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Removal of toxic organics in wetlands: a mechanistic model

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REMOVAL OF TOXIC ORGANICS IN WETLANDS: A MECHANISTIC MODEL

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the Requirements for the degree of Master of Science in Civil Engineering in

The Department of Civil and Environmental Engineering

by

Luz Edith Flórez
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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ ii

LIST OF TABLES .................................................................................................................. v

LIST OF FIGURES ............................................................................................................... vi

ABSTRACT ............................................................................................................................ ix

CHAPTER 1.  INTRODUCTION ............................................................................................. 1
   1.1. Background .................................................................................................................. 1
   1.2. Objectives .................................................................................................................. 6

CHAPTER 2. DEVELOPMENT OF MODEL ........................................................................ 7
   2.1. Toxicant Removal Concept in Tanks-in-series Model (TIS) ....................................... 7
   2.2. Assimilation Model for Toxic Organics in Wetlands ................................................ 8
   2.3. System Component Budgets ..................................................................................... 8
      2.3.1. Solid Budget ..................................................................................................... 9
      2.3.2. DOC Budget ................................................................................................... 11
      2.3.3. Toxicant Budget ............................................................................................ 13
   2.4. Speciation ................................................................................................................. 14
   2.5. Development of Equation of Assimilation and Removal ....................................... 15

CHAPTER 3. EFFECT OF REMOVAL EFFICIENCY
   BY NUMBER OF CELLS IN SERIES (N) ........................................................................ 19
   3.1. Introduction .............................................................................................................. 19
   3.2. Definition of Parameters ......................................................................................... 20
   3.3. Analysis of Sensitivity ............................................................................................ 22

CHAPTER 4. IMPACT OF SORPTION AND VOLATILIZATION ON THE
   ASSIMILATORY FUNCTION ($v_t$) FOR PRIORITY ORGANIC
   POLLUTANTS .................................................................................................................... 28
   4.1. Introduction .............................................................................................................. 28
   4.2. Definition of Parameters ........................................................................................ 30
   4.3. Mapping of Assimilation Function, $v_t$, for Different Classes of Organics ............ 31
      4.3.1. Mapping on Logarithmic Space Defined by Sorption ($K_{p.m}$) versus
             Henry’s constant (He) ......................................................................................... 31
      4.3.2. Mapping on Logarithmic Space Defined by Sorption to Colloids
             ($K_{doc.DOC}$) versus Henry’s constant (He) .................................................. 36
   4.4. Conclusions .............................................................................................................. 36

CHAPTER 5. SENSITIVITY ANALYSIS OF THE ASSIMILATORY PROCESS .......... 48
   5.1. Introduction ............................................................................................................. 48
   5.2. Definition of Parameters ....................................................................................... 49
   5.3. Sensitivity of Removal Efficiency by DOC .............................................................. 49
LIST OF TABLES

3.1. Fixed Parameters for Analysis in the Different Kinds of Wetlands (Pardue, 1992) .. 23

3.2. Fixed Parameters for Hexachlorobenzene and Nahpthalene (Pardue, 1992) .......... 24
LIST OF FIGURES


2.1. The Tanks-in-series Model for Mixing in a Treatment Wetland (Kadlec and Knight, 1996) ......................................................................................... 7

3.1. Removal Efficiency for Different Number of Cells in Series in Bottomland Hardwood Forest Wetlands (Hexachlorobenzene) ........................................... 26

3.2. Removal Efficiency for Different Number of Cells in Series in Freshwater Marsh (Hexachlorobenzene) ............................................................................. 26

3.3. Removal Efficiency for Different Number of Cells in Series in Bottomland Hardwood Forest Wetlands (Naphthalene) ...................................................... 27

3.4. Removal Efficiency for Different Number of Cells in Series in Freshwater Marsh (Naphthalene). ...................................................................................... 27

4.1. Mapping for Organic Pollutants for the Assimilation Function $v_t$ (m/year) on a Logarithmic Space Defined by Sorption ($K_{p,m}$) versus Henry’s Constant (He). Total Recycle (R=1) is Assumed in Bottomland Hardwood Forest Wetlands........ 32

4.2. Mapping for Organic Pollutants for the Assimilation Function $v_t$ (m/year) on a Logarithmic Space Defined by Sorption ($K_{p,m}$) versus Henry’s Constant (He). Total Recycle (R=1) is Assumed in Freshwater Marsh Wetland .......................... 33

4.3. Mapping for Organic Pollutants for the Assimilation Function $v_t$ (m/year) on a Logarithmic Space Defined by Sorption ($K_{p,m}$) versus Henry’s Constant (He). No Recycle (R=0) is Assumed in Bottomland Hardwood Forest Wetlands ............ 34

4.4. Mapping for Organic Pollutants for the Assimilation Function $v_t$ (m/year) on a Logarithmic Space Defined by Sorption ($K_{p,m}$) versus Henry’s Constant (He). No Recycle (R=0) is Assumed in Freshwater Marsh Wetlands ........................................ 35

4.5. Mapping for Organic Pollutants of Net Loss Rate $v_t$ (m/year) on a Logarithmic Space Defined by Sorption to Colloids ($K_{doc,DOC}$) versus Henry’s Constant (He). Total Recycle (R=1) is Assumed in Bottomland Hardwood Forest Wetlands ................................................................. 37

4.6. Mapping for Organic Pollutants of Net Loss Rate $v_t$ (m/year) on a Logarithmic Space Defined by Sorption to Colloids ($K_{doc,DOC}$) versus Henry’s Constant (He). Total Recycle (R=1) is Assumed in Freshwater Marsh Wetlands... 38
4.7. Mapping for Organic Pollutants of Net Loss Rate \( v_t \) (m/year) on a Logarithmic Space Defined by Sorption to Colloids \( (K_{doc}.DOC) \) versus Henry’s Constant \( (He) \). No Recycle \( (R=0) \) is Assumed in Bottomland Hardwood Forest Wetlands................................................................. 39

4.8. Mapping for Organic Pollutants of Net Loss Rate \( v_t \) (m/year) on Logarithmic Space Defined by Sorption to Colloids \( (K_{doc}.DOC) \) versus Henry’s Constant \( (He) \). No Recycle \( (R=0) \) is Assumed in Freshwater Marsh Wetland........ 40

4.9. Two Regions on a Logarithmic Space Defined by Sorption \( (K_p.m \) or \( K_{doc}.DOC \)) versus Volatilization \( (He) \)........................................................................................................ 41

4.10. Mapping for Organic Pollutants (Halogenated Aliphatic Hydrocarbons, Nitrosamines, PCBs and PAHs) on Logarithmic Space Defined by Sorption \( (K_p.m) \) versus Volatilization \( (He) \) in Bottomland Hardwood Forest Wetlands ...... 42

4.11. Mapping for Organic Pollutants (Halogenated Ethers, Monocyclic Aromatics, Pesticides, and Phthalate Esters) on Logarithmic Space Defined by Sorption \( (K_p.m) \) versus Volatilization \( (He) \) in Bottomland Hardwood Forest Wetlands................................................................. 43

4.12. Mapping for Organic Pollutants (Halogenated Aliphatic Hydrocarbons, Nitrosamines, PCBs and PAHs) on Logarithmic Space Defined by Sorption \( (K_p.m) \) versus Volatilization \( (He) \) in Freshwater Marsh Wetlands.......................... 44

4.13. Mapping for Organic Pollutants (Halogenated Ethers, Monocyclic Aromatics, Pesticides, and Phthalate Esters) on Logarithmic Space Defined by Sorption \( (K_p.m) \) versus Volatilization \( (He) \) in Freshwater Marsh Wetlands ...... 45

5.1. Removal Efficiency versus DOC for Hexachlorobenzene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year ...... 51

5.2. Removal Efficiency versus DOC for Naphthalene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year ...... 52

5.3. Removal Efficiency versus DOC for Hexachlorobenzene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year ......................... 53

5.4. Removal Efficiency versus DOC for Naphthalene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year ......................... 54

5.5. Removal Efficiency versus \( DOC_b \) for Hexachlorobenzene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year ...... 55

5.6. Removal Efficiency versus \( DOC_b \) for Naphthalene in Bottomland Forest Wetlands, Hydraulic Loading Rate = 20 m/year ......................... 56
5.7. Removal Efficiency versus $\text{DOC}_b$ for Hexachlorobenzene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year ...................... 57

5.8. Removal Efficiency versus $\text{DOC}_b$ for Naphthalene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year ...................... 58

5.9. Removal Efficiency versus $K_w$ for Hexachlorobenzene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year ...... 60

5.10. Removal Efficiency versus $K_w$ for Naphthalene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year .... 61

5.11. Removal Efficiency versus $K_w$ for Hexachlorobenzene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year ...................... 62

5.12. Removal Efficiency versus $K_w$ for Naphthalene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year ...................... 63

5.13. Effect in the Assimilatory Process ($v_t$) by Depth of the Sediment Bed ($Z_b$) for Hexachlorobenzene in Bottomland Hardwood Forest Wetlands ...................... 65

5.14. Effect in the Assimilatory Process ($v_t$) by Depth of the Sediment Bed ($Z_b$) for Naphthalene in Bottomland Hardwood Forest Wetlands ...................... 65

5.15. Effect in the Assimilatory Process ($v_t$) by Depth of the Sediment Bed ($Z_b$) for Hexachlorobenzene in Freshwater Marsh Wetland ...................... 66

5.16. Effect in the Assimilatory Process ($v_t$) by Depth of the Sediment Bed ($Z_b$) for Naphthalene in Freshwater Marsh Wetland ...................... 66
ABSTRACT

The ability of removing toxic organic compounds in natural systems is important due to the capacity of these toxicants to increase risk of diseases when they are ingested by humans. This study developed a mechanistic model to estimate the removal efficiency of toxic organics in wetlands using the tanks-in-series model. Sensitivity analyses were performed for different values of the hydraulic loading rate and two kinds of wetlands: bottomland hardwood forest and freshwater marsh. It was observed the effect in the removal efficiency by the number of cell in series was principally perceived for values of N between 1 and 4; that for both kind of wetlands. The most hydraulic loading rate, the less removal of organic compounds was observed in both kinds of wetlands and for the different values of N.

For the same value of hydraulic loading rate, number of sections considered (N) and the same kind of wetland, soluble organics (low K_{ow}) as naphthalene were more assimilated than hydrophobic organics (high K_{ow}) as hexachlorobenzene.

Two zones were well defined on the logarithmic space defined by Sorption versus Henry’s Constant for two conditions total recycle and no recycle: Air zone and sediment zone.

Removal efficiency went down when the value of DOC in the water column went up for insoluble organics as hexachlorobenzene. For soluble organics as naphthalene no effect was observed. That was observed in both kinds of wetlands.

Removal efficiency has no a large dependence of the value of DOC in the sediment bed, in both kinds of wetlands and for both kind of compounds (lower and higher K_{ow} value).
The higher $K_w$ of the pollutant, the higher removal in both of the kind of wetlands was observed in this analysis.

It was observed that removal efficiency is higher when the sediment bed depth is higher until determined values depending of the kind of pollutant.

It was observed that removal efficiency is higher for soluble organics as naphthalene than for hydrophobic organics as hexachlorobenzene, and in addition higher removal efficiency is observed in bottomland hardwood forest wetlands than in freshwater marshes.
CHAPTER 1. INTRODUCTION

1.1. Background

Fate of toxic organic compounds in runoff into aquatic systems is a problem that must be resolved by understanding how natural systems assimilate organics and the effects of the pollutants on the general function of these ecosystems (Pardue, 1992). Organic toxicants in water can increase risk of cancer; produce blood, nervous system, cardiovascular system or reproductive problems, anemia, and other problems when they are ingested by humans. The problem of removal of these toxicants has attracted the attention of many researchers in the last thirty years. Contamination in lakes has been widely studied. The removal of organics in wetlands has not been widely studied; however, studies have shown that toxic organics are readily removed in wetlands and constructed wetlands are a good technology for controlling and removing organic pollutants (Kadlec and Knight, 1996; Yang et al, 1995; Bourquin, 1977; Lunz, 1979).

Wetlands are defined as those areas that are either inundated or saturated at a frequency and duration to maintain saturated conditions in the soil (EPA, 1988). The importance of wetlands around the world has growth up since 1986 with the Piracicaba Conference, and also with different conferences in Chattanooga (1988), Cambridge (1990), Sydney (1992), and Guangzhou (1994) (Wood, 1995). In the US there are more than 270 millions of acres of natural wetlands, and in states like Alaska, Florida, Louisiana, Maine and South Caroline they occupy more than one quarter of the total area of the state (Kadlec and Knight, 1996).

The construction of wetlands is a relatively new technology that began in the 1970s (Kadlec and Knight, 1996). Each day wetlands become more important for the
necessity of using renewable, naturally occurring energies such as solar radiation, the kinetic energy of wind, the chemical-free energy of rainwater, surface water, and groundwater (Kadlec and Knight, 1996). These systems are more commonly used for municipal wastewater treatment in small communities, especially due to the low cost, and because these kinds of communities don’t have land restrictions.

Different processes act in aquatic systems to remove organic toxicants: evaporation, volatilization, photolysis (chemical decomposition due to the action of light), chemical reactions, and microbial degradation (Chapra and Reckhow, 1983), adsorption of the contaminants, uptake by system biota, and mass transfer processes as advection, dispersion, and diffusion (Pardue, 1992).

Volatilization is the most important mechanism of transport for elimination of a large number of the organic priority pollutants from aquatic systems (Jaffe and Ferrara, 1983). Volatilization of organic compounds from waters is affected by system factors such as wind and water turbulence, and depth of the solute in water. Also, characteristics of the solute affect this process; they are vapor pressure and solubility, which give the Henry’s constant, a measure of the capacity of the compound to volatilize.

Wetlands are systems that have a wide range of chemical transformations due to the ample variety of oxidation states that can occur naturally in them. Also, bacterial degradation is abundant due to the large biological diversity from the smallest viruses to the largest trees (Kadlec and Knight, 1996). In addition to these reactive processes, adsorption of contaminants in wetlands is efficient due to the high organic matter content of these systems (Kadlec and Knight, 1996).
In 1988 O’Connor developed a model that described the fate of sorptive toxic substances in freshwater systems. This model developed equations that defined the steady-state distribution of sorbing toxics such as heavy metals, inorganic and organic chemicals, and radionuclides. Due to the fact that the food chain was not included in the equations of mass balance, the developed equations are mainly appropriate to rivers, reservoirs and oligotrophic, rather than eutrophic lakes. Chapra (1991) later referred to the former computational frameworks (Thomann and Mueller, 1987; O’Connor, 1988a, 1988b, 1988c; Thomann and Di Toro, 1983; Chapra and Reckhow, 1983; Di Toro and Paquin, 1984) as the “Manhattan College Framework” and used them as a base to develop a model for organic contaminants in lakes. These works developed simple mechanistic models for toxicants in lakes and streams.

In this work, these models will be used as a base to develop a conceptual model for calculating the removal efficiency of toxic organics in wetlands. Due to the negative effects in the human health and the environment that toxic organics produce, it is necessary to develop a model that describes the removal efficiency of these toxicants in wetlands when they receive them, and to know how the different parameters affect this concentration.

There are two kind of mathematical models: statistical and mechanistic models. The first one is based on data sets from existing wetlands and these models are not necessarily designed with an idea of how the systems work. On the other hand, the mechanistic models express mathematically the cause-effect relationships (Chapra and Reckhow, 1983). Statistical models need adequate data bases that are not available for many wetlands and pollutants. So, mechanistic models are the more practical option.
However, when statistical data is available, both of these models can be used together (Chapra, 1991).

This research has two fundamental differences with the Chapra and Manhattan College framework. First of all, this model will have a “third phase” due to the high levels of dissolved organic carbon present in wetlands (Pardue, 1992). DOC is the organic carbon that passes through a 0.45 μm filter. DOC is determined by oxidation to carbon dioxide and by measurement of carbon dioxide by infrared spectrometry (Van Hall and others, 1963; Menzel and Vaccaro, 1964). In most of wetlands the concentration of DOC is greater than in the other types of aquatic systems. This is because of the presence of emergent plants in these environments (Thurman, 1985). It is the reason why in wetlands this “third phase” may be an important factor. It will make the sediment-water interactions more important than in previous efforts.

Secondly, this model would not idealize the wetlands as a well-mixed reactor. This model will use the tanks-in-series (TIS) model advocated by the Water Pollution Control Federation (1990). The use of the TIS approach builds on development of a previous 3-phase model by Pardue (1992). In this approach, the wetland is not idealized as a completely mixed tank. The wetland may be considered as divided into a number of equal sized cells (N), each one completely mixed. Values from 2 to 5 have been observed in operating SF treatment wetlands (Kadlec and Knight, 1996). A value of N = 1 corresponds to a totally mixed wetland, and a value of N=∞ is the plug flow extreme. Fractional numbers are allowable too. Even wetlands with aspect ratio of 25:1 may be represented by N=1 or N=2 (Kadlec and Knight, 1996). For determining N is better from the dimensionless variance (Levenspiel, 1972). N is given by one divided by the square
of the variance \( (N = 1/\sigma^2) \). Several studies have found different values for the normalized variance from which the value of \( N \) can be calculated for constructed wetlands (Kadlec, 1994; Stairs, 1993; TVA, 1990; Fisher, 1990; Bavor et al, 1988; Herskowitz, 1986; and Rosendahl, 1981).

Figure 1.1 shows a schematic model of assimilation for organics in wetlands. As showed in this figure, the DOC phase is present to remove the toxicants in wetlands. This figure will be used in chapter 2 in order to develop the necessary budgets for the model.


EPA has developed a list of organic pollutants which has been used in this work.
1.2. Objectives

The overall objective of this work is to develop a mechanistic model for estimating the removal efficiency of toxic organics in wetlands. The specific objectives were:

(i.) Evaluation of the effect on removal efficiency by the number of cells in series (N) in wetlands.

(ii.) Evaluation of the effect in the assimilatory process by the value of DOC in the sediment bed and the overlying water, the decay rate of the toxicant in water \( (K_w) \), and depth of the sediment bed \( (Z_b) \).

(iii.) Determination of the impact of sorption and volatilization on the assimilatory process for priority organic pollutants in wetlands.

(iv.) Determination of the effect of the kind of wetland (bottomland hardwood forest and freshwater marsh) on the assimilatory process.
CHAPTER 2. DEVELOPMENT OF MODEL

2.1. Toxicant Removal Concept in Tanks-in-series Model (TIS)

The TIS model was advocated by the WPCF (1990) for wastewater lagoons and it stated that lagoons can be partitioned into a number of equal sized pieces (N), each one presumed to be completely mixed (Kadlec and Knight, 1996). Wetlands can be conceptualized in the same way. Figure 2.1 shows the tanks-in-series model for mixing in a treatment wetland (Kadlec and Knight, 1996).

![Figure 2.1. The Tanks-in-series Model for Mixing in a Treatment Wetland. (Kadlec and Knight, 1996)](image)

In Figure 2.1 for jth tank the mass balance equation is (Kadlec and Knight, 1996):

\[ Q_{j-1} \cdot C_{j-1} - Q_j \cdot C_j = R_j = k \cdot A_j \cdot (C_j - C^*) \]

For making the model simpler, we are going to suppose rain and ET are balanced, thus

\[ Q_j = Q_{j-1} \]
2.2. Assimilation Model for Toxic Organics in Wetlands

In a simple way, the steady-state pollutant budget can be represented by (Chapra, 1991):

\[ C = \beta C_{in} \]

Where:

- \( C \): pollutant concentration (g/m³)
- \( \beta \): assimilation transfer function
- \( C_{in} \): inflow pollutant concentration (g/m³)

This equation in its simplest form, relates the response of an ecosystem (\( C \)) to a stimulus pollutant load (\( C_{in} \)). \( \beta \) is a proportionality factor that quantifies the capacity for assimilation that the system has for a given pollutant. \( \beta \) is made up of two components: the chemical, physical and biological processes (\( v_i \)) that contribute to assimilation and the amount of water that is added to the system (\( q \)).

\[ \beta = \frac{q}{q + v_i} \]

Using a mechanistic approach, the assimilation function can be estimated based on a mass balance.

2.3. System Component Budgets

First, we consider that the wetland is composed of a series of \( N \) sections that are completely mixed. Each wetland section consists of a water column and a sediment bed. Within each water column and sediment bed are solids, water and colloidal DOC. A mass balance of solids, water and DOC can be made for each wetland section, and
pollutants partition between each one of these phases, leading to a mass balance for the pollutant in the wetland.

2.3.1. Solid Budget

Suspended solids are important in the function of wetlands as a transporter of other components (Kadlec and Kadlec, 1978). Mass balance of solids in the water column in the jth tank is given by (Figure 1.1):

\[
V_j \frac{dm}{dt} = Q_j m_j - Q_{j-1} m_{j-1} - v_s A_j m_j + v_u A_j(1 - \phi) \rho
\]

Where:

- \( V \): volume of the tank considered, m³.
- \( m \): suspended solids concentration in the inlet (j-1) or outlet (j), g/m³.
- \( t \): time, years.
- \( Q \): water flow rate through the wetland, m³/year.
- \( v_s \): settling velocity of suspended solids, m/year.
- \( A \): wetland surface area, m².
- \( v_u \): the upward mass-transfer coefficient of solids due to sediment resuspension or scour, m/year.
- \( \phi \): sediment porosity
- \( \rho \): density of sediment solids, g/m³.

In the bed:

\[
\frac{d(V_b, m_b)}{dt} = v_s A_j m_j - v_u A_j (1 - \phi) \rho - v_b A_j (1 - \phi) \rho
\]

Where the suffix b indicates that the parameter is considered in the bed, and:
v_b: burial velocity or sedimentation rate, m/year.

At steady-state:

\[ 0 = Q_m \cdot m_j - v_s \cdot A_j \cdot m_j + v_u \cdot A_j (1 - \phi) \rho \]  
\[ 0 = v_s \cdot A_j \cdot m_j - v_u \cdot A_j (1 - \phi) \rho - v_b \cdot A_j (1 - \phi) \rho \]  

(2.1) \hspace{1cm} (2.2)

In Equation 2.2:

\[ (1 - \phi) \rho = \frac{m_j \cdot v_s}{v_u + v_b} \]

Replacing in Equation 2.1:

\[ 0 = Q_m \cdot m_j - Q \cdot m_j - v_s \cdot A_j \cdot m_j + v_u \cdot A_j \cdot m_j \cdot \frac{v_u}{v_u + v_b} \]

\[ m_j = \frac{Q \cdot m_j - 1}{Q + v_s \cdot A_j - \frac{v_u \cdot A_j \cdot v_s}{v_u + v_b}} \]

Dividing by A_j:

\[ m_j = \frac{q_j \cdot m_j - 1}{q_j + v_s - \frac{v_u \cdot v_b}{v_u + v_b}} = \frac{q_j \cdot m_j - 1}{q_j + v_s (1 - \frac{v_u}{v_u + v_b})} \]

Where:

q: hydraulic loading rate, m/year.  (q = Q/A)

If Fr (resuspension ratio) = (v_u/( v_u + v_b)), then the suspended solid concentration in the wetland (m) in the jth tank is:

\[ m_j = \frac{q_j \cdot m_j - 1}{q_j + v_s (1 - Fr)} \]
2.3.2. **DOC Budget**

The model assumes two sources of DOC to the water column: input from upstream ecosystems and the diffusive flux of material from the sediment bed.

DOC is lost from the water column as diffusive flux to the sediment bed and that DOC exported from the system in stream flow.

Water Column, in the jth tank:

\[
V_j \frac{dDOC_j}{dt} = Q_{j-1} \cdot DOC_{j-1} - Q_j \cdot DOC_j - (DOC_j - DOC_{bj} \cdot \phi_j) \cdot v_d \cdot A_j
\]

Where:

\(v_d\): diffusion mass-transfer coefficient, m/year.

Sediment bed in the jth tank:

\[
V_{bj} \cdot \phi_{bj} \frac{dDOC_{bj}}{dt} = V_{bj} \cdot k_p \cdot DOC_{bj} + (DOC_j - DOC_{bj} \cdot \phi_j) \cdot v_d \cdot A_j
\]

Where:

\(k_p\): production/leaching rate of DOC in the bed, 1/year.

At steady-state:

\[
0 = Q_{j-1} \cdot DOC_{j-1} - Q_j \cdot DOC_j - (DOC_j - DOC_{bj} \cdot \phi_j) \cdot v_d \cdot A_j \quad (2.3)
\]

\[
0 = V_{bj} \cdot k_p \cdot DOC_{bj} + (DOC_j - DOC_{bj} \cdot \phi_j) \cdot v_d \cdot A_j \quad (2.4)
\]

In Equation 2.4:

\[
0 = DOC_{bj}(V_{bj} \cdot k_p - v_d \cdot A_j \cdot \phi_b) + DOC_j \cdot v_d \cdot A_j
\]

\[
DOC_{bj}(-V_{bj} \cdot k_p + v_d \cdot A_j \cdot \phi_b) = DOC_j \cdot v_d \cdot A_j
\]
Replacing in Equation 2.3:

\[ 0 = Q_{j-1} \cdot DOC_{j-1} - Q_j \cdot DOC_j - DOC_j \cdot v_d \cdot A_j - \frac{DOC_j \cdot v_d \cdot A_j}{(v_d \cdot A_j \cdot \phi_b - V_{bj} \cdot k_p)} \cdot v_d \cdot A_j \]

\[ DOC_j = \frac{Q \cdot DOC_{j-1}}{Q + A_j v_d - \frac{(v_d A_j)^2 \cdot \phi_b}{(v_d \cdot A_j \cdot \phi_b - V_{bj} \cdot k_p)}} \]

\[ DOC_j = \frac{q \cdot DOC_{j-1}}{q + v_d - \frac{v_d^2 \cdot A_j \cdot \phi_b}{(v_d \cdot A_j \cdot \phi_b - V_{bj} \cdot k_p)}} \]

\[ V_{bj} = Z_{bj} \cdot A_j \]

\[ DOC_j = \frac{q \cdot DOC_{j-1}}{q + v_d - \frac{v_d \cdot \phi_b}{(v_d \cdot \phi_b - Z_{bj} \cdot k_p)}} \]

\[ DOC_j = \frac{q \cdot DOC_{j-1}}{q + v_d(1 - \frac{v_d \cdot \phi_b}{(v_d \cdot \phi_b - Z_{bj} \cdot k_p)})} \]

\[ DOC_j = \frac{q \cdot DOC_{j-1}}{q + v_d(\frac{v_d \cdot \phi_b - Z_{bj} \cdot k_p - v_d \cdot \phi_b}{(v_d \cdot \phi_b - Z_{bj} \cdot k_p)})} \]

\[ DOC_j = \frac{q \cdot DOC_{j-1}}{q + v_d(\frac{Z_{bj} \cdot k_p}{(Z_{bj} \cdot k_p - v_d \cdot \phi_b)})} \]

12
2.3.3. Toxicant Budget

In the water column:

\[
V_j \left( \frac{dC_{wj}}{dt} \right) = Q_{j-1} * C_{wj-1} - Q_j * C_{wj} - k_w * V_j * C_{wj} \\
- v_v * A_j * f_{dwj} * C_{wj} - v_v * A_j * f_{pwj} * C_{wj} + v_v * A_j * C_{bj} * f_{pbj} \\
+ v_d * A_j \left( f_{dbj} * C_{bj} - f_{dwj} * C_{wj} \right) + v_d * A_j \left( f_{docwj} * C_{wj} - f_{docbj} * C_{bj} \right)
\]

(2.5)

Where \( j \) and \( j-1 \) indicate the tank considered, and:

- \( C_{wj} \): total concentration of the pollutant in the water, g/m³.
- \( C_{bj} \): total concentration of the pollutant in the bed, g/m³.
- \( k_w \): decay rate of the toxicant in water, 1/year.
- \( f_{dw} \): fraction dissolved in the water column.
- \( f_{pw} \): fraction in particulate form in the water column.
- \( f_{db} \): fraction dissolved in the bed.
- \( f_{pb} \): fraction in particulate form in the bed.
- \( f_{docw} \): fraction associated with DOC in the water column.
- \( f_{docb} \): fraction associated with DOC in the bed.
- \( v_v \): volatilization rate constant, m/year.

Sediment bed:

\[
V_{bj} \left( \frac{dC_{bj}}{dt} \right) = v_v * A_j * f_{pwj} * C_{wj} - k_b * V_b * C_{bj} - v_v * A_j * C_{bj} - v_b * A_j * C_{bj} \\
+ v_d * A_j \left( f_{dwj} * C_{wj} - f_{dbj} * C_{bj} \right) + v_d * A_j \left( f_{docwj} * C_{wj} - f_{docbj} * C_{bj} \right)
\]

(2.6)

Where:

- \( k_b \): degradation rate of the toxicant in the bed, 1/year.
2.4. Speciation

Speciation of toxic organics in fractions into the three phases (water, DOC, and particulate) requires knowledge of sorption processes in these various phases (Pardue, 1992).

Analyzing a system with water-soluble and particulate phases only, sorption of toxicant organics can be described by:

\[ C_p = K_p C_w \]

Where:
- \( C_p \): concentration of the toxicant on the particulate, g/g
- \( C_w \): concentration of the toxicant in water, g/m³
- \( K_p \): the partition coefficient between particulates and water, m³/g

In a system with water and DOC phases, sorption can be described by:

\[ C_{doc} = K_{doc} C_w \]

Where:
- \( C_{doc} \): concentration of the toxicant associated with DOC, g/g.
- \( K_{doc} \): the partition coefficient between DOC and water, m³/g.

The fraction of particulate, DOC-associate and dissolved toxicant can be described in a general way as:

\[ f = \frac{C^*}{C_T} \]

Where:
- \( f \): fraction of toxicant in the respective phase.
- \( C^* \): concentration of the contaminant in the respective phase, g/m³.
- \( C_T \): total concentration of the toxicant in the system, g/m³.
$C_T$ is equal to the sum of the concentrations of the toxicant in the three phases (dissolved, particulate and DOC-associated), and the sum of the fractions in the three phases is equal to 1 in the column water and in the sediment bed. With the sorption relationships and the definition of the fraction of toxicant in each phase, we can derive the following equations (Pardue, 1992):

$$f_d = \frac{C^*}{C_T} = \frac{1}{1 + Kp.m + K_{doc}.DOC}$$

$$f_{doc} = \frac{C_{doc}^*}{C_T} = \frac{1}{1 + \frac{1}{K_{doc}.DOC} + \frac{Kp.m}{K_{doc}.DOC}}$$

$$f_p = \frac{C_p^*}{C_T} = \frac{1}{1 + \frac{1}{Kp.m} + \frac{K_{doc}.DOC}{Kp.m}}$$

2.5. Development of Equation of Assimilation and Removal

For making the model simpler, suppose rain and ET are balanced, thus $Q = Q_j = Q_{j-1}$, and the mass balance will be reduced to:

$$Q.C_{j-1} - Q.C_j = R_j = k.A_j.(C_j - C^*)$$

$$Q.C_{j-1} - Q.C_j - QC^* + QC^* = k.A_j.(C_j - C^*)$$

$$Q.(C_j - C^*) - Q.(C_j - C^*) = k.A_j.(C_j - C^*)$$

$$Q.(C_j - C^*) = (k.A_j + Q).(C_j - C^*)$$

$$\frac{(C_j - C^*)}{(C_j - C^*)} = \frac{Q}{(kA_j + Q)} = \frac{1}{kA_j + Q} = \frac{1}{k} + \frac{1}{q_j}$$

If $C^* = 0$, then:
\[
\frac{C_j}{C_{j-1}} = \frac{1}{kA_j} \frac{1}{(\frac{kA_j}{Q} + 1)}
\]

\[A_j = \frac{A_{total}}{N}, \text{ and } \frac{Q}{A} = q, \text{ then:}\]

\[
\frac{C_j}{C_{j-1}} = \frac{1}{kA_{total}} \frac{1}{(\frac{kA_{total}}{NQ} + 1)} = \frac{1}{(\frac{k}{Nq} + 1)}
\]

The fraction of pollutant in the outlet will be:

\[
\frac{C_{out}}{C_{N-1}} = \frac{1}{(\frac{k}{Nq} + 1)}
\]

And this fraction with respect to the concentration of pollutant in the inlet is:

\[
\frac{C_{out}}{C_{in}} = \frac{1}{(\frac{k}{Nq} + 1)^N}
\]  \hspace{1cm} (2.7)

In the steady state, equations 2.5 and 2.6 are equal zero. Also, dividing by \( A_j \), and making \( q_j = Q/A_j \), and \( q_{j-1} = Q/A_{j-1} = Q/A_j \) because \( A_j = A_{j-1} = A_{total} / N \). \hspace{1cm} (2.8)

\[
0 = q_{j-1} * C_{Wj-1} - q_j * C_{Wj} - kW * Z_{Wj} * C_{Wj} - v_s * fdw_{Wj} * C_{Wj} - v_s * fpw_{Wj} * C_{Wj} + v_s * C_b * fpb_j + v_d (fdh_j * C_b - f_{dwj} * C_{Wj}) + v_d (fdcb_j * C_b - fdocw_j * C_{Wj})
\]

\[
0 = v_s * fpw_{Wj} * C_{Wj} - k_b * Z_{bj} * C_{bj} - v_u * C_{bj} - v_b * C_{bj} + v_d (f_{dwj} * C_{Wj} - f_{dbj} * C_{bj}) + v_d (fdocw_{bj} * C_{Wj} - fdocb_{bj} * C_{bj})
\]  \hspace{1cm} (2.9)

In Equation 2.9:

\[
C_{bj} = \frac{C_{Wj}(v_s * fpw_{Wj} + v_d * f_{dwj} + v_d * fdocw_{Wj})}{(k_b * Z_{bj} + v_u + v_b + v_d * f_{dbj} + v_d * fdocb_{bj})}
\]
Replace $C_{b_j}$ in equation 2.8:

$$0 = q_{j-1} * C_{w_j} - 1 - C_{w_j}(q_j + k_v * Z_{w_j} + v_v * f_{dw_j} + v_s * f_{pw_j} + v_d * f_{docw_j}) + C_{w_j} * \left( \frac{v_s * f_{pw_j} + v_d * f_{docw_j}}{k_b * Z_{b_j} + v_u + v_b + v_d * f_{db_j} + v_d * f_{docb_j}} \right) * (v_u * f_{pb_j} + v_d * f_{db_j} + v_d * f_{docb_j})$$

In view of the high concentration of solids in the bed ($f_{db} \approx 1$) (O’Connor, 1988) the recycle ratio ($R$), is given by:

$$R = \frac{(v_u + v_d * f_{db_j} + v_d * f_{docb_j})}{(k_b * Z_{b_j} + v_u + v_b + v_d * f_{db_j} + v_d * f_{docb_j})} \quad (2.10)$$

Then:

$$C_{w_j} = C_{w_j} - 1 \left( \frac{q_{j-1}}{(q_j + k_v * Z_{w_j} + v_v * f_{dw_j}) + (1 - R)(v_s * f_{pw_j} + v_d * f_{docw_j})} \right)$$

$$\quad (2.11)$$

If $v_t$ is the sum of physical, chemical, and biological assimilatory process:

$$v_t = (k_v * Z_{w_j} + v_v * f_{dw_j}) + (1 - R)(v_s * f_{pw_j} + v_d * f_{docw_j}) \quad (2.12)$$

Doing:

$f_{dw_j} = f_{dw} = \text{constant}$

$Z_{wj} = Z_w = \text{constant}$

$f_{pwj} = f_{pw} = \text{constant}$

$f_{docwj} = f_{docw} = \text{constant}$

$f_{dbj} = f_{db} = \text{constant}$
\[ f_{do\text{bj}} = f_{do\text{eb}} = \text{constant} \]

\[ Z_{bj} = Z_{b} = \text{constant} \]

Then for the tank N, respect to the inlet, and replacing k by \( v_i \):

\[
C_{out} = C_{in} \left( \frac{q}{q + \frac{w}{N}} \right)^N
\]

\[ (2.13) \]
CHAPTER 3. EFFECT OF REMOVAL EFFICIENCY BY NUMBER OF CELLS IN SERIES (N)

3.1. Introduction

N is defined as the number of completely mixed sections in which a wetland can be divided. Different values of N affect the calculated assimilation and removal efficiency of toxicants in natural systems like wetlands. Values of N between 1 and ∞ can be considered. A value of N=1 indicates that the wetland can be considered as one totally mixed section, and it is called the single continuous stirred tank reactor (CSTR) (Kadlec and Knight, 1996). On the other hand, a value of N=∞ represents the plug flow reactor (PFR) (Kadlec and Knight, 1996). Investigations have reported that values between 2 and 8 should be considered for constructed wetlands based on tracer studies (Stairs, 1993; Kadlec, 1994).

The factor of proportionality β was defined in Chapter 2 as the capacity for assimilation that the system has for a given pollutant. For wetlands with N totally mixed sections, assimilation can be defined as:

\[ C_{out} = C_{in} \left( \frac{q}{q + \frac{N}{N}} \right)^N \]  

(2.13)

Then β is defined by:

\[ \beta = \left( \frac{q}{q + \frac{N}{N}} \right)^N \]
Where $v_t$ is given by Equation 2.11:

$$v_t = \left( kw * Z_{w/ j} + v_r * f_{d/w} \right) + (1 - R) \left( v_r * f_{p/w} + v_d * f_{d/w} + v_d * f_{d/c/w} \right)$$  \hspace{1cm} (2.12)$$

The removal efficiency (R.E.) for a pollutant is given for the amount of pollutant removed:

$$RE = 1 - \frac{C_{out}}{C_{in}}$$

$$RE = 1 - \beta$$

$$RE = 1 - \left( \frac{q}{q + \frac{v}{N}} \right)^N$$

$$RE(\%) = \left[ 1 - \left( \frac{q}{q + \frac{v}{N}} \right)^N \right] * 100$$ \hspace{1cm} (3.1)$$

Using this equation and considering values of N=1 to N=8, we will get the effect of the N value on the calculated removal of the pollutant. Also, fractional values were considered (Kadlec and Knight, 1996).

It is important to define until what point the value of N have an effect on the values of calculated removal efficiency, and if taking one or another value, the design of a wetland is being too conservative resulting in lost of land.

3.2. Definition of Parameters

This analysis will compare two kinds of wetlands: bottomland hardwood forest wetlands and freshwater marshes, and two organic compounds: hexachlorobenzene (log $K_{ow}$=6.41) and naphthalene (log $K_{ow}$ = 3.29). The compounds are representative of larger
classes of compounds since most of the organics on the list of priority pollutants have log $K_{\text{ow}}$ (octanol-water partition coefficient) between 2.5 and 7. Tables 3.1 and 3.2 show the fixed parameters considered in this analysis. Parameters were obtained from laboratory and field measurements made by Pardue (1992).

From Chapra (1991), the resuspension velocity can be calculated by Equation 3.2.

$$v_u = Fr \cdot v_{sb}$$  \hspace{1cm} (3.2)

Where:

$Fr$: Resuspension ratio defined as:

$$Fr = \frac{v_u}{v_u + v_b}$$

$v_{sb}$: a scaled settling velocity defined as:

$$v_{sb} = \frac{m}{(1 - \phi) \rho} v_s$$

Equation 3.2 was deducted from Equation 3.2 and the definitions of Fr and $v_{sb}$.

$$v_u = \left(\frac{m}{\rho(1 - \phi)}\right) v_s - v_b$$  \hspace{1cm} (3.3)

For estimating the mass transfer diffusion coefficient, $v_d$, O’Connor (1988a) presented the following equation for hydraulically smooth surfaces as:

$$\frac{U^*}{v_d} = \left(\Gamma o.Sc^{2/3}\right) / \kappa^{1/3}$$  \hspace{1cm} (3.4)

Where:

$U^*$: shear velocity, cm/s.

$\Gamma o$: the dimensional thickness of the viscous sublayer = $U^*\partial/u$.

$\partial$: the thickness of the viscous sublayer.
ν: the kinematic viscosity of the water, cm²/s.

Sc: the Schmitt number = ν/D.

κ: von Karman constant.

D: molecular diffusion coefficient, cm²/s.

The values of νd in Table 3.1 were calculated using the correspondent value of D in the same table for each kind of wetland; ν, the kinematic viscosity (20°C) = 1.0105*10⁻² cm²/s; U* is estimated as 0.1 cm/s (suggested shear velocity for low turbulent freshwater water bodies, O’Connor, 1988a); Ïo, estimated as 10 from the shear velocity (O’Connor, 1984); κ, the Von Karman’s constant is 0.4 (Pardue, 1992).

Typical hydraulic loading rates for constructed surface-flow wetlands are between 0.7 to 5.0 cm/d (Kadlec and Knight, 1996). The analyses in this work were performed for values of hydraulic loading rate of 1, 10 and 20 m/year.

3.3. Analysis of Sensitivity

Figures 3.1 to 3.4 show the result for this analysis. Results are discussed below.

For hexachlorobenzene: As observed in Figures 3.1 and 3.2, the effect of N on the removal efficiency of hexachlorobenzene occurs for values of N between 1 and 4. For values of N above 4, there is not a strong variation in the removal efficiency with changes in N, since hexachlorobenzene is essentially completely removed. We can also say that there is not a considerable influence of the kind of wetland (bottomland hardwood forest and freshwater marsh) on the removal of hexachlorobenzene. As expected, the greater the hydraulic loading rate, the lower the removal of hexachlorobenzene is observed in both kinds of wetlands and for the different values of N.
Table 3.1 Fixed Parameters for Analysis in the Different Kinds of Wetlands (Pardue, 1992).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bottomland Hardwood</th>
<th>Freshwater Marsh</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Interval</td>
<td>Used value in the analysis</td>
<td>Interval</td>
</tr>
<tr>
<td>( v_b ) (cm/yr)</td>
<td>0.18</td>
<td>1.8E-3 m/yr</td>
<td>0.66 cm/yr</td>
</tr>
<tr>
<td>( v_s ) (m/yr)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>( v_d ) (m/yr)</td>
<td>50</td>
<td>50</td>
<td>64.6</td>
</tr>
<tr>
<td>( m_b ) (g/m³)</td>
<td>0.85*10^6</td>
<td>0.85*10^6</td>
<td>0.14*10^6</td>
</tr>
<tr>
<td>( m ) (g/m³)</td>
<td>10-156</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>DOC (g/m³)</td>
<td>7.2-24</td>
<td>10</td>
<td>21-80</td>
</tr>
<tr>
<td>DOC(_b) (g/m³)</td>
<td>12.4 - 28.5</td>
<td>25</td>
<td>10.5 – 245</td>
</tr>
<tr>
<td>D (cm²/d)</td>
<td>2.76</td>
<td>2.76</td>
<td>4.04</td>
</tr>
<tr>
<td>( \rho ) (g/cm³)</td>
<td>0.85</td>
<td>0.85</td>
<td>0.14</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>0.6</td>
<td>0.6</td>
<td>0.82</td>
</tr>
<tr>
<td>( v_u ) (m/yr)</td>
<td>1.29*10^-2</td>
<td>1.32*10^-2</td>
<td></td>
</tr>
<tr>
<td>( k_w ) (1/yr)</td>
<td>1-100</td>
<td>10</td>
<td>1-100</td>
</tr>
</tbody>
</table>
Table 3.2. Fixed Parameters for Hexachlorobenzene and Naphthalene (Pardue, 1992).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hexachlorobenzene</th>
<th></th>
<th>Naphthalene</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bottomland</td>
<td>Freshwater</td>
<td>Bottomland</td>
<td>Freshwater</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hardwood</td>
<td>Marsh</td>
<td>Hardwood</td>
<td>Marsh</td>
<td></td>
</tr>
<tr>
<td>$k_{doc}$ (m³/g)</td>
<td>$10^{-1.62}$</td>
<td>$10^{-1.62}$</td>
<td>$10^{-2.73}$</td>
<td>$10^{-2.80}$</td>
<td></td>
</tr>
<tr>
<td>$k_{p}$ (m³/g)</td>
<td>$10^{-2.28}$</td>
<td>$10^{-2.31}$</td>
<td>$10^{-4.29}$</td>
<td>$10^{-3.77}$</td>
<td></td>
</tr>
<tr>
<td>$v_v$ (m/yr)</td>
<td>110</td>
<td>110</td>
<td>150</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>$k_b$ (1/yr)</td>
<td>4.95</td>
<td>9.78</td>
<td>39.8</td>
<td>44.9</td>
<td></td>
</tr>
</tbody>
</table>
**For naphthalene:** Similar trends were observed for naphthalene. For the same value of hydraulic loading rate, number of sections considered (N) and the same kind of wetland, naphthalene is more assimilated than hexachlorobenzene. As observed in Figures 3.3 and 3.4, it can be said that the effect on the removal efficiency of the value of N is larger for values of N between 1 and 4 than for values of N above 4. There is not considerable variation in the removal efficiency with N for values of N over 4, since naphthalene is completely removed. We can also say, as in the case of hexachlorobenzene, that there is not a considerable influence of the kind of wetland (bottomland hardwood forest and freshwater marsh) for the removal of naphthalene. The higher the hydraulic loading rate, the lower the removal of naphthalene is observed in both kinds of wetlands and for the different values of N.

Although N does affect the removal of hexachlorobenzene and naphthalene for values between 1 and 4, the assimilation function, $\beta$, is dominated by the highly efficient biodegradation, sorption, and volatilization processes which make up $\nu_t$. Even at very high loading rates ($q = 20$), removal efficiency exceeds 80%. More water soluble, less biodegradable compounds may be more poorly removed and the effect of the number of tanks-in-series may be more important.

In general, if we are designing constructed wetlands and assume N=1 we are over designing the wetland. Values of between 2 and 8 are commonly found in treatment wetlands and very large natural wetlands may require more units in series.
Figure 3.1. Removal Efficiency for Different Number of Cells in Series in Bottomland Hardwood Forest Wetlands (Hexachlorobenzene).

Figure 3.2. Removal Efficiency for Different Number of Cells in Series in Freshwater Marsh (Hexachlorobenzene).
Figure 3.3. Removal Efficiency for Different Number of Cells in Series in Bottomland Hardwood Forest Wetlands (Naphthalene).

Figure 3.4. Removal Efficiency for Different Number of Cells in Series in Freshwater Marsh (Naphthalene).
CHAPTER 4. IMPACT OF SORPTION AND VOLATILIZATION ON THE ASSIMILATORY FUNCTION ($v_t$) FOR PRIORITY ORGANIC POLLUTANTS

4.1. Introduction

Sorption, the partitioning of organics onto solids, and volatilization, the transfer of organics from the water to air, are important fate processes in wetlands. The relative importance of these processes determines whether chemicals will remain in the bed for biological or chemical reactions to occur or simply transfer to the air phase. In this chapter we analyze the way sorption and volatilization act together to remove toxicants from wetlands. This analysis was performed by plotting values of $v_t$ on a logarithmic space defined by the sorption parameter (the partition coefficient, $K_p$) and the volatilization parameter (given by the Henry’s constant, a measure of the tendency of the compound to volatilize).

Using equation 2.12 defined in chapter 2, we calculate $v_t$:

$$v_t = (kw*Z_{w_j} + v_r*fd_{w_j}) + (1 - R)(v_r*fp_{w_j} + n_{a} + nd_{w_j} + n_{a} * fdoc_{w_j})$$  \hspace{1cm} (2.12)

The coefficient of volatilization mass-transfer $v_v$ can be calculated with Whitman’s two-film model (Whitman, 1923; Lewis and Whitman, 1924).

$$v_v = k_i \frac{He}{He + RTa \left( \frac{k_i}{k_g} \right)}$$  \hspace{1cm} (4.1)

where

He: Henry’s constant, atm m³/ mole.

R: the universal gas constant, $8.206 \times 10^{-5}$ atm m³/K.mole.

$k_i$: the liquid-film mass-transfer coefficient, m/yr.
**k_g:** the gas-film mass transfer coefficient, m/yr.

**T_a:** absolute temperature, °K.

Equation 4.2 is useful to calculate the gas-film coefficient which is correlated with the evaporation of water (Mills et al, 1982).

\[
k_g = 61320 \left( \frac{18}{M} \right)^{0.25} U_w
\]  

(4.2)

where:

**M:** molecular weight

**U_w:** wind velocity, m/s.

Liquid-film mass-transfer is correlated with the oxygen mass-transfer coefficient (\(K_L, \text{ m/yr}\)) (Mills et al, 1982). Equation 4.3 shows this correlation.

\[
k_f = \left( \frac{32}{M} \right)^{0.25} K_L
\]  

(4.3)

where:

\[
K_L = 0.728 U_w^{0.5} - 0.317 U_w + 0.0372 U_w^2
\]

\(K_L\) has unit of m/d.

The partition coefficients, \(K_p\) and \(K_{doc}\), are related with the organic carbon content of the particulate and colloidal matter, as (Pardue, 1992):

\[
K_p = f_{oc} \cdot K_{oc}
\]  

(4.4)
\[ K_{doc} = (f_{oc,\text{colloid}}) K_{oc} \]  \hspace{1cm} (4.5)

where:

\( f_{oc} \): the fraction or organic carbon in the particulate matter.

\( f_{oc,\text{colloid}} \): the fraction of organic carbon in the colloidal matter.

\( K_{oc} \): the normalized organic carbon partition coefficient, m³/g.

As in this research we are quantifying colloidal organic carbon as DOC, then
\( f_{oc,\text{colloid}} = 1 \), and equation 4.5 change to:

\[ K_{doc} = K_{oc} \]  \hspace{1cm} (4.6)

Several investigations have found empirical relationships between \( K_{ow} \) and \( K_{oc} \) (Schwartzenbach and Westall, 1981; Karickhoff et al., 1979; and Lyman et al., 1982), however in this work we will use the one established by Karickhoff et al (1979), which was developed for neutral organic chemicals. Equation 4.7 was developed by Karickhoff to estimate the organic-carbon partition coefficient (\( K_{oc} \)) from the octanol-water partition coefficient (\( K_{ow} \)).

\[ K_{oc} = 6.17 \times 10^{-7} K_{ow} \]  \hspace{1cm} (4.7)

Combinations of Equations 4.4 and 4.7, and equations 4.6 and 4.7 result in equations 4.8 and 4.9 respectively:

\[ K_p = 6.17 \times 10^{-7} f_{oc} K_{ow} \]  \hspace{1cm} (4.8)

\[ K_{doc} = 6.17 \times 10^{-7} K_{ow} \]  \hspace{1cm} (4.9)

4.2. Definition of Parameters

Table 3.1 shows the fixed parameters for each wetland type. Other fixed values include: \( R = 8.21 \times 10^{-5} \text{ atm-m}^3/\text{mole-}^o\text{K} \); \( U_w = 2.24 \text{ m/s} \); \( T_a = 273^o\text{K} \); \( M = 200 \text{ g/gmole} \);
For the development of this analysis data for Henry’s constant and $K_{ow}$ for organic pollutants were tabulated as in Appendix A. Sensitivity analyses were performed for two extreme cases: no recycle of organics from the sediment bed ($R=0$) and total recycle of organics from the sediment bed ($R=1$).

4.3. Mapping of the Assimilation Function, $v_t$, for Different Classes of Organics

4.3.1. Mapping on Logarithmic Space Defined by Sorption ($K_p.m$) versus Henry’s Constant ($He$)

In this first part, sorption was represented by the product of $K_p$, the partition coefficient, and $m$, the mass of suspended solids in the water column. Figures 4.1 and 4.2 show the plot for the organic pollutants into a bottomland hardwood forest and freshwater marsh wetlands for total recycle ($R=1$). In both figures there can be defined three spaces differentiated by the value of $v_t$: one space for $v_t$ less than 10, one space for values of $v_t$ between 10 and 100 and another one for $v_t$ higher than 100. For both wetland types, the limit between the first ($v_t<10$) and the second space ($10<v_t<100$) is at $\log He = 6.1$ and $\log (K_p.m) = -1$. The limit between the second ($10<v_t<100$) and third spaces ($v_t>100$) is on the order of $\log He = -4.2$ and $\log (K_p.m) = -2$. The difference between values of these limits for each kind of wetland is insignificant, and therefore, we conclude that the wetland type does not have big influence on the type of process that dominates the system (volatilization or sorption).

In the second case ($R=0$), we defined only two spaces: one where $v_t$ is less than 100 and the second, where $v_t$ is higher than 100. For this case, the limit between spaces is on the order of $\log He = 5$ and $\log (K_p.m) = -1$, and the same conclusion can be drawn: the kind of wetland does not have big influence in the type of process that dominates the system.
Figure 4.1. Mapping for Organic Pollutants for the Assimilation Function $v_t$ (m/year) on a Logarithmic Space Defined by Sorption ($K_{p,m}$) versus Henry’s Constant ($H_e$). Total Recycle ($R=1$) is Assumed in Bottomland Hardwood Forest Wetlands.
Figure 4.2. Mapping for Organic Pollutants for the Assimilation Function \( v_t \) (m/year) on a Logarithmic Space Defined by Sorption (\( K_{p,m} \)) versus Henry’s Constant (He). Total Recycle (R=1) is Assumed in Freshwater Marsh Wetland.
Figure 4.3. Mapping for Organic Pollutants for the Assimilation Function $v_t$ (m/year) on a Logarithmic Space Defined by Sorption ($K_{p,m}$) versus Henry’s Constant ($H_e$). No Recycle ($R=0$) is Assumed in Bottomland Hardwood Forest Wetlands.
Figure 4.4. Mapping for Organic Pollutants for the Assimilation Function $\nu_t$ (m/year) on a Logarithmic Space Defined by Sorption ($K_{p,m}$) versus Henry’s Constant (He). No Recycle (R=0) is Assumed in Freshwater Marsh Wetlands.
4.3.2. **Mapping on Logarithmic Space Defined by Sorption to Colloids ($K_{\text{doc}}$-DOC) versus Henry’s Constant (He)**

In this second mapping, sorption was represented by the product of $K_{\text{doc}}$ and DOC, to represent the partition of organics to colloidal DOC. Figures 4.5 and 4.6 show the mapping plots for organic pollutants in a bottomland hardwood forest and freshwater marsh wetlands for total recycle (R=1). As in the first part of this analysis, in both figures three spaces can be defined differentiated by the value of the assimilation function, $v_t$: one space for $v_t$ less than 10, one space for values of $v_t$ between 10 and 100 and another one for $v_t$ higher than 100. In both cases, the limit between the first ($v_t<10$) and the second space ($10<v_t<100$) is on the order of log $He = 6.1$ and log ($K_{\text{doc}}$ DOC) = 0.5. Also, the limit between the second ($10<v_t<100$) and third spaces ($v_t>100$) is on the order of log $He = -4.2$ and log ($K_{\text{doc}}$ DOC) = -1. The difference between values of these limits for each kind of wetland is insignificant, and therefore, we can say that the kind of wetland does not have big influence in the type of process that dominates the system (volatilization or sorption).

In the second case (R=0), we defined only two spaces: one, the space where $v_t$ is less than 100 and the second is where $v_t$ is higher than 100. Again, the difference between limits is insignificant for each kind of wetland. For this case, the limit between spaces is in the order of log $He = 5$ and log ($K_{\text{doc}}$ DOC) = 0.5 and the same conclusion can be drawn: the kind of wetland does not have big influence in the type of process that dominates the system.

4.4. **Conclusions**

Figure 4.9 shows two zones that are well defined analyzing Figures 4.1 to 4.8:

Air zone: To this zone belong the contaminants that are insoluble (high Log He)
Figure 4.5. Mapping for Organic Pollutants of Net Loss Rate $v_t$ (m/year) on a Logarithmic Space Defined by Sorption to Colloids ($K_{doc}$-DOC) versus Henry’s Constant (He). Total Recycle ($R=1$) is Assumed in Bottomland Hardwood Forest Wetlands.
Figure 4.6. Mapping for Organic Pollutants of Net Loss Rate $v_t$ (m/year) on a Logarithmic Space Defined by Sorption to Colloids ($K_{doc}$-DOC) versus Henry’s Constant (He). Total Recycle (R=1) is Assumed in Freshwater Marsh Wetlands.
Figure 4.7. Mapping for Organic Pollutants of Net Loss Rate $v_t$ (m/year) on a Logarithmic Space Defined by Sorption to Colloids ($K_{doc}$-DOC) versus Henry’s Constant (He). No Recycle ($R=0$) is Assumed in Bottomland Hardwood Forest Wetlands.
Figure 4.8. Mapping for Organic Pollutants of Net Loss Rate $v_t$ (m/year) on a Logarithmic Space Defined by Sorption to Colloids ($K_{doc}$-DOC) versus Henry’s Constant (He). No Recycle ($R=0$) is Assumed in Freshwater Marsh Wetland.
Figure 4.9. Two Regions on a Logarithmic Space Defined by Sorption ($K_{p,m}$ or $K_{doc}$.DOC) versus Volatilization (He)
Figure 4.10. Mapping for Organic Pollutants (Halogenated Aliphatic Hydrocarbons, Nitrosamines, PCBs and PAHs) on Logarithmic Space Defined by Sorption (Kp.m) versus Volatilization (He) in Bottomland Hardwood Forest Wetlands.
Figure 4.11. Mapping for Organic Pollutants (Halogenated Ethers, Monocyclic Aromatics, Pesticides, and Phthalate Esters) on Logarithmic Space Defined by Sorption (Kp.m) versus Volatilization (He) in Bottomland Hardwood Forest Wetlands.
Figure 4.12. Mapping for Organic Pollutants (Halogenated Aliphatic Hydrocarbons, Nitrosamines, PCBs and PAHs) on Logarithmic Space Defined by Sorption (Kp.m) versus Volatilization (He) in Freshwater Marsh Wetlands.
Figure 4.13. Mapping for Organic Pollutants (Halogenated Ethers, Monocyclic Aromatics, Pesticides, and Phthalate Esters) on Logarithmic Space Defined by Sorption ($K_p m$) versus Volatilization ($H_e$) in Freshwater Marsh Wetlands.
and that sorb weakly (low Log ($K_p$ m) or low Log ($K_{doc}$ DOC)). They always have high removal rates (i.e., $v_t > 50$ m/yr), because they are almost wholly in dissolved form and they are subject to strong volatilization.

Sediment zone: To this zone belong the contaminants that are strong sorbers (high Log ($K_p$ m) or high Log ($K_{doc}$ DOC)), and the contaminants that being soluble (low Log He), they sorb weakly (low Log ($K_p$ m) or low Log ($K_{doc}$ DOC)). Their removal depends on sediment-water interactions. In the case of no recycle ($R=0$) they have high removal ($v_t > 50$ m/yr). In contrast, in the case of total recycle ($R=1$) they have relatively low removal ($v_t <10$ m/yr).

In contrast with Chapra’s report (1991), for wetlands the water zone is not well defined. We can say that in the case of wetlands this zone can disappear because of the presence of plants and other components in the water column, also the water column is not too large as in lakes.

There is not a big difference between the graphics with $K_{doc}$ DOC and $K_p$ m as the terms of sorption. Also, there is not a big difference in the results for each kind of wetland.

EPA has published a list of priority pollutants, in which they are classified in the following categories (Callahan, 1979):

- Pesticides
- PCBs and related compounds
- Halogenated Aliphatic Hydrocarbons
- Halogenated Ethers
- Monocyclic Aromatics (MAHs)
• Phthalate Esters
• Polycyclic Aromatic Hydrocarbons (PAHs)
• Nitrosamines and miscellaneous compounds

Figures 4.10 to 4.13 show the localization into Figure 4.9 of the different pollutants. Figures 4.10 and 4.11 shows the mapping for these organic pollutants in bottomland hardwood forest wetlands. Figures 4.12 and 4.13 shows the mapping of these pollutants in freshwater marsh wetlands. We can observe than halogenated aliphatic hydrocarbons are in the air zone, it means that they have always high value of \( v_i \) (high removal). On the other hand, phthalate esters are in the sediment zone and it means that their removal depends of recycle. The other pollutants are divided in the two zones, passing some ones from sediment zone to the air zone when comparing bottomland hardwood forest and freshwater marsh wetlands.
5.1. Introduction

Diverse characteristics of wetlands act to define the efficiency of removal in these natural systems. Some of these are: the concentration of DOC in the water column and in the porewater of the sediment bed, the decay rate of the toxicant in the water column ($K_w$), and the depth of the sediment bed ($z_b$). Changes in these parameters in the wetland can produce increases or decreases in the removal efficiency of toxic organics. It is very important to know how these changes affect the assimilatory processes of contaminants in wetlands for different values of the hydraulic loading rate, and in different kinds of wetlands.

The removal efficiency of contaminants in wetlands can be calculated by equation 3.1:

\[
RE(\%) = \left[1 - \left(\frac{q}{q + \frac{N}{N}}\right)^N\right] \times 100
\]  

(3.1.)

where $v_t$ is calculated using equation 2.12.

\[
v_t = (k_w \cdot Z_{wj} + v_r \cdot f d_{wj}) + (1 - R) (v_s \cdot fp_{wj} + v_d \cdot f d_{wj} + v_d \cdot f d_{ocw})
\]

(2.12)

In this chapter, using these equations, sensitivity analyses were performed to find the effect of the parameters above. Several values will be used in order to analyze the
effect on the removal efficiency of these parameters for hexachlorobenzene and naphthalene in bottomland hardwood forest and freshwater marsh wetlands.

5.2. Definition of Parameters

The fixed parameters for each kind of wetland (bottomland hardwood forest wetlands and freshwater marshes) and for the different toxicants (hexachlorobenzene and naphthalene) were presented in Tables 3.1 and 3.2. Typical hydraulic loading rates for constructed surface-flow wetlands are between 0.7 to 5.0 cm/d or 256 to 1825 cm/yr (Kadlec and Knight, 1996). The analysis was executed for values of hydraulic loading rate of 1, 10 and 20 m/year.

5.3. Sensitivity of Removal Efficiency by DOC

Previous studies determined ranges over which the DOC value is observed for both bottomland hardwoods and freshwater marshes site (Pardue, 1992). These concentrations are between 7.2 and 24 g/m³ for DOC for bottomland hardwood forest wetlands and 21 and 80 g/m³ for DOC in freshwater marsh wetlands. This range was placed in the model and Figures 5.1 to 5.4 shows the results. Different values of q (between 1 and 20 m/year) were utilized in the analysis, but only the graphics with q= 20 m/yr are shown here. It can be observed that increasing DOC in the system, results in lower removal of hexachlorobenzene in both wetland types. This observation supports a statement by Thurman (1985), that several factors may inhibit the assimilation of organic contaminants including DOC in wetlands. The decrease in the removal efficiency (and in the assimilation) is due to several factors. Volatilization is diminished in the presence of DOC since hydrophobic organics partition into DOC. Also, contaminant recycle from the bed increases. This is not observed for naphthalene, which is removed independently.
of the DOC concentration. The value of $K_{ow}$ strongly influences these results has for each compound. It is a high value of $K_{ow}$ in hexachlorobenzene ($\log K_{ow}=6.41$) and the lower value of $K_{ow}$ for naphthalene ($\log K_{ow} = 3.29$) which are the basis for calculating the partition coefficients $K_p$ and, of course, $v_t$. Removal of hexachlorobenzene is lower than for naphthalene (e.g., for $N =1$ the difference is about 5% more removal of naphthalene than hexachlorobenzene). Slightly higher removal efficiency is observed in bottomland hardwood forest wetlands than in freshwater marshes. Since wetlands have the highest concentrations of DOC of any aquatic system due to the high plant productivity of these systems (Pardue, 1992), we can made the conclusion that wetlands possibly will have less efficiency at absorbing certain organics, specially organics with high $K_{ow}$.

5.4. Sensitivity of Removal Efficiency by $DOC_b$

Values between 12.4 and 28.5 g/m³ for bottomland hardwood forest wetlands and 10.5 and 245 g/m³ for freshwater marshes were substituted into the model for $DOC_b$ (the concentration of DOC in the porewater) and Figures 5.4 to 5.8 show the results. Again, different values of $q$ between 1 and 20 were utilized in the analysis, but only the graphics with $q=20$ m/yr are showed here. It can be observed that the amount of $DOC_b$ in the system has no practical influence on the removal efficiency for hexachlorobenzene and naphthalene. Some influence can be observed in the removal efficiency for hexachlorobenzene in freshwater marsh wetland, but it is very slight (about 1%). However, it was observed that the removal efficiency for naphthalene is about 5% higher than for hexachlorobenzene. Again, slightly higher removal efficiency is observed in bottomland hardwood forest wetlands than in freshwater marshes (about 1-2%).
Figure 5.1. Removal Efficiency versus DOC for Hexachlorobenzene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year.
Figure 5.2. Removal Efficiency versus DOC for Naphthalene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year.
Figure 5.3. Removal Efficiency versus DOC for Hexachlorobenzene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year.
Figure 5.4. Removal Efficiency versus DOC for Naphthalene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year.
Figure 5.5. Removal Efficiency versus DOC_b for Hexachlorobenzene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year.
Figure 5.6. Removal Efficiency versus DOC\textsubscript{b} for Naphthalene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year.
Figure 5.7. Removal Efficiency versus DOC$_b$ for Hexachlorobenzene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year.
Figure 5.8. Removal Efficiency versus DOC$_b$ for Naphthalene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year.
5.5. Sensitivity of Removal Efficiency to the Decay Rate of the Toxicant in Water ($k_w$)

This sensitivity analysis was performed to determine the effect of the biodegradation in the water column. Since wetlands are vegetated, it is probable that a higher biodegradation rate in the water column, $k_w$, will be present with the biofilm on the plants, than might be observed in lakes, for example. Values between 1 and 100/yr for bottomland hardwood forest wetlands and freshwater marshes were put into the model and Figures 5.9 to 5.12 shows the results. In this case, again values of $q$ of 2, 10 and 20 were utilized in the analysis, but only the graphics with $q= 20$ m/yr are showed here. It can be observed that the higher $k_w$ of the pollutant, the higher removal in both of the kind of wetlands. Increases of 5% in removal efficiency were observed with increases from 1 to 100 /yr for $k_w$. As in the analysis of the other parameters, higher removal efficiency was observed for naphthalene than for hexachlorobenzene. In the case, once more, slightly higher removal efficiency is observed in bottomland hardwood forest wetlands than in freshwater marshes.

5.6. Sensitivity of Removal Efficiency by Depth of the Bed ($Z_b$)

Data from Table 3.1 and 3.2 were inserted into the model and different values of bed depth ($Z_b$) between 0.01 to 1 m were analyzed. We can observe in Figures 5.13 to 5.16 that removal of naphthalene is more dependent of the depth of the bed because $v_t$ is somewhat more variable in depths over 0.1 m, but for hexachlorobenzene $v_t$ becomes nearly constant at ~ 0.1 m in the depth. It is observed for both kinds of wetlands that $v_t$ becomes constant for depths over 0.3 m. These Figures show the fact that assimilation of naphthalene is higher than assimilation of hexachlorobenzene in both kinds of wetlands.
Figure 5.9. Removal Efficiency versus $K_w$ for Hexachlorobenzene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year.
Figure 5.10. Removal Efficiency versus $K_w$ for Naphthalene in Bottomland Hardwood Forest Wetlands, Hydraulic Loading Rate = 20 m/year.
Figure 5.11. Removal Efficiency versus $K_w$ for Hexachlorobenzene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year.
Figure 5.12. Removal Efficiency versus $K_w$ for Naphthalene in Freshwater Marsh Wetland, Hydraulic Loading Rate = 20 m/year.
We can conclude that the ideal depth of the bed is about 0.3 m, which gives the best removal efficiency for any toxic organic, and any higher value does not improve the removal efficiency.

5.7. Conclusions

Some conclusions can be drawn on the effect that the different characteristics of wetlands have in the removal efficiency.

First of all, the removal efficiency goes down when the value of DOC in the water column goes up, but it is observed only for hexachlorobenzene (high $K_{ow}$) and not for naphthalene (lower $K_{ow}$). This observation was observed in both kinds of wetlands (bottomland hardwood forest and freshwater marsh wetlands).

Secondly, the removal efficiency is not changed with the value of DOC in the sediment bed, in both kinds of wetlands and for both kind of compounds (lower and higher $K_{ow}$ values).

Third, it can be observed that the higher $K_{w}$ of the pollutant, the higher removal in both of the kind of wetlands. Although dramatic changes in $K_{w}$ do not significantly alter $v_{t}$.

Also, the removal efficiency is higher when the sediment bed depth is higher until a value of 0.1 m for pollutants with high value of $K_{ow}$ and 0.4 m for pollutant with low value of $K_{ow}$. Over those values, the removal efficiency became a constant value in both kinds of wetlands.

Another observation is that the removal efficiency is higher for naphthalene than for hexachlorobenzene, and, in addition, slightly higher removal efficiencies are observed in bottomland hardwood forest wetlands than in freshwater marshes.
Figure 5.13. Effect in the Assimilatory Process ($v_t$) by Depth of the Sediment Bed ($Z_b$) for Hexachlorobenzene in Bottomland Hardwood Forest Wetlands.

Figure 5.14. Effect in the Assimilatory Process ($v_t$) by Depth of the Sediment Bed ($Z_b$) for Naphthalene in Bottomland Hardwood Forest Wetlands.
Figure 5.15. Effect in the Assimilatory Process ($v_t$) by Depth of the Sediment Bed ($Z_b$) for Hexachlorobenzene in Freshwater Marsh Wetland.

Figure 5.16. Effect in the Assimilatory Process ($v_t$) by Depth of the Sediment Bed ($Z_b$) for Naphthalene in Freshwater Marsh Wetland.
6.1. Conclusions

The objectives of this study were to development a mechanistic model for estimating the removal efficiency of toxic organics in wetlands, and to use this model to evaluate the effect on removal efficiency by a number of parameters. These include the number of cells in series (N) in wetlands, the value of DOC in the sediment bed and the overlying water, the decay rate of the toxicant in water ($K_w$), the depth of the sediment bed ($Z_b$). Variations in these parameters were used to determine the impact of sorption and volatilization in the assimilatory process for priority organic pollutants in wetlands; and to determine the effect of the kind of wetland (bottomland hardwood forest and freshwater marsh) on the assimilatory process. The model was constructed giving emphasis to the importance of the DOC phase and the number of cells (N) in which the wetland can be divided.

Based on the analysis done, the following conclusions are given:

- The effect in the removal efficiency of the value of N (number of cells) is principally perceived for values of N between 1 and 4. For values of N above 4, there is not variation in the removal efficiency with N.

- There is not a considerable influence of the kind of wetland (bottomland hardwood forest and freshwater marsh) on the removal of organic compounds for different values of the number of cells considered.

- The greater hydraulic loading rate, the lower the removal of organic compounds as observed in both kinds of wetlands and for the different values of N.
For the same value of the hydraulic loading rate, the number of cells considered (N) and the same kind of wetland, more soluble organics with low $K_{ow}$ such as naphthalene are more assimilated than hydrophobic organics (high $K_{ow}$) as hexachlorobenzene.

Two zones are well defined on the logarithmic space defined by Sorption ($K_{doc}$ DOC or $K_{p,m}$) versus Henry’s Constant (He) for two conditions total recycle (R=1) and no recycle (R=0) in two kinds of wetlands (freshwater marsh and bottomland hardwood forest): Air zone (compounds with high removal rates (i.e., $v_t > 50$ m/yr), independent of the recycle) and sediment zone (their removal depends on sediment-water interactions).

Halogenated aliphatic hydrocarbons are in the air zone, it means that they have always high value of $v_t$ (high removal). On the other hand, phthalate esters are in the sediment zone and it means that their removal depends of recycle. The other pollutants are divided into the two zones, some passing from the sediment zone to the air zone when comparing bottomland hardwood forest and freshwater marsh wetlands.

Removal efficiency goes down when the value of DOC in the water column goes up, but it is observed only for insoluble organics as hexachlorobenzene (high $K_{ow}$) and not for soluble organics as naphthalene (low $K_{ow}$). This observation is seen in both kinds of wetlands (bottomland hardwood forest and freshwater marsh wetlands). Therefore, we can say that wetlands may be less efficient to remove certain organics due to the DOC phase.
Removal efficiency has no a large dependence of the value of DOC in the sediment bed, in both kinds of wetlands and for both kind of compounds (lower and higher K\textsubscript{ow} value). Some dependence is observed for insoluble organics as hexachlorobenzene which sorbs strongly to particles.

The higher Kw of the pollutant, the higher removal in both of the kind of wetlands. This effect is less predominant in wetlands than in lakes due to the water depth, which is higher in lakes than in wetlands.

Removal efficiency is higher when the sediment bed depth is higher until a value of 0.1 m for pollutants with high value of K\textsubscript{ow} and 0.4 m for pollutant with low value of K\textsubscript{ow}. Over those values, the removal efficiency got a constant value in both kinds of wetlands.

In general, we can say that removal efficiency is higher for soluble organics as naphthalene than for hydrophobic organics as hexachlorobenzene, and in addition higher removal efficiency is observed in bottomland hardwood forest wetlands than in freshwater marshes. This contradicts the idea that wetlands with high substrate organic carbon are better to remove organic compounds, and confirm the results found by Pardue (1992).

6.2. Limitations of the Model

This model can be used to identify the effect of parameters like DOC on the sediment bed and in the water column, depth of the bed and others in the removal efficiency of other kinds of wetlands and other kind of compounds.
This model has some limitations. First of all, the incomplete understanding of assimilation process in wetlands such as the magnitude of the volatilization mass transfer coefficient.

A second limitation is the unknown concentration of organics in the biotic components of the system (i.e., plants and fish). This model does not have a term to consider the bioconcentration and bioaccumulation, and they can influence the assimilation processes.

Third, a lack of data can limit the model. However, new research into different kinds of wetlands can provide data to calculate a particular removal efficiency for some compound in a specific wetland.

This model can be used too in the design of new constructed wetlands. With the basic data and determining the characteristics to be controlled, the designer can determine the features of the wetland that can enrich the goals of the design.
REFERENCES


## APPENDIX

### PHYSICAL DATA FOR PRIORITY POLLUTANTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{Log } K_{ow} )</th>
<th>( \text{He (atm-m}^3/\text{M)} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrolein</td>
<td>0.01</td>
<td>5.66*10^{-5}</td>
<td>Mabey et al, 1982</td>
</tr>
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<td>Acrylonitrile</td>
<td>0.25</td>
<td>8.8*10^{-5}</td>
<td>Mabey et al, 1982</td>
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<td>Benzene</td>
<td>2.13</td>
<td>4.39*10^{-3}</td>
<td>Mackay, 1982</td>
</tr>
<tr>
<td>Bromoform</td>
<td>2.30</td>
<td>5.00*10^{-3}</td>
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<td>2.73</td>
<td>2.30*10^{-2}</td>
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<td>2.61*10^{-3}</td>
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</tr>
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<td>Toluene</td>
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VITA

Luz Edith Flórez was born to Rodolfo Flórez and Alba E. Agudelo in Bucaramanga, Colombia, South America, on March 15, 1966. Luz Edith received her primary education in the Escuela Anexa a la Normal, and her secondary education in the Colegio de Santander in Bucaramanga. She subsequently graduated from the Universidad Industrial de Santander, in Bucaramanga, with Bachelor of Science degree in civil engineering (March, 1990). Luz Edith worked for one year at Dinco Ltda, in Bucaramanga, Colombia, as civil engineer, supervising construction of buildings. At the present she works for Ecopetrol, the Colombian national oil company, since 1992.