific RBCs and the multimedia resultant concentration for the different media are presented in Figures 5.13 through 5.17. In these figures the RBCs values are shown using horizontal lines since they are constants. These RBCs have limitations that must be considered before use, they are outlined in RBC Table Users Guide (EPA, 1999).

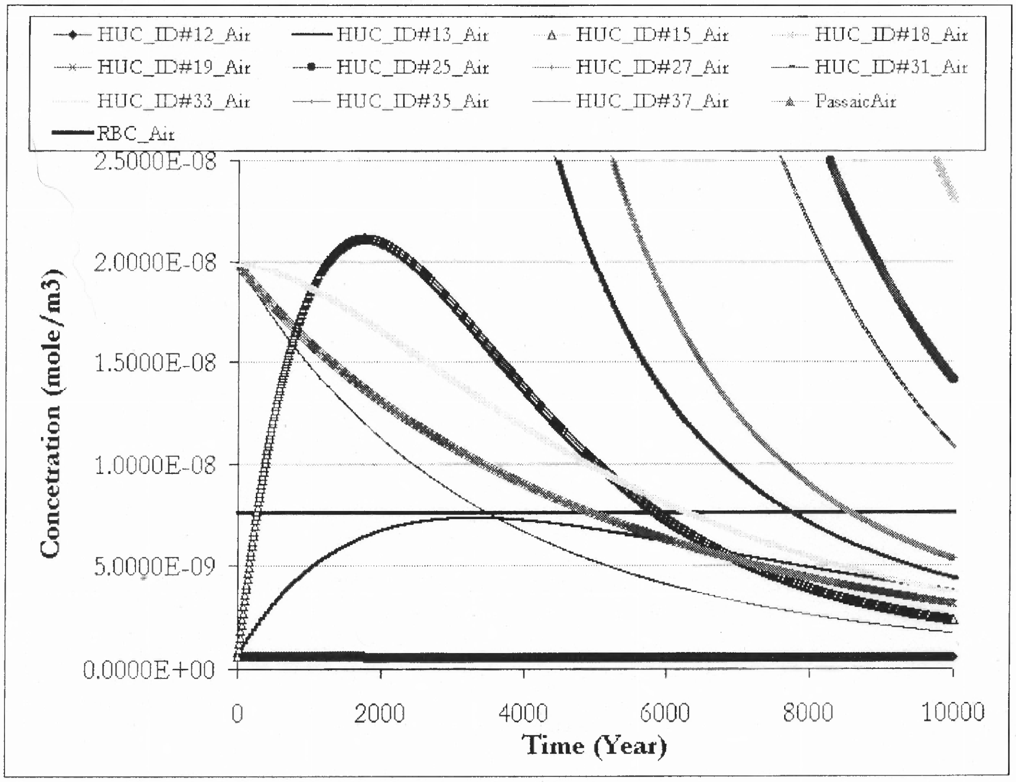


Figure 5.13 Simulation vs. Air RBC of TCE

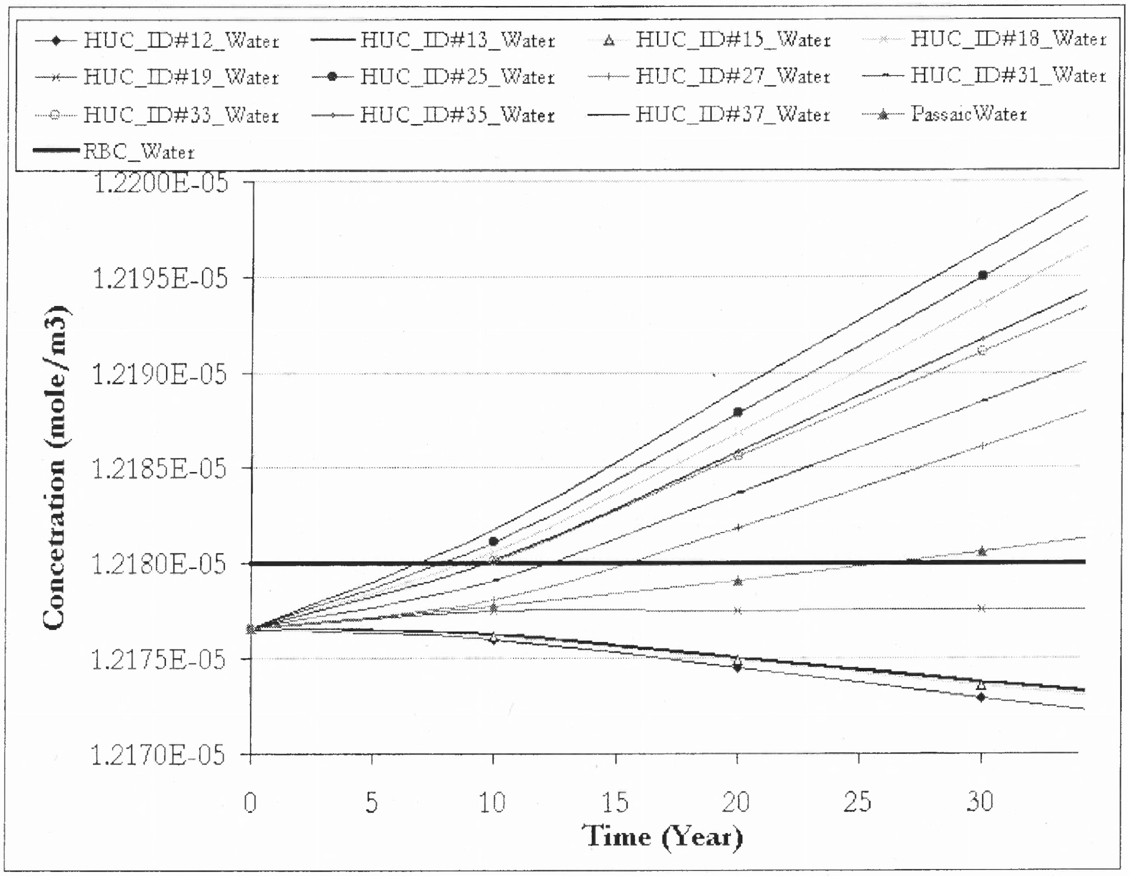


Figure 5.14 Simulation vs. Water RBC of TCE

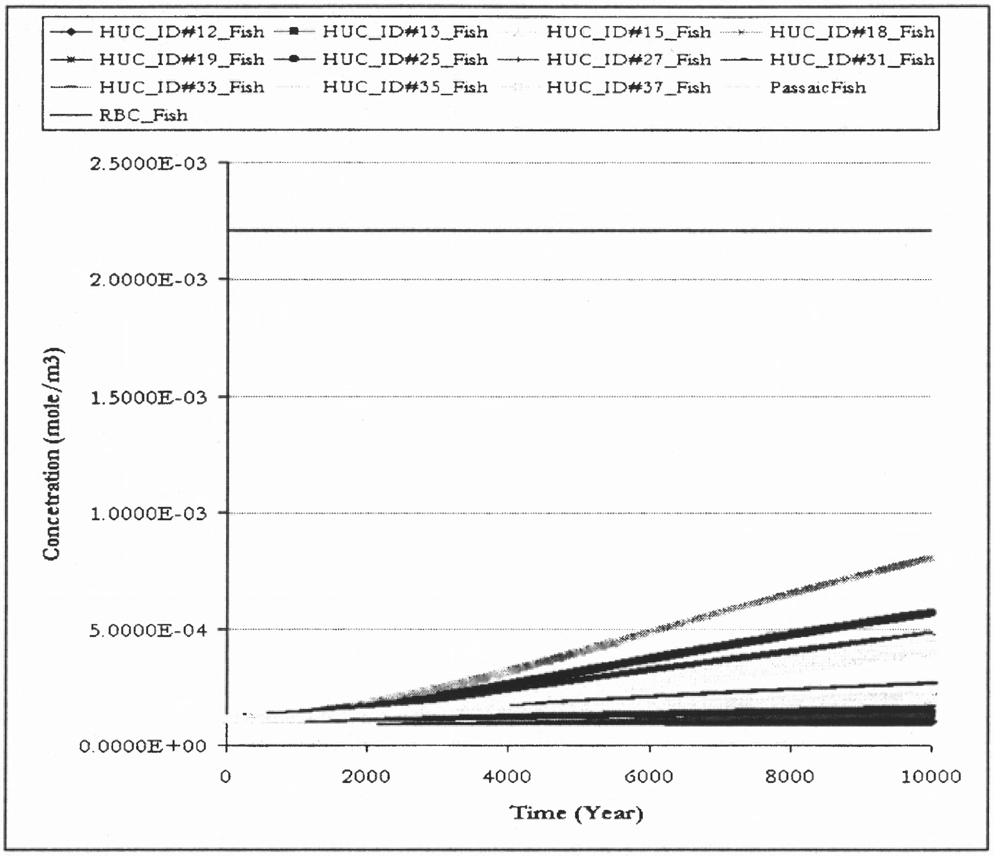


Figure 5.15 Simulation vs. Edible Fish RBC of TCE

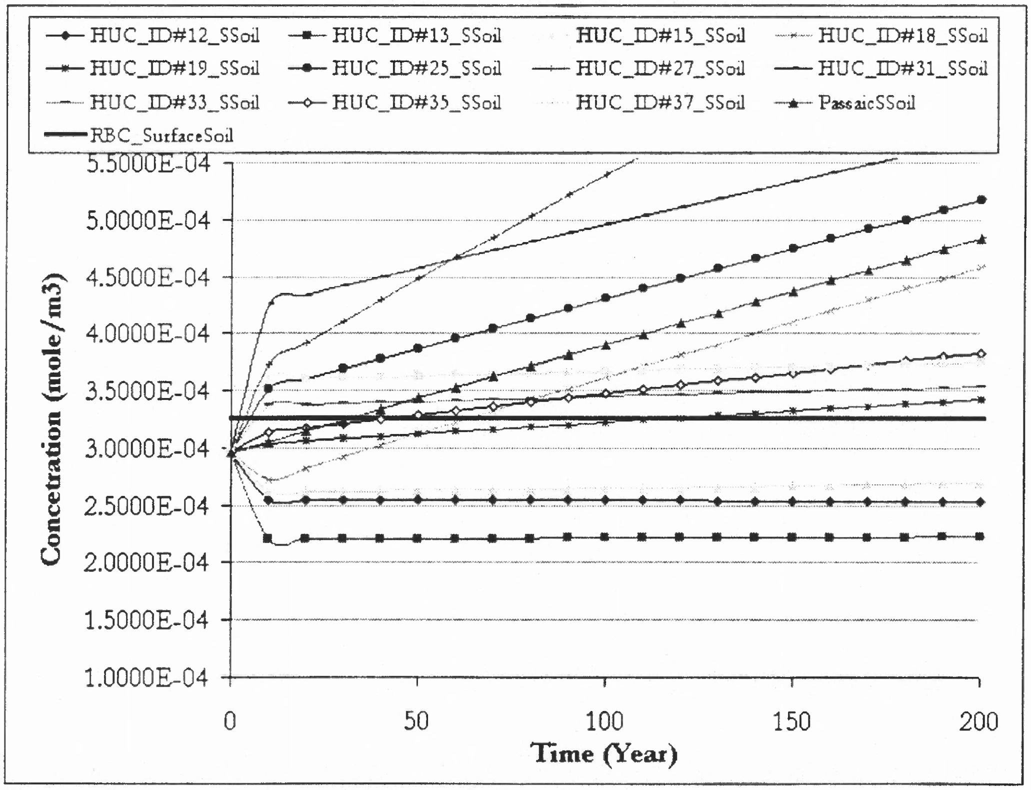


Figure 5.16 Simulation vs. Surface RBCs of TCE

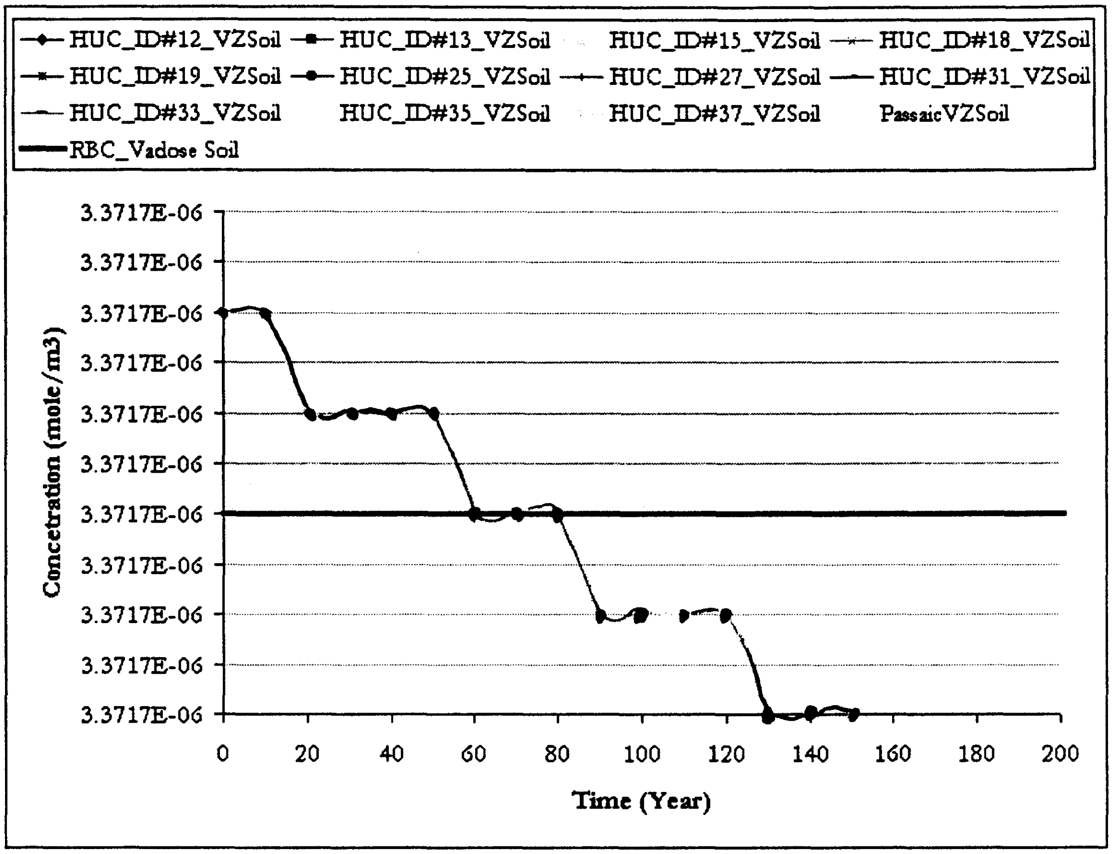


Figure 5.17 Simulation vs. Vadose RBCs of TCE

In the above figures, using the initial concentrations shown in Table 5.2, the ambient air RBC of TCE is reached in a reasonable amount of time for only HUC#15 and is not reached for HUC# 12 and 13. For these three non-urban sub-watersheds, the initial concentrations used are much lower than the RBC (only 8% of the RBC) and consequently, they increased with time by receiving advective inflows from neighboring sub-watersheds. For sub-watersheds HUC# 33, 19 and 37 the initial concentrations are 260% of the RBC. Here the concentrations decrease with time and reach acceptable levels after a long period, a time greater than 1000 years. And for the remaining urban sub-watersheds where the initial levels are 5000% of the RBC, the required time to reach the RBC level is even higher. For these latter sub-watersheds the "Non-attainment" designation may be appropriate for TCE since no reduction measure will reduce the background levels to acceptable exposure concentration in a reasonable time frame. The non-attainment designation area is available from EPA but only for certain criteria contaminants such as NOx, SOx, Ozone and particulate, using extensive monitoring data. The current model can be used to make a better use of these data by estimating the time required for the non-attainment areas to reach attainment and to extend the classification to organic contaminants.

The water exposure concentrations estimated with the multimedia model are compared with RBC using the 1.59E3 $\mu g/m^3$ initial concentration. The exposure levels attain the RBC in less than 10 years in HUC# 37, 25, 18, 35 and 33 as they steadily increase with time. Also in HUC# 31, 27 and in the entire watershed as one unit, the RBC is reached after 12, 16 and 26 years, respectively. In these units, the high water background levels coupled with the high background concentration in the air compartment contribute to the increase in water concentration. Although most of these units do not receive any advective inflows or release, the multimedia transfers affect the water concentration with time. This is a significant advantage in using multimedia approach. This is an important observation with regulatory implications in that the medium of concern may indeed represent a sink rather than a source of contamination. Therefore, to curtail environmental exposures in this case will require an understanding of the contaminant transfer from air and soil to the water bodies and for any reduction measure to be effective, the sources (air and soil compartments) must be first addressed. The exposure concentrations in HUC# 19, 15, 13 and 12 are less than the RBC and thus would not require any further reduction effort in contaminant release.

The edible fish concentrations shown in Figure 5.13 display similar characteristics with the water concentrations. The fish concentration is basically derived from the water and sediment concentrations in the present multimedia model. In the current RBC analysis, it is shown in Figure 5.15 that the exposure via consumption of fish is not significant in a near future. The migration pathway to the groundwater from soil concentration is shown in Figure 5.17 to decrease with time and reach RBC after 60 years using the current background data. Because the simulation was performed using zero root soil concentration, no significant contribution is made to the vadose soil compartment and the levels decrease due to leaching and degradation losses.

Finally, the surface soil concentrations shown in Figure 5.16 are strongly influenced by the air concentration via deposition and foliage losses. With the exception of HUC# 12, 13 and 15 the environmental exposure concentrations from the multimedia model quickly reach the RBC. The estimated time is less than 10 years for HUC# 31, 27, 37, 25 and 33. This time is about 50 years or less for HUC# 35, 18, 19 and the Passaic River Basin as one unit. It should be kept in mind that the above analysis, although detailed in scope, was performed using reported national background concentrations which may not be representative of the Passaic River Basin releases. However, such an analysis will provide environmental regulators with a wealth of knowledge on the relative importance of the sources and sinks of a contaminant and assist them in making effective long-term decisions in reducing environmental exposures of toxic chemicals.

CHAPTER 6

CONCLUSIONS

In the present study, a multimedia dynamic model was successfully developed and implemented for the assessment of 5 priority contaminants in the Passaic River Watershed in northern New Jersey. The results of this model were used to identify the major sinks of contamination, the important transport vectors, the relative importance of each source on the overall contamination and the analysis of different scenarios that can be used to curtail a particular pollution. A successful validation of the current model was carried out. Finally, the importance in using accurate environmental background concentration and advective influxes into the watershed environment was investigated. These points are developed into this closing chapter of the present research and constitute the contribution of this dissertation to the field of environmental assessment.

6.1 Model Development

The goal of the present research was to develop an assessment tool for the prediction of organic contaminants fate in the Passaic River Watershed. This assessment was carried out using actual landscape and the available toxic release data. The main parts of this development included the formulation of the modeling approach to be used, the collection of landscape and contaminant release database and development and implementation of the code used to carry out the assessment.

A dynamic unsteady state fugacity (Level IV Fugacity) was developed as an improvement over the existing steady state non-equilibrium model (Level III), to take full advantage of the type of information provided by the level IV model. On such important advantage is the introduction of variable wind speed and wind direction regimes. This effect of up wind locations on local contamination has been recognized by researchers but never quantified using a simple model. As a result of the present model, it was observed that for certain contaminants (e.g. Toluene) these advective inflows are indeed important and their actual impact was quantitatively estimated and compared to other gains of contaminant in the watershed such as the releases.

As part of the present model development, a greater level of spatial resolution was sought after and the improvement in using a greater resolution was characterized. The watershed was modeled in two separate modes; the entire watershed as one environmental unit was done in current models, and the watershed composed of 11 sub-watersheds, each representing a separate unit. This division of the Passaic River Watershed improved the model results of environmental concentrations by several orders of magnitude, especially for immobile compartments such the soil layers and the sediment compartment. Another advantage in using the sub-watershed representation was the estimation of cross boundary contribution to local contamination. Furthermore, this contribution is comparable to the local release and environmental decisions can be more effectively made in reducing contamination. Finally, because the model is developed using GIS data sets, its results are also displayed in spatial format, time series representation of media concentrations and tables of mass distribution, intermedia transfers and gain and losses of contaminant mass in the 7 bulk compartments.

An integral part of the multimedia model development was the landscape characterization, because the landscape parameters such as organic carbon content are as important as the contaminant physical and chemical properties in the multimedia model. They have a direct impact on the fate and transport of the contaminant and were collected and re-derived using the soil database from the New Jersey Department of Environmental

Protection, the Soil Conservation Services soil data and United State Geological Survey. Because these data were not appropriate for multimedia application in their present form, a significant part of this study was directed at deriving appropriate data, specifically, the re-definition of the soil, atmosphere and hydrologic data on a watershed basis -- see Chapter 3. As a result a complete landscape database of the Passaic River Watershed is now readily available on most hydrologic parameters and the methodology outlined can be used for other watersheds in New Jersey and elsewhere. It was recommended that future landscape data be made available for hydrologic units such as watershed instead of the current legislative unit such as a county. The watershed represents a much better representation of the actual environment processes such as advective water flows.

The final part of the model formulation involved the characterization of the environmental background concentrations and summarizing the contaminant releases in the Passaic River Watershed. The release summary was performed using the EPA TRI database and was done for each of the 11 sub-watersheds that comprise the Passaic River Basin. Because the TRI data were distributed per county basis, a new analysis was performed to derive them on a watershed basis using geocoding in ArcView GIS. Although the TRI database does not account for all the releases in an environmental unit, it is still a better tool for the assessment of contaminants using a multimedia model mainly, because it provided the contaminant in term of mass. The second part of the contaminant input summary was the characterization of the background and advective inflows. Background concentrations for the five priority contaminants are used in the present model. However, these data were not specific as they are provided on a per state or national basis. The present model was designed to handle contaminant input using mass input (TRI), background (e.g. initial values) concentrations and advective inflows for cross boundary contributions. These features combined to make the present multimedia model a much better assessment tool than the existing multimedia models reviewed in this research, specially for large environmental units like a watershed.

6.2 Validation and Results

A numerical model by definition estimates actual environmental process using simplifying assumptions. Therefore, before such a model can be accepted for popular use, it must be first validated using actual field data. However, this type of validation is feasible in control environment applications (e.g. laboratory setting) and for site specific model application where all the parameters are measured with little variation. For large area applications such as watershed, regional or continental, true validation is not possible and thus, the accuracy of the present model was checked by comparing its results against the results of another established and peer reviewed multimedia mode. The model chosen for this validation was "ChemCAN version4" which was developed to assess the fate of contaminants in different Canadian provinces (Mackay, 1996). Furthermore, there is little or no extensive monitoring data for the 5 priority contaminants used and the release data are not well characterized.

The present model was successfully validated and the compartment concentrations that resulted from the models simulations were very similar for the air, water, fish and sediment compartments. The points of divergence between the two models results were in the soil layers concentrations with the surface soil of the present model having higher concentrations than the ChemCAN soil layer while the root and vadose soil have lower concentrations than the ChemCAN soil. This difference is attributed to the way the two models represent the soil compartment, as one uniformly mixed compartment in ChemCAN and as composed of 3 distinct layers with very different physical characteristics in the present model. It was observed that for all the contaminants, the ChemCAN soil concentrations were within the range of three soil layers (surface, root and vadose) in the present multimedia model.

The multimedia model was used to simulate the release of 5 priority contaminants for different simulation periods. The results were mapped into GIS and provided a spatial assessment of the contamination. A detailed analysis was performed for toluene and less detailed descriptions of the remaining contaminants were also accomplished. These results are summarized as follows:

1. When background concentrations are not included, the current releases reached steady levels only after very long period of simulation. For example, this time is in the order of 2000 years for toluene. It can be concluded that the steady state model (Level III or lower) concentrations are not practical because of the excessive time duration needed to reach such levels, and thus the level IV provided a significant improvement over the existing level III modeling approach.
2. The use of reported background concentrations causes uncertainties in the model results, primarily the lack of temporal variation in the air and water media. The background concentrations are scarcely available and only for air and water, thus arbitrary values must be assigned to the remaining 5 bulk compartments. In our analysis, a zero concentration was used for these compartments and the model resulted in steady increase in concentration there but showed little variation in air and water compartments. Here also it can be concluded that the current releases have limited impact on the overall watershed exposure concentration if we assume that the reported background concentrations are accurate.

3. The impact of advective inflows and background concentrations were analyzed separately in the assessment of toluene. It was observed that the background concentrations were much more important to the overall contamination than the advective inflows. Similar values were used for both advective and background contributions.
4. The distribution of the contaminants in the environment was according to the contaminant physical characteristics. Xylene-Toluene pair showed a relatively fair distribution among the air, water and soil compartment while the TCE-1-1-1 Trichloroethane pair was mainly distributed in the soil and air. Finally, Naphthalene distributed almost entirely in the soil compartments (greater than 90% of total mass).
5. For 5 contaminants the air-vegetation root soil-vegetation and vegetation surface soil were important processes in their intermedia transfers. The Xylene-Toluene pair also had important air-surface soil exchanges because of their relatively high volatility. The naphthalene has also a strong air-water intermedia transfer in addition to the above transfers. This latter part is attributed to the naphthalene high volatility, which removes it from soil, water and vegetation in favor of the air compartment.
6. Finally, because all the 5 chemicals have relatively high sorption capacity, the surface soil to surface water or leaching through soil layers are the least important intermedia transfers in the Passaic River environment.

6.3 Scenario Analysis

One of the main objectives in developing the present multimedia model was the need to have an assessment tool capable of performing contamination reduction scenario analysis. For this purpose a dynamic (Level IV) fugacity model was developed to provide the behavior of a particular contaminant with time, and to observe the changes caused by contaminant release rates. This ability was fully deployed by setting environmental background concentrations at or near the risk-based concentrations in air, water, fish, surface soil and vadose soil and estimating the required time to reach acceptable levels. Acceptable level here is synonymous with RBC value and the analysis was performed essentially for TCE.

The air background levels were higher than the air RBC value for all the environmental units except HUC# 12, 13 and 15. In HUC# 12 and 13 the RBC value is never reached while the HUC# 15 air concentration increase pass it. Furthermore, it was shown that although no release occur in these units, the exposure level changed with time accounting for the advective exchange between approximate environmental units. For the remaining units, the predicted exposure levels reached acceptable levels only after very long period (order of 1000 years). This could be designated as non-attainment areas as per the high level of background levels and insignificant effect that any reduction in contaminant release will have on the overall exposure levels.

Because of the intermedia transfers represented in the multimedia model, the predicted exposure concentrations in water and surface soil increased for certain environmental units and reached RBC level in relatively short period of time (e.g. 10 years) while other units showed decisive improvement in contamination levels. These points helped highlighted the advantages in using multimedia models by showing a decrease or increase in media concentrations instead of no variation whith a traditional modeling approach. The vadose zone soil concentrations showed a continuous decline since this compartment receive no gains while allowing for degradation and leaching losses.

APPENDIX A

CONTAMINANTS' PHYSICAL AND CHEMICAL PROPERTIES SUMMARY

The contaminant properties that impact its fate in the environment are important in multimedia modeling. These properties are described in Chapter 1 for PCB and Dioxin and in Chapter 3 for the five contaminants used in the present dissertation. These properties are summarized below. Also provided is a summary of the characteristics of aquatic biota in the harbor.

PROGRAM 'QWASI', CALCULATION OF THE FATE OF DOXIN IN THE NY HARBOR

Physical-chemical, Partitioning and Related Properties

```
-----------------------------------------------------------------
| Temperature in deg C                                  |    12      |
| Temperature in deg K                                  |    285     |
| Gas constant (J/mol K)                                |   8.314    |
| Molecular mass (g/mol)                                |    322     |
| Melting point (deg C) (system temp. for liquids)      |    305     |
| Solubility (g/m3)                                     | 5.99E-08   |
| Solubility (mol/m3)                                   | 1.86E-10   |
| Vapor pressure (Pa)                                   | 2.00E-07   |
| Subcooled liquid vapor pressure (Pa)                  | 2.15E-04   |
| Fugacity ratio                                        | 9.30E-04   |
| Henry's Law constant (Pa.m3/mol)                      | 1.08E+03   |
| Air-water partition coefficient                       | 4.54E-01   |
```

```
| Log octanol-water partition coefficient        |    6.80     |

| Octanol-water partition coefficient            |  6.31E+06   |

| Organic carbon partition coefficient           |  2.59E+06   |


PROGRAM 'FISH',UPTAKE AND CLEARARCE CHARACTERISTICS OF DIOXIN


LOG Kow                                   6.8

MOLECULAR MASS g/mol                      322

HENRY'S LAW CONSTANT (Pa m3/mol)          3.34

Z VALUES mol/m3.Pa FOR WATER              .2994012

             LIPID (OCTANOL)              1889095

             FISH                         132236.6

             FOOD                         94454.73

             PARTICLES                    133838.6

             BULK WATER                   3.903562


ENVIRONMENTAL CONDITIONS AND FISH PROPERTIES


FISH VOLUME m3 and cm3                    2.83266E-03         2832.66

VOLUME FRACTION LIPID IN FISH             .07

LIPID VOLUMES m3 and cm3                  1.982862E-04         198.2862

FEEDING RATE % BY VOLUME PER DAY          2

VOLUME FRACTION LIPID IN FOOD             .05

GROWTH RATE FRACTION BY VOLUME PER DAY              .001
```

```
METABOLISM RATE CONSTANT AND HALF TIME (h)           .000275       2520

METABOLISM RATE CONSTANT & HALF TIME (days)          .0066         105

GILL UPTAKE RESISTANCE (WATER) TIME (h)              .001

GILL UPTAKE RESISTANCE (ORGANIC) TIME (h)            300

GUT ABSORPTION PARAMETER (WATER)                     .0000001

GUT ABSORPTION PARAMETER (ORGANIC)                   2

GUT ABSORPTION EFFICIENCY                            .3800897

EQUILIBRIUM BIOCONCENTRATION FACTOR                  441670.3

ACTUAL BIOCONCENTRATION FACTOR                       23537.04

GUT DIGESTION FACTOR QD                              3

SUSPENDED PARTICULATE CONCENTRATION g/m3             64.63

SUSPENDED PARTICULATE VOLUME FRACTION                2.692916E-05

SUSPENDED PARTICULATE DENSITY kg/m3                  2400

ORGANIC C CONTENT OF SUSP PARTICULATES               .072

RATIO OF FOOD TO WATER FUGACITIES                    1


PROGRAM 'QWASI', CALCULATION OF THE FATE OF PCB in NY HARBOR


Physical-chemical, Partitioning and Related Properties

 ------------------------------------------------------------

| Temperature in deg C                     |    12    |

| Temperature in deg K                     |   285    |

| Gas constant (J/mol K)                   |  8.314   |

| Molecular mass (g/mol)                   |   326    |
```

```
| Melting point (deg C) (system temp. for liquids)   |     12      |
| Solubility (g/m3)                                  |  2.40E-02   |
| Solubility (mol/m3)                                |  7.36E-05   |
| Vapor pressure (Pa)                                |  9.00E-04   |
| Subcooled liquid vapor pressure (Pa)               |  9.00E-04   |
| Fugacity ratio                                     |  1.00E+00   |
| Henry's Law constant (Pa.m3/mol)                   |  1.22E+01   |
| Air-water partition coefficient                    |  5.16E-03   |
| Log octanol-water partition coefficient            |    6.60     |
| Octanol-water partition coefficient                |  3.98E+06   |
| Organic carbon partition coefficient               |  1.63E+06   |
```

```
PROGRAM 'FISH',UPTAKE AND CLEARARCE CHARACTERISTICS OF PCB


LOG Kow                                   6.6
MOLECULAR MASS g/mol                      326
HENRY'S LAW CONSTANT (Pa m3/mol)         12.2
Z VALUES mol/m3.Pa FOR WATER              8.196721E-02
              LIPID (OCTANOL)             326317.3
              FISH                        22842.21
              FOOD                        16315.86
              PARTICLES                   23118.93
              BULK WATER                  .7045406
```

APPENDIX B

PASSAIC RIVER WATERSHED LANDSCAPE CHARACTERISTICS

Sub-Watershed HUC# 12

LANDSCAPE CHARATERISTICS & CONTAMINANT FUGACITY CAPACITIES

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density(kg/m
1-Air	1000	2.052e+011	0.0004036	1.186
2-Water	3.5	7.217e+007	0.001492	1000
3-Surface Soil	0.2	3.691e+007	0.03175	1490
4- Sediment	0.05	1.031e+006	0.007341	1140
5-Vegetation	0.5	6.924e+007	0.0369	900
6-RootZone Soil	0.56	1.033e+008	0.001323	1737
7-VadoseZone Soil	9.13	1.685e+009	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	6.67e-012	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	6.7e-006	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.289	0.0004036	1.186	
3-2 SSoil Water	0.239	0.001489	1000	
3-3 SSoil Particles	0.472	0.06627	2650	0.029
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02187	900	
5-3 Plant Roots	0.5	0.05194	900	
6-1 RZSoil Gas	0.22	0.0004036	1.186	
6-2 RZSoil Water	0.2	0.001489	1000	
6-3 RZSoil Particles	0.58	0.00457	2650	0.002
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC#13

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density(kg/m3)
1-Air	1000	2.25e+011	0.0004036	1.186
2-Water	3.5	5.253e+007	0.001492	1000
3-Surface Soil	0.25	5.25e+007	0.03689	1463
4- Sediment	0.05	7.505e+005	0.007341	1140
5-Vegetation	0.5	7.663e+007	0.03347	900
6-RootZone Soil	0.54	1.134e+008	0.0008701	1721
7-VadoseZone Soil	0.8	1.68e+008	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	6.67e-012	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	6.7e-006	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.288	0.0004036	1.186	
3-2 SSoil Water	0.257	0.001489	1000	
3-3 SSoil Particles	0.455	0.07998	2650	0.035
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02187	900	
5-3 Plant Roots	0.5	0.04507	900	
6-1 RZSoil Gas	0.22	0.0004036	1.186	
6-2 RZSoil Water	0.21	0.001489	1000	
6-3 RZSoil Particles	0.57	0.002285	2650	0.001
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 15

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density
1-Air	1000	1.238e+011	0.0004036	1.186
2-Water	3.5	2.775e+007	0.001492	1000
3-Surface Soil	0.19	2.202e+007	0.0307	1539
4- Sediment	0.05	3.964e+005	0.007341	1140
5-Vegetation	0.5	3.127e+007	0.02994	900
6-RootZone Soil	0.55	6.376e+007	0.001815	1747
7-VadoseZone Soil	9.15	1.061e+009	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	1.17e-011	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	6.7e-006	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.27	0.0004036	1.186	
3-2 SSoil Water	0.24	0.001489	1000	
3-3 SSoil Particles	0.49	0.0617	2650	0.027
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02189	900	
5-3 Plant Roots	0.5	0.03798	900	
6-1 RZSoil Gas	0.21	0.0004036	1.186	
6-2 RZSoil Water	0.21	0.001489	1000	
6-3 RZSoil Particles	0.58	0.00457	2650	0.002
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 18

1-Air	1000	1.333e+011	0.0004036	1.186
2-Water	3.5	1.056e+007	0.001494	1000
3-Surface Soil	0.2	2.605e+007	0.03069	1531
4- Sediment	0.05	1.508e+005	0.007341	1140
5-Vegetation	0.5	6.899e+006	0.02332	900
6-RootZone Soil	0.6	7.815e+007	0.006419	1747
7-VadoseZone Soil	0.95	1.237e+008	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC conter
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	1.01e-011	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	1.3e-005	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.278	0.0004036	1.186	
3-2 SSoil Water	0.232	0.001489	1000	
3-3 SSoil Particles	0.49	0.0617	2650	0.027
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02188	900	
5-3 Plant Roots	0.5	0.02475	900	
6-1 RZSoil Gas	0.21	0.0004036	1.186	
6-2 RZSoil Water	0.21	0.001489	1000	
6-3 RZSoil Particles	0.58	0.01143	2650	0.005
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 19

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density
1-Air	1000	3.545e+011	0.0004036	1.186
2-Water	3.5	7.756e+007	0.001492	1000
3-Surface Soil	0.23	7.644e+007	0.02595	1498
4- Sediment	0.05	1.108e+006	0.007341	1140
5-Vegetation	0.5	9.448e+007	0.02953	900
6-RootZone Soil	0.53	1.762e+008	0.001054	1721
7-VadoseZone Soil	3.04	1.01e+009	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	7.92e-012	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	6.7e-006	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.268	0.0004036	1.186	
3-2 SSoil Water	0.268	0.001489	1000	
3-3 SSoil Particles	0.464	0.05484	2650	0.024
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02187	900	
5-3 Plant Roots	0.5	0.0372	900	
6-1 RZSoil Gas	0.22	0.0004036	1.186	
6-2 RZSoil Water	0.21	0.001489	1000	
6-3 RZSoil Particles	0.57	0.002285	2650	0.001
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 25

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density
1-Air	1000	1.965e+011	0.0004036	1.186
2-Water	3.5	2.016e+007	0.001494	1000
3-Surface Soil	0.24	4.578e+007	0.02302	1574
4- Sediment	0.05	2.88e+005	0.007341	1140
5-Vegetation	0.5	1.399e+007	0.02373	900
6-RootZone Soil	0.62	1.183e+008	0.00386	1737
7-VadoseZone Soil	9.02	1.721e+009	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	1.2e-011	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	1.3e-005	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.286	0.0004036	1.186	
3-2 SSoil Water	0.193	0.001489	1000	
3-3 SSoil Particles	0.521	0.04342	2650	0.019
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.0219	900	
5-3 Plant Roots	0.5	0.02557	900	
6-1 RZSoil Gas	0.22	0.0004036	1.186	
6-2 RZSoil Water	0.2	0.001489	1000	
6-3 RZSoil Particles	0.58	0.006855	2650	0.003
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 27

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density
1-Air	1000	6.218e+010	0.0004036	1.186
2-Water	3.5	9.938e+006	0.001494	1000
3-Surface Soil	0.22	1.306e+007	0.02161	1485
4- Sediment	0.05	1.42e+005	0.007341	1140
5-Vegetation	0.5	8.797e+006	0.02582	900
6-RootZone Soil	0.6	3.561e+007	0.002318	1711
7-VadoseZone Soil	9.07	5.382e+008	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	1.14e-011	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	1.3e-005	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.278	0.0004036	1.186	
3-2 SSoil Water	0.26	0.001489	1000	
3-3 SSoil Particles	0.462	0.0457	2650	0.02
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02189	900	
5-3 Plant Roots	0.5	0.02974	900	
6-1 RZSoil Gas	0.23	0.0004036	1.186	
6-2 RZSoil Water	0.2	0.001489	1000	
6-3 RZSoil Particles	0.57	0.00457	2650	0.002
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 31

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density
1-Air	1000	5.049e+010	0.0004036	1.186
2-Water	3.5	7.784e+006	0.001494	1000
3-Surface Soil	0.19	9.171e+006	0.01736	1466
4- Sediment	0.05	1.112e+005	0.007341	1140
5-Vegetation	0.5	3.152e+006	0.02438	900
6-RootZone Soil	0.58	2.799e+007	0.005915	1638
7-VadoseZone Soil	9.12	4.402e+008	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	1.2e-011	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	1.3e-005	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.247	0.0004036	1.186	
3-2 SSoil Water	0.321	0.001489	1000	
3-3 SSoil Particles	0.432	0.03885	2650	0.017
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.0219	900	
5-3 Plant Roots	0.5	0.02686	900	
6-1 RZSoil Gas	0.27	0.0004036	1.186	
6-2 RZSoil Water	0.18	0.001489	1000	
6-3 RZSoil Particles	0.55	0.01143	2650	0.005
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 33

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density
1-Air	1000	1.805e+011	0.0004036	1.186
2-Water	3.5	1.802e+007	0.001494	1000
3-Surface Soil	0.25	4.383e+007	0.02296	1507
4- Sediment	0.05	2.574e+005	0.007341	1140
5-Vegetation	0.5	2.608e+007	0.02636	900
6-RootZone Soil	0.63	1.104e+008	0.003225	1694
7-VadoseZone Soil	2.69	4.716e+008	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	1.14e-011	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	1.3e-005	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.266	0.0004036	1.186	
3-2 SSoil Water	0.266	0.001489	1000	
3-3 SSoil Particles	0.468	0.04799	2650	0.021
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02189	900	
5-3 Plant Roots	0.5	0.03084	900	
6-1 RZSoil Gas	0.23	0.0004036	1.186	
6-2 RZSoil Water	0.21	0.001489	1000	
6-3 RZSoil Particles	0.56	0.006855	2650	0.003
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 35

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density
1-Air	1000	1.389e+011	0.0004036	1.186
2-Water	3.5	1.314e+007	0.001494	1000
3-Surface Soil	0.18	2.433e+007	0.02583	1599
4- Sediment	0.05	1.878e+005	0.007341	1140
5-Vegetation	0.5	2.959e+006	0.02228	900
6-RootZone Soil	0.64	8.651e+007	0.005652	1780
7-VadoseZone Soil	9.07	1.226e+009	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	1.5e-011	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	1.3e-005	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.276	0.0004036	1.186	
3-2 SSoil Water	0.194	0.001489	1000	
3-3 SSoil Particles	0.53	0.04799	2650	0.021
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02191	900	
5-3 Plant Roots	0.5	0.02264	900	
6-1 RZSoil Gas	0.21	0.0004036	1.186	
6-2 RZSoil Water	0.19	0.001489	1000	
6-3 RZSoil Particles	0.6	0.00914	2650	0.004
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Sub-Watershed HUC# 37

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density
1-Air	1000	3.71e+011	0.0004036	1.186
2-Water	3.5	3.299e+007	0.001494	1000
3-Surface Soil	0.24	8.677e+007	0.02152	1521
4- Sediment	0.05	4.714e+005	0.007341	1140
5-Vegetation	0.5	5.389e+007	0.02672	900
6-RootZone Soil	0.63	2.278e+008	0.003158	1668
7-VadoseZone Soil	16.3	5.893e+009	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	7.92e-012	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	1.3e-005	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.28	0.0004036	1.186	
3-2 SSoil Water	0.235	0.001489	1000	
3-3 SSoil Particles	0.485	0.04342	2650	0.019
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02187	900	
5-3 Plant Roots	0.5	0.03157	900	
6-1 RZSoil Gas	0.24	0.0004036	1.186	
6-2 RZSoil Water	0.21	0.001489	1000	
6-3 RZSoil Particles	0.55	0.006855	2650	0.003
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

Watershed PASSAIC

Main Compartment	Height(m)	Volume(m3)	Z (mol/Pa.m3)	Bulk-Density(kg/m
1-Air	1000	2.041e+012	0.0004036	1.186
2-Water	3.5	3.426e+008	0.001493	1000
3-Surface Soil	0.217	4.217e+008	0.02675	1516
4- Sediment	0.05	4.895e+006	0.007341	1140
5-Vegetation	0.5	3.874e+008	0.02759	900
6-RootZone Soil	0.589	1.145e+009	0.002522	1719
7-VadoseZone Soil	7.12	1.384e+010	0.002999	1738

Sub-Compartment	VolumeFraction	Z(mole/Pa.m3)	Density(kg/m3)	OC content
1-1 Pure Air	1	0.0004036	1.186	
1-3 Aerosols	9.41e-012	2.07	2400	
2-2 Pure water	1	0.001489	1000	
2-3 Water Particles	8.77e-006	0.4139	2400	0.2
2-4 Aquatic Biota	1e-006	0.1009	1000	
3-1 SSoil Gas	0.275	0.0004036	1.186	
3-2 SSoil Water	0.246	0.001489	1000	
3-3 SSoil Particles	0.479	0.05484	2650	0.024
4-2 Sediment Pore water	0.9	0.001489	1000	
4-3 Sediment Particles	0.1	0.06001	2400	0.029
5-1 Plant Foliage	0.5	0.02188	900	
5-3 Plant Roots	0.5	0.03329	900	
6-1 RZSoil Gas	0.225	0.0004036	1.186	
6-2 RZSoil Water	0.203	0.001489	1000	
6-3 RZSoil Particles	0.572	0.005713	2650	0.0025
7-1 VZSoil Gas	0.17	0.0004036	1.186	
7-2 VZSoil Water	0.28	0.001489	1000	
7-3 VZSoil Particles	0.55	0.00457	2650	0.002

APPENDIX C

ENVIRONMENTAL PROCESS RATES

The environmental processes controlling the fate and transport of the 5 priority contaminants in the present multimedia model were estimated and the results for Naphthalene are presented below. These processes differ for each chemical in the different sub-watersheds since the latter are different as shown in Appendix B. Furthermore, the introduction of spatial resolution in the present model showed a marked difference in these processes, this is observed by comparing the processes when modeling the entire watershed as one environmental unit against the sub-watersheds representation. Finally, since the multimedia model is dynamic (Level IV), these rates are time dependent and are displayed after 1000 years of simulation and using only the TRI releases as contaminant input.

Sub-Watershed HUC#12

```
TOTAL GAIN:
Emisions
Compt:            mol/h             kg/h              kg/year
1                 0.2637            0.0338            296.1
2                 0                 0                 0
3                 0                 0                 0
4                 0                 0                 0
5                 0                 0                 0
6                 0                 0                 0
7                 0                 0                 0
Total:            0.2637            0.0338            296.1

Advection:        mol/h             kg/h              kg/year
1_AIR:            0                 0                 0
2_WATER:          0                 0                 0

-------------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:      mol/h             kg/h              kg/year
1                 0.0152            0.001949          17.07
2                 0.0003274         4.197e-005        0.3676
3                 0.002851          0.0003655         3.202
4                 8.305e-006        1.065e-006        0.009326
5                 1.727e-005        2.214e-006        0.01939
6                 1.399e-008        1.794e-009        1.572e-005
7                 4.031e-009        5.167e-010        4.527e-006
Total:            0.01841           0.00236           20.67

Advection:        mol/h             kg/h              kg/year
1_AIR:            0.1128            0.01447           126.7
2_WATER:          9.356e-006        1.199e-006        0.01051

INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment       Rates(mol/h)      Rates(kg/y)       Dvalues(mol/Pa.h) Half-Lif
1 TO 2            2.026e-005        0.02276           4687              251.5
1 TO 3            5.405e-005        0.0607            1.25e+004         1245
1 TO 5            0.0269            30.21             6.221e+006        0.003112
2 TO 1            0.0003136         0.3522            4615              251.5
2 TO 4            1.087e-005        0.01221           160               6986
3 TO 1            0.0182            20.44             1.186e+004        1245
3 TO 2            0.0006619         0.7433            431.4             4.699e+0
3 TO 6            0.0003504         0.3935            228.4             4.841e+0
4 TO 2            2.425e-006        0.002723          11.58             4364
5 TO 1            0.02723           30.58             6.221e+006        0.003112
5 TO 3            0.02202           24.73             5.03e+006         0
6 TO 3            4.084e-010        4.587e-007        19.07             4.841e+0
6 TO 5            0.0003504         0.3935            1.636e+007        1.263e+0
6 TO 7            4.482e-009        5.034e-006        209.3             9703
7 TO 2            3.212e-011        3.608e-008        209.3             3.9e+005
```

```
INDIVIDUAL PROCESS RATES or FLUX
          mol/h            kg/year
____________AIR WATER INTERFACE_________________________________
Adsorption from Air:                     1.995e-005        0.221
Volatilization from Water:               0.0003136         3.473
Aerolols Dry Deposition:                 1.418e-009        1.571e-
Wet Deposition - Rain Dissolution:       3.087e-007        0.00341
____________AIR SOIL INTERFACE__________________________________
Adsorption from Air:                     5.128e-005        0.568
Volatilization from Soil:                0.0182            201.6
Aerolols Dry Deposition:                 1.418e-009        1.571e-
Wet Deposition - Rain Dissolution:       2.762e-006        0.0306
____________AIR PLANT INTERFACE_________________________________
Adsorption by Foliar Plant:              0.0269            297.9
Volatilization from Plants:              0.02723           301.6
Net Deposition onto Plants:              1.969e-018        2.181e-
____________WATER SEDIMENT INTERFACE____________________________
Adsorption to Sediment Layer:            6.917e-007        0.00766
Desorption from Sediment:                2.132e-006        0.02361
Sediment Deposition:                     1.018e-005        0.1128
Sediment Resuspension:                   2.932e-007        0.00324
Sediment Burial:                         2.932e-007        0.00032
____________SURFACE SOIL(1) SURFACE WATER INTERFACE_____________
Surface Water Runoff:                    0.0006603         7.314
Soil Erosion:                            1.557e-006        0.01725
____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE_________
Difusion(Air+Water) into Soil2:          2.926e-005        0.3241
Difusion(Air+Water) into Soil1:          4.084e-010        4.524e-
Infiltration/Leaching to Soil2:          0.0003211         3.557
____________PLANT ROOT ZONE SOIL(2) INTERFACE___________________
Net Plant Uptake:                        0.0003504         3.881
____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE_____
Leaching/Infiltration:                   4.482e-009        4.965e-
____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE___________
Leaching:                                3.212e-011        3.558e-


INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment       Rates(mol/h)      Rates(kg/h)       Rates(kg/y)
1                 0.04574           0.005864          51.37
2                 0.0006846         8.776e-005        0.7688
3                 0.02207           0.002829          24.79
4                 1.087e-005        1.394e-006        0.01221
5                 0.02725           0.003493          30.6
6                 0.0003504         4.492e-005        0.3935
7                 4.482e-009        5.747e-010        5.034e-006
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)      Rates(kg/h)       Rates(kg/y)
1                 0.02697           0.003458          30.29
2                 0.0003245         4.16e-005         0.3644
3                 0.01921           0.002463          21.57
4                 2.425e-006        3.109e-007        0.002723
5                 0.04925           0.006313          55.31
6                 0.0003504         4.492e-005        0.3935
7                 3.212e-011        4.118e-012        3.608e-008
```

Sub-Watershed HUC#13

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TOTAL GAIN:
Emisions
Compt:              mol/h             kg/h              kg/year
1                   0                 0                 0
2                   0                 0                 0
3                   0                 0                 0
4                   0                 0                 0
5                   0                 0                 0
6                   0                 0                 0
7                   0                 0                 0
Total:              0                 0                 0

Advection:          mol/h             kg/h              kg/year
1_AIR:              0                 0                 0
2_WATER:            0                 0                 0

-------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:        mol/h             kg/h              kg/year
1                   3.137e-005        4.022e-006        0.03523
2                   5.097e-007        6.535e-008        0.0005724
3                   7.576e-006        9.712e-007        0.008508
4                   1.247e-008        1.598e-009        1.4e-005
5                   3.356e-008        4.302e-009        3.769e-005
6                   1.483e-011        1.901e-012        1.665e-008
7                   5.856e-012        7.507e-013        6.576e-009
Total:              3.95e-005         5.064e-006        0.04436

Advection:          mol/h             kg/h              kg/year
1_AIR:              0.0002224         2.851e-005        0.2497
2_WATER:            5.267e-008        6.752e-009        5.915e-005
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INDIVIDUAL PROCESS RATES or FLUX
mol/h               kg/year
 ____________AIR WATER INTERFACE________________________________________
Adsorption from Air:                    2.733e-008        0.0003027
Volatilization from Water:              4.883e-007        0.005408
Aerolols Dry Deposition:                1.942e-012        2.151e-008
Wet Deposition - Rain Dissolution:      4.199e-010        4.651e-006
 ____________AIR SOIL INTERFACE________________________________________
Adsorption from Air:                    1.203e-007        0.001332
Volatilization from Soil:               3.645e-005        0.4037
Aerolols Dry Deposition:                1.942e-012        2.151e-008
Wet Deposition - Rain Dissolution:      5.874e-009        6.507e-005
 ____________AIR PLANT INTERFACE________________________________________
Adsorption by Foliar Plant:             5.471e-005        0.606
Volatilization from Plants:             5.53e-005         0.6126
Net Deposition onto Plants:             4.1e-021          4.542e-017
 ____________WATER SEDIMENT INTERFACE_______________________________________
Adsorption to Sediment Layer:           1.077e-009        1.193e-005
Desorption from Sediment:               3.2e-009          3.545e-005
Sediment Deposition:                    1.585e-008        0.0001756
Sediment Resuspension:                  4.403e-010        4.877e-006
Sediment Burial:                        4.403e-010        4.944e-007
 ____________SURFACE SOIL(1) SURFACE WATER INTERFACE_______________________
Surface Water Runoff:                   1.172e-006        0.01298
Soil Erosion:                           3.436e-009        3.806e-005
 ____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE___________________
Difusion(Air+Water) into Soil2:         3.133e-008        0.000347
Difusion(Air+Water) into Soil1:         4.425e-013        4.902e-009
Infiltration/Leaching to Soil2:         5.993e-007        0.006639
 ____________PLANT ROOT ZONE SOIL(2) INTERFACE__________________________
Net Plant Uptake:                       6.305e-007        0.006984
 ____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE_______________
Leaching/Infiltration:                  8.294e-012        9.187e-008
 ____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE_____________________
Leaching:                               5.326e-013        5.899e-009
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INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment         Rates(mol/h)        Rates(kg/y)         Dvalues(mol/Pa.h)   Half-Life
1 TO 2              2.775e-008          3.117e-005          3411                253.3
1 TO 3              1.262e-007          0.0001417           1.551e+004          1455
1 TO 5              5.471e-005          0.06144             6.725e+006          0.003186
2 TO 1              4.883e-007          0.0005483           3360                253.3
2 TO 4              1.693e-008          1.901e-005          116.5               6841
3 TO 1              3.645e-005          0.04093             1.478e+004          1455
3 TO 2              1.175e-006          0.00132             476.7               7.032e+004
3 TO 6              6.307e-007          0.0007083           255.8               5.802e+004
4 TO 2              3.641e-009          4.089e-006          8.43                4364
5 TO 1              5.53e-005           0.06211             6.725e+006          0.003186
5 TO 3              4.578e-005          0.05142             5.567e+006          0
6 TO 3              4.425e-013          4.97e-010           12.71               5.802e+004
6 TO 5              6.305e-007          0.0007081           1.81e+007           1.655e+015
6 TO 7              8.294e-012          9.314e-009          238.2               5556
7 TO 2              5.326e-013          5.981e-010          238.2               3.417e+004
```

```
INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment        Rates(mol/h)        Rates(kg/h)        Rates(kg/y)
1                  9.224e-005          1.182e-005         0.1036
2                  1.207e-006          1.547e-007         0.001355
3                  4.591e-005          5.886e-006         0.05156
4                  1.693e-008          2.17e-009          1.901e-005
5                  5.534e-005          7.094e-006         0.06214
6                  6.307e-007          8.085e-008         0.0007083
7                  8.294e-012          1.063e-012         9.314e-009
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)       Rates(kg/h)         Rates(kg/y)
1                  5.486e-005          7.033e-006         0.06161
2                  5.052e-007          6.477e-008         0.0005673
3                  3.825e-005          4.904e-006         0.04296
4                  3.641e-009          4.667e-010         4.089e-006
5                  0.0001011           1.296e-005         0.1135
6                  6.305e-007          8.083e-008         0.0007081
7                  5.326e-013          6.828e-014         5.981e-010
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Sub-Watershed HUC#15

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TOTAL GAIN:
Emisions
Compt:             mol/h               kg/h               kg/year
1                  0                   0                  0
2                  0                   0                  0
3                  0                   0                  0
4                  0                   0                  0
5                  0                   0                  0
6                  0                   0                  0
7                  0                   0                  0
Total:             0                   0                  0

Advection:         mol/h               kg/h               kg/year
1_AIR:             0                   0                  0
2_WATER:           0                   0                  0

---------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:       mol/h               kg/h               kg/year
1                  0.001925            0.0002468          2.162
2                  3.094e-005          3.967e-006         0.03475
3                  0.0002789           3.575e-005         0.3132
4                  7.764e-007          9.954e-008         0.000872
5                  1.289e-006          1.652e-007         0.001447
6                  2.065e-009          2.648e-010         2.319e-006
7                  3.891e-010          4.988e-011         4.37e-007
Total:             0.002237            0.0002867          2.512

Advection:         mol/h               kg/h               kg/year
1_AIR:             0.01839             0.002358           20.65
2_WATER:           1.687e-005          2.163e-006         0.01895
```

```
INDIVIDUAL PROCESS RATES or FLUX
mol/h             kg/year
 ____________AIR WATER INTERFACE____________________________________
Adsorption from Air:                    1.609e-006        0.01782
Volatilization from Water:              2.964e-005        0.3283
Aerolols Dry Deposition:                2.006e-010        2.222e-006
Wet Deposition - Rain Dissolution:      2.462e-008        0.0002727
 ____________AIR SOIL INTERFACE_____________________________________
Adsorption from Air:                    5.921e-006        0.06558
Volatilization from Soil:               0.001699          18.82
Aerolols Dry Deposition:                2.006e-010        2.222e-006
Wet Deposition - Rain Dissolution:      3.6e-007          0.003987
 ____________AIR PLANT INTERFACE____________________________________
Adsorption by Foliar Plant:             0.002576          28.54
Volatilization from Plants:             0.002601          28.81
Net Deposition onto Plants:             5.738e-019        6.356e-015
 ____________WATER SEDIMENT INTERFACE_______________________________
Adsorption to Sediment Layer:           6.539e-008        0.0007242
Desorption from Sediment:               1.993e-007        0.002207
Sediment Deposition:                    9.624e-007        0.01066
Sediment Resuspension:                  2.742e-008        0.0003037
Sediment Burial:                        2.742e-008        3.079e-005
 ____________SURFACE SOIL(1) SURFACE WATER INTERFACE________________
Surface Water Runoff:                   8.052e-005        0.8919
Soil Erosion:                           1.544e-007        0.001711
 ____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE____________
Difusion(Air+Water) into Soil2:         4.279e-006        0.0474
Difusion(Air+Water) into Soil1:         5.87e-011         6.502e-007
Infiltration/Leaching to Soil2:         2.209e-005        0.2447
 ____________PLANT ROOT ZONE SOIL(2) INTERFACE______________________
Net Plant Uptake:                       2.636e-005        0.292
 ____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE________
Leaching/Infiltration:                  4.692e-010        5.197e-006
 ____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE______________
Leaching:                               3.094e-012        3.427e-008

INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment       Rates(mol/h)      Rates(kg/y)       Dvalues(mol/Pa.h) Half-Life(h
1 TO 2            1.634e-006        0.001835          1802              253.4
1 TO 3            6.284e-006        0.007057          6930              1318
1 TO 5            0.002576          2.893             2.841e+006        0.003077
2 TO 1            2.964e-005        0.03329           1775              253.4
2 TO 4            1.028e-006        0.001154          61.53             6404
3 TO 1            0.001699          1.908             6530              1318
3 TO 2            8.067e-005        0.0906            310.1             3.771e+004
3 TO 6            2.637e-005        0.02961           101.3             5.614e+004
4 TO 2            2.267e-007        0.0002546         4.453             4364
5 TO 1            0.002601          2.921             2.841e+006        0.003077
5 TO 3            0.00208           2.336             2.272e+006        0
6 TO 3            5.87e-011         6.593e-008        16.45             5.614e+004
6 TO 5            2.636e-005        0.02961           7.387e+006        3.26e+014
6 TO 7            4.692e-010        5.269e-007        131.5             1.368e+004
7 TO 2            3.094e-012        3.475e-009        131.5             3.908e+005
```

```
INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment        Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.00433            0.0005551          4.862
2                  8.253e-005         1.058e-005         0.09269
3                  0.002086           0.0002674          2.343
4                  1.028e-006         1.318e-007         0.001154
5                  0.002603           0.0003336          2.923
6                  2.637e-005         3.38e-006          0.02961
7                  4.692e-010         6.015e-011         5.269e-007
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.002584           0.0003313          2.902
2                  3.067e-005         3.932e-006         0.03444
3                  0.001806           0.0002315          2.028
4                  2.267e-007         2.906e-008         0.0002546
5                  0.004681           0.0006001          5.257
6                  2.637e-005         3.38e-006          0.02961
7                  3.094e-012         3.967e-013         3.475e-009
```

Sub-Watershed HUC#18

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 TOTAL GAIN:
Emisions
Compt:             mol/h              kg/h               kg/year
1                  0                  0                  0
2                  0                  0                  0
3                  0                  0                  0
4                  0                  0                  0
5                  0                  0                  0
6                  0                  0                  0
7                  0                  0                  0
Total:             0                  0                  0

Advection:         mol/h              kg/h               kg/year
1_AIR:             0                  0                  0
2_WATER:           0                  0                  0

--------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:       mol/h              kg/h               kg/year
1                  0.0009902          0.0001269          1.112
2                  3.689e-006         4.73e-007          0.004143
3                  2.937e-005         3.765e-006         0.03298
4                  1.728e-007         2.215e-008         0.0001941
5                  1.04e-007          1.333e-008         0.0001168
6                  4.041e-009         5.18e-010          4.538e-006
7                  1.762e-010         2.259e-011         1.979e-007
Total:             0.001024           0.0001312          1.149

Advection:         mol/h              kg/h               kg/year
1_AIR:             0.00912            0.001169           10.24
2_WATER:           1.694e-006         2.172e-007         0.001903
```

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INDIVIDUAL PROCESS RATES or FLUX
mol/h              kg/year
 ____________AIR WATER INTERFACE_____________________________________
Adsorption from Air:                    2.921e-007        0.003236
Volatilization from Water:              3.517e-006        0.03896
Aerolols Dry Deposition:                3.15e-011         3.489e-007
Wet Deposition - Rain Dissolution:      4.413e-009        4.888e-005
 ____________AIR SOIL INTERFACE______________________________________
Adsorption from Air:                    3.392e-006        0.03757
Volatilization from Soil:               0.0001813         2.008
Aerolols Dry Deposition:                3.15e-011         3.489e-007
Wet Deposition - Rain Dissolution:      1.905e-007        0.00211
 ____________AIR PLANT INTERFACE_____________________________________
Adsorption by Foliar Plant:             0.0002931         3.247
Volatilization from Plants:             0.0002954         3.272
Net Deposition onto Plants:             4.511e-020        4.997e-016
 ____________WATER SEDIMENT INTERFACE________________________________
Adsorption to Sediment Layer:           7.777e-009        8.614e-005
Desorption from Sediment:               4.437e-008        0.0004915
Sediment Deposition:                    2.22e-007         0.002459
Sediment Resuspension:                  6.102e-009        6.759e-005
Sediment Burial:                        6.102e-009        6.853e-006
 ____________SURFACE SOIL(1) SURFACE WATER INTERFACE_________________
Surface Water Runoff:                   9.339e-006        0.1034
Soil Erosion:                           1.545e-008        0.0001711
 ____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE_____________
Difusion(Air+Water) into Soil2:         1.636e-006        0.01812
Difusion(Air+Water) into Soil1:         1.046e-010        1.159e-006
Infiltration/Leaching to Soil2:         7.842e-007        0.008686
 ____________PLANT ROOT ZONE SOIL(2) INTERFACE_______________________
Net Plant Uptake:                       2.415e-006        0.02675
 ____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE_________
Leaching/Infiltration:                  2.189e-010        2.424e-006
 ____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE_______________
Leaching:                               1.35e-011         1.495e-007
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INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment        Rates(mol/h)        Rates(kg/y)         Dvalues(mol/Pa.h)  Half-Life(
1 TO 2             2.966e-007          0.0003331           684.1              256.8
1 TO 3             3.584e-006          0.004025            8267               1270
1 TO 5             0.0002931           0.3292              6.761e+005         0.002852
2 TO 1             3.517e-006          0.00395             673.9              256.8
2 TO 4             2.298e-007          0.0002581           44.03              3239
3 TO 1             0.0001813           0.2036              7824               1270
3 TO 2             9.355e-006          0.01051             403.8              3.424e+004
3 TO 6             2.42e-006           0.002718            104.5              6.295e+004
4 TO 2             5.047e-008          5.668e-005          1.695              2879
5 TO 1             0.0002954           0.3318              6.761e+005         0.002852
5 TO 3             0.000219            0.2459              5.012e+005         0
6 TO 3             1.046e-010          1.175e-007          70.6               6.295e+004
6 TO 5             2.415e-006          0.002712            1.63e+006          2.071e+013
6 TO 7             2.189e-010          2.458e-007          147.7              5.737e+004
7 TO 2             1.35e-011           1.516e-008          147.7              4.058e+004
```

```
INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment        Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.0004802          6.156e-005         0.5393
2                  9.702e-006         1.244e-006         0.0109
3                  0.0002226          2.854e-005         0.25
4                  2.298e-007         2.946e-008         0.0002581
5                  0.0002955          3.789e-005         0.3319
6                  2.42e-006          3.102e-007         0.002718
7                  2.189e-010         2.806e-011         2.458e-007
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.000297           3.807e-005         0.3335
2                  3.747e-006         4.803e-007         0.004208
3                  0.000193           2.475e-005         0.2168
4                  5.047e-008         6.471e-009         5.668e-005
5                  0.0005144          6.595e-005         0.5777
6                  2.416e-006         3.097e-007         0.002713
7                  1.35e-011          1.73e-012          1.516e-008
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Sub-Watershed HUC#19

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 TOTAL GAIN:
Emisions
Compt:            mol/h              kg/h               kg/year
1                 0                  0                  0
2                 0                  0                  0
3                 0                  0                  0
4                 0                  0                  0
5                 0                  0                  0
6                 0                  0                  0
7                 0                  0                  0
Total:            0                  0                  0

Advection:        mol/h              kg/h               kg/year
1_AIR:            0                  0                  0
2_WATER:          0                  0                  0

-----------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:      mol/h              kg/h               kg/year
1                 0.0006556          8.405e-005         0.7363
2                 1.51e-005          1.936e-006         0.01696
3                 0.000125           1.603e-005         0.1404
4                 3.742e-007         4.797e-008         0.0004202
5                 4.688e-007         6.01e-008          0.0005265
6                 4.048e-010         5.19e-011          4.546e-007
7                 1.382e-010         1.772e-011         1.552e-007
Total:            0.0007966          0.0001021          0.8947

Advection:        mol/h              kg/h               kg/year
1_AIR:            0.003702           0.0004746          4.158
2_WATER:          2.341e-006         3.002e-007         0.00263
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INDIVIDUAL PROCESS RATES or FLUX
mol/h              kg/year
 ____________AIR WATER INTERFACE__________________________________
Adsorption from Air:                     5.352e-007        0.005928
Volatilization from Water:               1.447e-005        0.1602
Aerolols Dry Deposition:                 4.516e-011        5.002e-007
Wet Deposition - Rain Dissolution:       8.228e-009        9.114e-005
 ____________AIR SOIL INTERFACE___________________________________
Adsorption from Air:                     1.567e-006        0.01735
Volatilization from Soil:                0.0005784         6.406
Aerolols Dry Deposition:                 4.516e-011        5.002e-007
Wet Deposition - Rain Dissolution:       1.234e-007        0.001367
 ____________AIR PLANT INTERFACE__________________________________
Adsorption by Foliar Plant:              0.000903          10
Volatilization from Plants:              0.0009132         10.12
Net Deposition onto Plants:              9.455e-020        1.047e-015
 ____________WATER SEDIMENT INTERFACE_____________________________
Adsorption to Sediment Layer:            3.191e-008        0.0003534
Desorption from Sediment:                9.604e-008        0.001064
Sediment Deposition:                     4.697e-007        0.005202
Sediment Resuspension:                   1.321e-008        0.0001463
Sediment Burial:                         1.321e-008        1.484e-005
 ____________SURFACE SOIL(1) SURFACE WATER INTERFACE______________
Surface Water Runoff:                    3.472e-005        0.3846
Soil Erosion:                            6.026e-008        0.0006674
 ____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE__________
Difusion(Air+Water) into Soil2:          1.021e-006        0.01131
Difusion(Air+Water) into Soil1:          1.23e-011         1.362e-007
Infiltration/Leaching to Soil2:          9.697e-006        0.1074
 ____________PLANT ROOT ZONE SOIL(2) INTERFACE____________________
Net Plant Uptake:                        1.072e-005        0.1187
 ____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE______
Leaching/Infiltration:                   1.809e-010        2.004e-006
 ____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE____________
Leaching:                                3.308e-012        3.665e-008
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INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment        Rates(mol/h)       Rates(kg/y)        Dvalues(mol/Pa.h)  Half-Life
1 TO 2             5.435e-007         0.0006103          5037               253.5
1 TO 3             1.691e-006         0.001899           1.567e+004         1718
1 TO 5             0.000903           1.014              8.368e+006         0.003156
2 TO 1             1.447e-005         0.01625            4960               253.5
2 TO 4             5.016e-007         0.0005633          172                7014
3 TO 1             0.0005784          0.6495             1.452e+004         1718
3 TO 2             3.478e-005         0.03906            873.1              3.922e+00
3 TO 6             1.072e-005         0.01204            269                5.671e+00
4 TO 2             1.093e-007         0.0001227          12.45              4364
5 TO 1             0.0009132          1.026              8.368e+006         0.003156
5 TO 3             0.0007491          0.8412             6.864e+006         0
6 TO 3             1.23e-011          1.381e-008         25.62              5.671e+00
6 TO 5             1.072e-005         0.01203            2.232e+007         2.947e+01
6 TO 7             1.809e-010         2.032e-007         376.9              6954
7 TO 2             3.308e-012         3.715e-009         376.9              1.298e+00
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INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment          Rates(mol/h)         Rates(kg/h)          Rates(kg/y)
1                    0.001506             0.0001931            1.691
2                    3.543e-005           4.543e-006           0.03979
3                    0.0007508            9.625e-005           0.8431
4                    5.016e-007           6.43e-008            0.0005633
5                    0.0009137            0.0001171            1.026
6                    1.072e-005           1.374e-006           0.01204
7                    1.809e-010           2.32e-011            2.032e-007
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)         Rates(kg/h)          Rates(kg/y)
1                    0.0009052            0.000116             1.017
2                    1.497e-005           1.919e-006           0.01681
3                    0.0006239            7.998e-005           0.7006
4                    1.093e-007           1.401e-008           0.0001227
5                    0.001662             0.0002131            1.867
6                    1.072e-005           1.374e-006           0.01203
7                    3.308e-012           4.241e-013           3.715e-009
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Sub-Watershed HUC#25

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 TOTAL GAIN:
Emisions
Compt:               mol/h                kg/h                 kg/year
1                    0.1139               0.0146               127.9
2                    0.001209             0.000155             1.358
3                    0                    0                    0
4                    0                    0                    0
5                    0                    0                    0
6                    0                    0                    0
7                    0                    0                    0
Total:               0.1151               0.01475              129.3

Advection:           mol/h                kg/h                 kg/year
1_AIR:               0                    0                    0
2_WATER:             0                    0                    0

--------------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:         mol/h                kg/h                 kg/year
1                    0.009552             0.001225             10.73
2                    0.0001869            2.397e-005           0.2099
3                    0.0003914            5.017e-005           0.4395
4                    8.933e-006           1.145e-006           0.01003
5                    1.404e-006           1.8e-007             0.001577
6                    2.031e-008           2.604e-009           2.281e-005
7                    1.586e-009           2.033e-010           1.781e-006
Total:               0.01014              0.0013               11.39

Advection:           mol/h                kg/h                 kg/year
1_AIR:               0.07245              0.009288             81.37
2_WATER:             0.0005015            6.429e-005           0.5632
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INDIVIDUAL PROCESS RATES or FLUX
           mol/h              kg/year
 ____________AIR WATER INTERFACE_________________________________________
Adsorption from Air:                   3.649e-006         0.04042
Volatilization from Water:             0.0001782          1.974
Aerolols Dry Deposition:               4.675e-010         5.178e-006
Wet Deposition - Rain Dissolution:     5.518e-008         0.0006112
 ____________AIR SOIL INTERFACE_________________________________________
Adsorption from Air:                   2.869e-005         0.3178
Volatilization from Soil:              0.002374           26.29
Aerolols Dry Deposition:               4.675e-010         5.178e-006
Wet Deposition - Rain Dissolution:     1.827e-006         0.02024
 ____________AIR PLANT INTERFACE_________________________________________
Adsorption by Foliar Plant:            0.003805           42.15
Volatilization from Plants:            0.003832           42.44
Net Deposition onto Plants:            8.448e-019         9.357e-015
 ____________WATER SEDIMENT INTERFACE____________________________________
Adsorption to Sediment Layer:          3.941e-007         0.004365
Desorption from Sediment:              2.294e-006         0.02541
Sediment Deposition:                   1.125e-005         0.1246
Sediment Resuspension:                 3.154e-007         0.003494
Sediment Burial:                       3.154e-007         0.0003542
 ____________SURFACE SOIL(1) SURFACE WATER INTERFACE_____________________
Surface Water Runoff:                  0.0001374          1.522
Soil Erosion:                          1.612e-007         0.001786
 ____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE_________________
Difusion(Air+Water) into Soil2:        1.496e-005         0.1657
Difusion(Air+Water) into Soil1:        5.33e-010          5.904e-006
Infiltration/Leaching to Soil2:        1.269e-005         0.1405
 ____________PLANT ROOT ZONE SOIL(2) INTERFACE___________________________
Net Plant Uptake:                      2.762e-005         0.306
 ____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE_____________
Leaching/Infiltration:                 1.808e-009         2.003e-005
 ____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE___________________
Leaching:                              1.279e-011         1.417e-007


INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment        Rates(mol/h)       Rates(kg/y)        Dvalues(mol/Pa.h)  Half-Life
1 TO 2             3.705e-006         0.004161           1306               256.5
1 TO 3             3.054e-005         0.03429            1.077e+004         1330
1 TO 5             0.003805           4.274              1.342e+006         0.002914
2 TO 1             0.0001782          0.2001             1287               256.5
2 TO 4             1.164e-005         0.01308            84.07              3542
3 TO 1             0.002374           2.666              1.012e+004         1330
3 TO 2             0.0001376          0.1545             586.6              3.102e+00
3 TO 6             2.765e-005         0.03105            117.9              6.703e+00
4 TO 2             2.609e-006         0.00293            3.236              2879
5 TO 1             0.003832           4.303              1.342e+006         0.002914
5 TO 3             0.002903           3.26               1.016e+006         0
6 TO 3             5.33e-010          5.986e-007         63.77              6.703e+00
6 TO 5             2.762e-005         0.03102            3.305e+006         8.358e+01
6 TO 7             1.808e-009         2.03e-006          216.3              3.492e+00
7 TO 2             1.279e-011         1.437e-008         216.3              3.853e+00
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INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment        Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.006383           0.0008183          7.169
2                  0.0001439          1.845e-005         0.1616
3                  0.002933           0.000376           3.294
4                  1.164e-005         1.493e-006         0.01308
5                  0.003833           0.0004914          4.305
6                  2.765e-005         3.545e-006         0.03105
7                  1.808e-009         2.318e-010         2.03e-006
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.00384            0.0004922          4.312
2                  0.0001899          2.434e-005         0.2132
3                  0.002539           0.0003255          2.851
4                  2.609e-006         3.345e-007         0.00293
5                  0.006734           0.0008633          7.563
6                  2.763e-005         3.542e-006         0.03103
7                  1.279e-011         1.64e-012          1.437e-008
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Sub-Watershed HUC#27

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 TOTAL GAIN:
Emisions
Compt:             mol/h              kg/h               kg/year
1                  0.1014             0.013              113.9
2                  0                  0                  0
3                  0                  0                  0
4                  0                  0                  0
5                  0                  0                  0
6                  0                  0                  0
7                  0                  0                  0
Total:             0.1014             0.013              113.9

Advection:         mol/h              kg/h               kg/year
1_AIR:             0                  0                  0
2_WATER:           0                  0                  0

-------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:       mol/h              kg/h               kg/year
1                  0.004351           0.0005578          4.886
2                  3.923e-005         5.03e-006          0.04406
3                  0.0003942          5.054e-005         0.4427
4                  1.87e-006          2.398e-007         0.002101
5                  1.392e-006         1.785e-007         0.001564
6                  6.921e-009         8.873e-010         7.772e-006
7                  1.012e-009         1.297e-010         1.136e-006
Total:             0.004788           0.0006138          5.377

Advection:         mol/h              kg/h               kg/year
1_AIR:             0.05866            0.007521           65.88
2_WATER:           8.186e-005         1.049e-005         0.09193
```

```
INDIVIDUAL PROCESS RATES or FLUX
            mol/h             kg/year
 ____________AIR WATER INTERFACE____________________________________
Adsorption from Air:                    2.589e-006        0.02868
Volatilization from Water:              3.74e-005         0.4143
Aerolols Dry Deposition:                3.151e-010        3.49e-006
Wet Deposition - Rain Dissolution:      3.831e-008        0.0004243
 ____________AIR SOIL INTERFACE_____________________________________
Adsorption from Air:                    9.533e-006        0.1056
Volatilization from Soil:               0.002066          22.88
Aerolols Dry Deposition:                3.151e-010        3.49e-006
Wet Deposition - Rain Dissolution:      8.007e-007        0.008869
 ____________AIR PLANT INTERFACE____________________________________
Adsorption by Foliar Plant:             0.003353          37.14
Volatilization from Plants:             0.003386          37.5
Net Deposition onto Plants:             6.901e-019        7.644e-015
 ____________WATER SEDIMENT INTERFACE_______________________________
Adsorption to Sediment Layer:           8.27e-008         0.0009161
Desorption from Sediment:               4.803e-007        0.00532
Sediment Deposition:                    2.361e-006        0.02615
Sediment Resuspension:                  6.605e-008        0.0007316
Sediment Burial:                        6.605e-008        7.417e-005
 ____________SURFACE SOIL(1) SURFACE WATER INTERFACE________________
Surface Water Runoff:                   0.0001488         1.649
Soil Erosion:                           1.991e-007        0.002206
 ____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE____________
Difusion(Air+Water) into Soil2:         1.044e-005        0.1156
Difusion(Air+Water) into Soil1:         1.93e-010         2.138e-006
Infiltration/Leaching to Soil2:         2.357e-005        0.261
 ____________PLANT ROOT ZONE SOIL(2) INTERFACE______________________
Net Plant Uptake:                       3.4e-005          0.3766
 ____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE________
Leaching/Infiltration:                  1.101e-009        1.219e-005
 ____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE______________
Leaching:                               8.117e-012        8.991e-008
```

```
INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment        Rates(mol/h)       Rates(kg/y)        Dvalues(mol/Pa.h)  Half-Life
1 TO 2             2.628e-006         0.002951           643.7              255.6
1 TO 3             1.034e-005         0.01161            2533               1597
1 TO 5             0.003353           3.766              8.214e+005         0.002994
2 TO 1             3.74e-005          0.042              634.2              255.6
2 TO 4             2.444e-006         0.002744           41.44              3203
3 TO 1             0.002066           2.32               2335               1597
3 TO 2             0.000149           0.1674             168.5              2.885e+00
3 TO 6             3.401e-005         0.03819            38.44              5.923e+00
4 TO 2             5.463e-007         0.0006135          1.595              2879
5 TO 1             0.003386           3.803              8.214e+005         0.002994
5 TO 3             0.002635           2.959              6.391e+005         0
6 TO 3             1.93e-010          2.168e-007         11.8               5.923e+00
6 TO 5             3.4e-005           0.03818            2.078e+006         3.026e+01
6 TO 7             1.101e-009         1.236e-006         67.3               1.954e+00
7 TO 2             8.117e-012         9.116e-009         67.3               3.874e+00
```

```
INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment          Rates(mol/h)         Rates(kg/h)          Rates(kg/y)
1                    0.005489             0.0007037            6.165
2                    0.0001522            1.951e-005           0.1709
3                    0.002645             0.0003391            2.97
4                    2.444e-006           3.133e-007           0.002744
5                    0.003387             0.0004343            3.804
6                    3.401e-005           4.36e-006            0.03819
7                    1.101e-009           1.411e-010           1.236e-006
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)         Rates(kg/h)          Rates(kg/y)
1                    0.003366             0.0004316            3.781
2                    3.985e-005           5.108e-006           0.04475
3                    0.002249             0.0002883            2.526
4                    5.463e-007           7.004e-008           0.0006135
5                    0.006021             0.0007718            6.761
6                    3.4e-005             4.359e-006           0.03818
7                    8.117e-012           1.041e-012           9.116e-009
```

Sub-Watershed HUC#31

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 TOTAL GAIN:
Emisions
Compt:               mol/h                kg/h                 kg/year
1                    0                    0                    0
2                    0                    0                    0
3                    0                    0                    0
4                    0                    0                    0
5                    0                    0                    0
6                    0                    0                    0
7                    0                    0                    0
Total:               0                    0                    0

Advection:           mol/h                kg/h                 kg/year
1_AIR:               0                    0                    0
2_WATER:             0                    0                    0

-----------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:         mol/h                kg/h                 kg/year
1                    0.001577             0.0002022            1.772
2                    9.338e-005           1.197e-005           0.1049
3                    7.017e-005           8.996e-006           0.07881
4                    4.438e-006           5.69e-007            0.004984
5                    2.113e-007           2.709e-008           0.0002373
6                    1.503e-008           1.926e-009           1.688e-005
7                    7.654e-010           9.813e-011           8.596e-007
Total:               0.001746             0.0002238            1.96

Advection:           mol/h                kg/h                 kg/year
1_AIR:               0.0236               0.003026             26.51
2_WATER:             0.0003669            4.704e-005           0.4121
```

```
INDIVIDUAL PROCESS RATES or FLUX
          mol/h            kg/year
 ___________AIR WATER INTERFACE__________________________________
Adsorption from Air:                     9.055e-007       0.01003
Volatilization from Water:               8.902e-005       0.986
Aerolols Dry Deposition:                 1.16e-010        1.285e-006
Wet Deposition - Rain Dissolution:       1.369e-008       0.0001517
 ___________AIR SOIL INTERFACE___________________________________
Adsorption from Air:                     1.975e-006       0.02187
Volatilization from Soil:                0.0003036        3.363
Aerolols Dry Deposition:                 1.16e-010        1.285e-006
Wet Deposition - Rain Dissolution:       2.972e-007       0.003292
 ___________AIR PLANT INTERFACE__________________________________
Adsorption by Foliar Plant:              0.0005772        6.393
Volatilization from Plants:              0.0005895        6.529
Net Deposition onto Plants:              1.223e-019       1.355e-015
 ___________WATER SEDIMENT INTERFACE_____________________________
Adsorption to Sediment Layer:            1.968e-007       0.00218
Desorption from Sediment:                1.14e-006        0.01262
Sediment Deposition:                     5.619e-006       0.06224
Sediment Resuspension:                   1.567e-007       0.001736
Sediment Burial:                         1.567e-007       0.000176
 ___________SURFACE SOIL(1) SURFACE WATER INTERFACE_______________
Surface Water Runoff:                    4.091e-005       0.4531
Soil Erosion:                            4.361e-008       0.0004831
 ___________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE___________
Difusion(Air+Water) into Soil2:          8.023e-006       0.08887
Difusion(Air+Water) into Soil1:          4.798e-010       5.314e-006
Infiltration/Leaching to Soil2:          4.475e-006       0.04956
 ___________PLANT ROOT ZONE SOIL(2) INTERFACE_____________________
Net Plant Uptake:                        1.248e-005       0.1382
 ___________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE_______
Leaching/Infiltration:                   9.174e-010       1.016e-005
 ___________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE_____________
Leaching:                                6.107e-012       6.765e-008


INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment      Rates(mol/h)      Rates(kg/y)      Dvalues(mol/Pa.h) Half-Life(h)
1 TO 2           9.193e-007        0.001032         504.3             255.7
1 TO 3           2.274e-006        0.002554         1248              2062
1 TO 5           0.0005772         0.6482           3.166e+005        0.002782
2 TO 1           8.902e-005        0.09997          496.7             255.7
2 TO 4           5.816e-006        0.006532         32.46             3044
3 TO 1           0.0003036         0.341            1083              2062
3 TO 2           4.095e-005        0.04599          146.1             1.869e+004
3 TO 6           1.25e-005         0.01404          44.59             3.759e+004
4 TO 2           1.296e-006        0.001456         1.249             2879
5 TO 1           0.0005895         0.662            3.166e+005        0.002782
5 TO 3           0.0004263         0.4787           2.29e+005         0
6 TO 3           4.798e-010        5.388e-007       28.63             3.759e+004
6 TO 5           1.248e-005        0.01402          7.446e+005        4.14e+012
6 TO 7           9.174e-010        1.03e-006        54.74             5.091e+004
7 TO 2           6.107e-012        6.858e-009       54.74             3.895e+005
```

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INFLUX RATES  INTO  INDIVIDUAL  COMPARTMENT
compartment        Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.0009821          0.0001259          1.103
2                  4.317e-005         5.534e-006         0.04848
3                  0.0004286          5.494e-005         0.4813
4                  5.816e-006         7.456e-007         0.006532
5                  0.0005897          7.56e-005          0.6622
6                  1.25e-005          1.602e-006         0.01404
7                  9.174e-010         1.176e-010         1.03e-006
TRANSFER RATES  OUT  OF  INDIVIDUAL  COMPARTMENT
Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.0005804          7.44e-005          0.6518
2                  9.483e-005         1.216e-005         0.1065
3                  0.0003571          4.578e-005         0.401
4                  1.296e-006         1.662e-007         0.001456
5                  0.001016           0.0001302          1.141
6                  1.248e-005         1.6e-006           0.01402
7                  6.107e-012         7.829e-013         6.858e-009
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Sub-Watershed HUC#33

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 TOTAL GAIN:
Emisions
Compt:             mol/h              kg/h               kg/year
1                  0.004446           0.00057            4.993
2                  0                  0                  0
3                  0                  0                  0
4                  0                  0                  0
5                  0                  0                  0
6                  0                  0                  0
7                  0                  0                  0
Total:             0.004446           0.00057            4.993

Advection:         mol/h              kg/h               kg/year
1_AIR:             0                  0                  0
2_WATER:           0                  0                  0

-----------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:       mol/h              kg/h               kg/year
1                  0.008266           0.00106            9.283
2                  0.0001196          1.533e-005         0.1343
3                  0.0009072          0.0001163          1.019
4                  5.629e-006         7.217e-007         0.006322
5                  2.751e-006         3.527e-007         0.00309
6                  2.208e-008         2.831e-009         2.48e-005
7                  1.956e-009         2.508e-010         2.197e-006
Total:             0.009301           0.001192           10.45

Advection:         mol/h              kg/h               kg/year
1_AIR:             0.06542            0.008387           73.47
2_WATER:           4.435e-005         5.686e-006         0.04981
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INDIVIDUAL PROCESS RATES or FLUX
mol/h                kg/year
 ____________AIR WATER INTERFACE________________________________________
Adsorption from Air:                        3.074e-006         0.03405
Volatilization from Water:                  0.000114           1.263
Aerolols Dry Deposition:                    3.741e-010         4.144e-006
Wet Deposition - Rain Dissolution:          4.712e-008         0.0005219
 ____________AIR SOIL INTERFACE_________________________________________
Adsorption from Air:                        1.804e-005         0.1998
Volatilization from Soil:                   0.00385            42.65
Aerolols Dry Deposition:                    3.741e-010         4.144e-006
Wet Deposition - Rain Dissolution:          1.604e-006         0.01777
 ____________AIR PLANT INTERFACE________________________________________
Adsorption by Foliar Plant:                 0.006625           73.39
Volatilization from Plants:                 0.006695           74.16
Net Deposition onto Plants:                 1.339e-018         1.483e-014
 ____________WATER SEDIMENT INTERFACE___________________________________
Adsorption to Sediment Layer:               2.52e-007          0.002792
Desorption from Sediment:                   1.445e-006         0.01601
Sediment Deposition:                        7.195e-006         0.0797
Sediment Resuspension:                      1.988e-007         0.002202
Sediment Burial:                            1.988e-007         0.0002232
 ____________SURFACE SOIL(1) SURFACE WATER INTERFACE____________________
Surface Water Runoff:                       0.0002953          3.271
Soil Erosion:                               3.983e-007         0.004411
 ____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE________________
Difusion(Air+Water) into Soil2:             2.788e-005         0.3088
Difusion(Air+Water) into Soil1:             5.771e-010         6.392e-006
Infiltration/Leaching to Soil2:             4.489e-005         0.4972
 ____________PLANT ROOT ZONE SOIL(2) INTERFACE__________________________
Net Plant Uptake:                           7.274e-005         0.8057
 ____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE____________
Leaching/Infiltration:                      2.347e-009         2.6e-005
 ____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE__________________
Leaching:                                   5.291e-011         5.861e-007
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INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment      Rates(mol/h)      Rates(kg/y)       Dvalues(mol/Pa.h) Half-Life(
1 TO 2           3.121e-006        0.003505          1168              256.5
1 TO 3           1.966e-005        0.02207           7354              1870
1 TO 5           0.006625          7.441             2.479e+006        0.00294
2 TO 1           0.000114          0.128             1150              256.5
2 TO 4           7.447e-006        0.008364          75.15             3500
3 TO 1           0.00385           4.324             6749              1870
3 TO 2           0.0002957         0.3321            518.4             3.346e+004
3 TO 6           7.277e-005        0.08172           127.6             6.345e+004
4 TO 2           1.644e-006        0.001847          2.893             2879
5 TO 1           0.006695          7.519             2.479e+006        0.00294
5 TO 3           0.005117          5.746             1.895e+006        0
6 TO 3           5.771e-010        6.481e-007        48.88             6.345e+004
6 TO 5           7.274e-005        0.08169           6.161e+006        2.613e+014
6 TO 7           2.347e-009        2.636e-006        198.8             2.924e+004
7 TO 2           5.291e-011        5.942e-008        198.8             1.149e+005
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INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment       Rates(mol/h)      Rates(kg/h)       Rates(kg/y)
1                 0.01066           0.001367          11.97
2                 0.0003005         3.852e-005        0.3375
3                 0.005137          0.0006585         5.768
4                 7.447e-006        9.548e-007        0.008364
5                 0.006698          0.0008587         7.522
6                 7.277e-005        9.329e-006        0.08172
7                 2.347e-009        3.009e-010        2.636e-006
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)      Rates(kg/h)       Rates(kg/y)
1                 0.006648          0.0008523         7.466
2                 0.0001214         1.557e-005        0.1364
3                 0.004219          0.0005408         4.738
4                 1.644e-006        2.108e-007        0.001847
5                 0.01181           0.001514          13.27
6                 7.275e-005        9.326e-006        0.0817
7                 5.291e-011        6.783e-012        5.942e-008
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Sub-Watershed HUC#35

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 TOTAL GAIN:
Emisions
Compt:            mol/h             kg/h              kg/year
1                 2.496             0.32              2803
2                 0.04727           0.00606           53.09
3                 0                 0                 0
4                 0                 0                 0
5                 0                 0                 0
6                 0                 0                 0
7                 0                 0                 0
Total:            2.543             0.3261            2856

Advection:        mol/h             kg/h              kg/year
1_AIR:            0                 0                 0
2_WATER:          0                 0                 0

-----------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:      mol/h             kg/h              kg/year
1                 0.114             0.01462           128.1
2                 0.001369          0.0001755         1.537
3                 0.001175          0.0001506         1.319
4                 6.592e-005        8.451e-006        0.07403
5                 4.718e-006        6.048e-007        0.005298
6                 4.265e-007        5.468e-008        0.000479
7                 2.264e-008        2.902e-009        2.542e-005
Total:            0.1167            0.01496           131

Advection:        mol/h             kg/h              kg/year
1_AIR:            1.029             0.1319            1155
2_WATER:          0.006641          0.0008514         7.458
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INDIVIDUAL PROCESS RATES or FLUX
mol/h            kg/year
____________AIR WATER INTERFACE__________________________________
Adsorption from Air:                        4.018e-005        0.445
Volatilization from Water:                  0.001305          14.45
Aerolols Dry Deposition:                    6.434e-009        7.127e-
Wet Deposition - Rain Dissolution:          5.828e-007        0.00645
____________AIR SOIL INTERFACE___________________________________
Adsorption from Air:                        0.0003652         4.045
Volatilization from Soil:                   0.008993          99.61
Aerolols Dry Deposition:                    6.434e-009        7.127e-
Wet Deposition - Rain Dissolution:          2.098e-005        0.2324
____________AIR PLANT INTERFACE__________________________________
Adsorption by Foliar Plant:                 0.01386           153.6
Volatilization from Plants:                 0.01397           154.8
Net Deposition onto Plants:                 4.715e-018        5.223e-
____________WATER SEDIMENT INTERFACE_____________________________
Adsorption to Sediment Layer:               2.885e-006        0.03195
Desorption from Sediment:                   1.693e-005        0.1875
Sediment Deposition:                        8.236e-005        0.9123
Sediment Resuspension:                      2.328e-006        0.02578
Sediment Burial:                            2.328e-006        0.00261
____________SURFACE SOIL(1) SURFACE WATER INTERFACE______________
Surface Water Runoff:                       0.0004784         5.299
Soil Erosion:                               6.35e-007         0.00703
____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE__________
Difusion(Air+Water) into Soil2:             7.827e-005        0.867
Difusion(Air+Water) into Soil1:             1.067e-008        0.00011
Infiltration/Leaching to Soil2:             3.466e-005        0.3839
____________PLANT ROOT ZONE SOIL(2) INTERFACE____________________
Net Plant Uptake:                           0.0001125         1.246
____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE______
Leaching/Infiltration:                      2.466e-008        0.00027
____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE____________
Leaching:                                   1.816e-010        2.011e-
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INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment       Rates(mol/h)      Rates(kg/y)       Dvalues(mol/Pa.h) Half-Life
1 TO 2            4.077e-005        0.04578           851.1             256.6
1 TO 3            0.0003864         0.4339            8067              1100
1 TO 5            0.01386           15.57             2.895e+005        0.002857
2 TO 1            0.001305          1.465             838.8             256.6
2 TO 4            8.524e-005        0.09573           54.81             3358
3 TO 1            0.008993          10.1              7624              1100
3 TO 2            0.0004791         0.538             406.1             2.675e+00
3 TO 6            0.0001129         0.1268            95.73             5.93e+004
4 TO 2            1.925e-005        0.02162           2.11              2879
5 TO 1            0.01397           15.69             2.895e+005        0.002857
5 TO 3            0.01038           11.65             2.15e+005         0
6 TO 3            1.067e-008        1.199e-005        66.35             5.93e+004
6 TO 5            0.0001125         0.1263            6.991e+005        3.979e+01
6 TO 7            2.466e-008        2.769e-005        153.3             5.376e+00
7 TO 2            1.816e-010        2.039e-007        153.3             3.874e+00
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INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment        Rates(mol/h)       Rates(kg/h)        Rates(kg/y
1                  0.02427            0.003111           27.26
2                  0.0005391          6.911e-005         0.6054
3                  0.01076            0.00138            12.09
4                  8.524e-005         1.093e-005         0.09573
5                  0.01398            0.001792           15.7
6                  0.0001129          1.448e-005         0.1268
7                  2.466e-008         3.161e-009         2.769e-005
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.01429            0.001832           16.05
2                  0.00139            0.0001782          1.561
3                  0.009585           0.001229           10.76
4                  1.925e-005         2.468e-006         0.02162
5                  0.02435            0.003122           27.35
6                  0.0001125          1.442e-005         0.1263
7                  1.816e-010         2.328e-011         2.039e-007
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Sub-Watershed HUC#37

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 TOTAL GAIN:
Emisions
Compt:             mol/h              kg/h               kg/year
1                  2.122              0.272              2383
2                  0                  0                  0
3                  0                  0                  0
4                  0                  0                  0
5                  0                  0                  0
6                  0                  0                  0
7                  0                  0                  0
Total:             2.122              0.272              2383

Advection:         mol/h              kg/h               kg/year
1_AIR:             0                  0                  0
2_WATER:           0                  0                  0

-------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:       mol/h              kg/h               kg/year
1                  0.108              0.01385            121.3
2                  0.001524           0.0001954          1.711
3                  0.01013            0.001299           11.38
4                  7.261e-005         9.309e-006         0.08155
5                  3.66e-005          4.692e-006         0.0411
6                  2.675e-007         3.43e-008          0.0003004
7                  2.647e-008         3.394e-009         2.973e-005
Total:             0.1198             0.01535            134.5

Advection:         mol/h              kg/h               kg/year
1_AIR:             0.5962             0.07643            669.5
2_WATER:           0.0005031          6.45e-005          0.565
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INDIVIDUAL PROCESS RATES or FLUX
mol/h          kg/year
     ____________AIR WATER INTERFACE_____________________________________
Adsorption from Air:                    3.577e-005        0.3962
Volatilization from Water:              0.001453          16.09
Aerolols Dry Deposition:                3.024e-009        3.35e-005
Wet Deposition - Rain Dissolution:      5.396e-007        0.005977
     ____________AIR SOIL INTERFACE______________________________________
Adsorption from Air:                    0.0002609         2.89
Volatilization from Soil:               0.05275           584.3
Aerolols Dry Deposition:                3.024e-009        3.35e-005
Wet Deposition - Rain Dissolution:      2.069e-005        0.2292
     ____________AIR PLANT INTERFACE_____________________________________
Adsorption by Foliar Plant:             0.08732           967.2
Volatilization from Plants:             0.08818           976.8
Net Deposition onto Plants:             8.49e-018         9.404e-014
     ____________WATER SEDIMENT INTERFACE________________________________
Adsorption to Sediment Layer:           3.212e-006        0.03558
Desorption from Sediment:               1.864e-005        0.2065
Sediment Deposition:                    9.171e-005        1.016
Sediment Resuspension:                  2.564e-006        0.0284
Sediment Burial:                        2.564e-006        0.002879
     ____________SURFACE SOIL(1) SURFACE WATER INTERFACE_________________
Surface Water Runoff:                   0.003607          39.96
Soil Erosion:                           4.473e-006        0.04954
     ____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE_____________
Difusion(Air+Water) into Soil2:         0.0003472         3.845
Difusion(Air+Water) into Soil1:         7.179e-009        7.952e-005
Infiltration/Leaching to Soil2:         0.0005573         6.172
     ____________PLANT ROOT ZONE SOIL(2) INTERFACE_______________________
Net Plant Uptake:                       0.0009041         10.01
     ____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE_________
Leaching/Infiltration:                  2.911e-008        0.0003225
     ____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE_______________
Leaching:                               1.182e-010        1.309e-006


INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment        Rates(mol/h)       Rates(kg/y)        Dvalues(mol/Pa.h)  Half-Life
1 TO 2             3.631e-005         0.04078            2138               256.7
1 TO 3             0.0002818          0.3164             1.659e+004         1569
1 TO 5             0.08732            98.06              5.141e+006         0.00293
2 TO 1             0.001453           1.632              2106               256.7
2 TO 4             9.492e-005         0.1066             137.6              3690
3 TO 1             0.05275            59.24              1.536e+004         1569
3 TO 2             0.003612           4.056              1052               3.059e+00
3 TO 6             0.0009044          1.016              263.4              5.946e+00
4 TO 2             2.121e-005         0.02382            5.296              2879
5 TO 1             0.08818            99.03              5.141e+006         0.00293
5 TO 3             0.06717            75.43              3.915e+006         0
6 TO 3             7.179e-009         8.063e-006         101.1              5.946e+00
6 TO 5             0.0009041          1.015              1.273e+007         1.101e+01
6 TO 7             2.911e-008         3.27e-005          410                2.856e+00
7 TO 2             1.182e-010         1.327e-007         410                6.962e+00
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INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment         Rates(mol/h)        Rates(kg/h)         Rates(kg/y)
1                   0.1424              0.01825             159.9
2                   0.003669            0.0004704           4.121
3                   0.06745             0.008647            75.75
4                   9.492e-005          1.217e-005          0.1066
5                   0.08822             0.01131             99.07
6                   0.0009044           0.0001159           1.016
7                   2.911e-008          3.732e-009          3.27e-005
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)        Rates(kg/h)         Rates(kg/y)
1                   0.08763             0.01123             98.42
2                   0.001548            0.0001984           1.738
3                   0.05726             0.007341            64.31
4                   2.121e-005          2.719e-006          0.02382
5                   0.1554              0.01992             174.5
6                   0.0009041           0.0001159           1.015
7                   1.182e-010          1.515e-011          1.327e-007
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PASSAIC WATERSHED

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 TOTAL GAIN:
Emisions
Compt:              mol/h               kg/h                kg/year
1                   5.101               0.654               5729
2                   0.04852             0.00622             54.49
3                   0                   0                   0
4                   0                   0                   0
5                   0                   0                   0
6                   0                   0                   0
7                   0                   0                   0
Total:              5.15                0.6602              5784

Advection:          mol/h               kg/h                kg/year
1_AIR:              0                   0                   0
2_WATER:            0                   0                   0

---------------------------------------------------------------------
LOSSES: Degradation/Reaction & Advection
Degradation:        mol/h               kg/h                kg/year
1                   0.2908              0.03728             326.5
2                   0.1105              0.01417             124.1
3                   0.03486             0.004469            39.15
4                   0.003657            0.0004689           4.107
5                   0.0001334           1.711e-005          0.1498
6                   5.077e-007          6.508e-008          0.0005701
7                   6.765e-008          8.673e-009          7.598e-005
Total:              0.4399              0.0564              494.1

Advection:          mol/h               kg/h                kg/year
1_AIR:              0.6843              0.08772             768.5
2_WATER:            0.02061             0.002642            23.15
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INDIVIDUAL PROCESS RATES or FLUX
            mol/h            kg/year
____________AIR WATER INTERFACE____________________________________
Adsorption from Air:                      0.000182         2.016
Volatilization from Water:                0.1057           1171
Aerolols Dry Deposition:                  1.826e-008       0.0002022
Wet Deposition - Rain Dissolution:        2.763e-006       0.03061
____________AIR SOIL INTERFACE_____________________________________
Adsorption from Air:                      0.0008025        8.889
Volatilization from Soil:                 0.1885           2088
Aerolols Dry Deposition:                  1.826e-008       0.0002022
Wet Deposition - Rain Dissolution:        5.486e-005       0.6076
____________AIR PLANT INTERFACE____________________________________
Adsorption by Foliar Plant:               0.3012           3337
Volatilization from Plants:               0.3042           3370
Net Deposition onto Plants:               4.215e-017       4.669e-013
____________WATER SEDIMENT INTERFACE_______________________________
Adsorption to Sediment Layer:             0.0002333        2.584
Desorption from Sediment:                 0.0009389        10.4
Sediment Deposition:                      0.004495         49.79
Sediment Resuspension:                    0.0001291        1.431
Sediment Burial:                          0.0001291        0.145
____________SURFACE SOIL(1) SURFACE WATER INTERFACE________________
Surface Water Runoff:                     0.01049          116.1
Soil Erosion:                             1.726e-005       0.1912
____________SURFACE SOIL(1) ROOT ZONE SOIL(2) INTERFACE____________
Difusion(Air+Water) into Soil2:           0.0008131        9.006
Difusion(Air+Water) into Soil1:           1.418e-008       0.0001571
Infiltration/Leaching to Soil2:           0.002303         25.51
____________PLANT ROOT ZONE SOIL(2) INTERFACE______________________
Net Plant Uptake:                         0.003116         34.51
____________ROOT ZONE SOIL(2) VADOSE ZONE SOIL(3) INTERFACE________
Leaching/Infiltration:                    7.503e-008       0.0008311
____________VADOSE ZONE SOIL(3) GROUNDWATER INTERFACE______________
Leaching:                                 6.914e-010       7.658e-006
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INTERMEDIA TRANSFER RATES BETWEEN BULK COMPARTMENTS
Compartment       Rates(mol/h)      Rates(kg/y)       Dvalues(mol/Pa.h) Half-Life(
1 TO 2            0.0001848         0.2075            2.223e+004        254.7
1 TO 3            0.0008577         0.9633            1.032e+005        1478
1 TO 5            0.3012            338.3             3.625e+007        0.002988
2 TO 1            0.1057            118.7             2.19e+004         254.7
2 TO 4            0.004728          5.31              979.5             5694
3 TO 1            0.1885            211.7             9.656e+004        1478
3 TO 2            0.0105            11.79             5381              3.62e+004
3 TO 6            0.003116          3.5               1597              5.819e+004
4 TO 2            0.001068          1.199             54.99             3731
5 TO 1            0.3042            341.6             3.625e+007        0.002988
5 TO 3            0.2362            265.3             2.814e+007        0
6 TO 3            1.418e-008        1.593e-005        416.6             5.819e+004
6 TO 5            0.003116          3.499             9.152e+007        5.489e+016
6 TO 7            7.503e-008        8.426e-005        2204              2.103e+004
7 TO 2            6.914e-010        7.765e-007        2204              3.041e+005
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INFLUX RATES INTO INDIVIDUAL COMPARTMENT
compartment        Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.5984             0.07671            672
2                  0.01176            0.001507           13.2
3                  0.2371             0.03039            266.2
4                  0.004728           0.0006061          5.31
5                  0.3043             0.03902            341.8
6                  0.003116           0.0003995          3.5
7                  7.503e-008         9.619e-009         8.426e-005
TRANSFER RATES OUT OF INDIVIDUAL COMPARTMENT
Rates(mol/h)       Rates(kg/h)        Rates(kg/y)
1                  0.3023             0.03875            339.5
2                  0.1104             0.01416            124
3                  0.2021             0.02591            226.9
4                  0.001068           0.0001369          1.199
5                  0.5404             0.06928            606.9
6                  0.003116           0.0003994          3.499
7                  6.914e-010         8.864e-011         7.765e-007
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