Modelling of fate and transport of toxic chemicals in natural water ways.

Ewa Maria Mietek. Barycka

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MODELLING OF FATE AND TRANSPORT OF TOXIC CHEMICALS

IN NATURAL WATER WAYS

by

Ewa Maria Mietek Barycka

A thesis
Submitted to the
Faculty of Graduate Studies and Research
through the Department of Civil Engineering
in Partial Fulfillment of the Requirements
for the Degree of Master of Science at
the University of Windsor

WINDSOR, ONTARIO, CANADA

1988
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ABSTRACT

The response of the St. Clair River and a simple aquatic food chain in Lake St. Clair to the release of hexachlorobenzene (HCB) and octachlorostyrene (OCS), from the highly industrialized "chemical valley" of Sarnia, is predicted in this study. Two components of the WASTOX fate and transport model are implemented in this project. The time-variable exposure concentration model simulates the transport, transfer and reaction of toxic chemicals in water bodies. It introduces the "moving sediment" layer and calculates the time-variable concentrations for coarse, medium and fine sediment. The food chain component of WASTOX estimates the environmental impact of predicted concentrations in a five-level food chain consisting of phytoplankton, benthic invertebrates, zooplankton, small and sport fish. Phytoplankton and benthic invertebrates are assumed to be steady-state species; time variable concentrations are calculated for all other trophic levels. Two possibilities are considered for the top predator, (a) the sport fish is treated as stationary species in the lake and (b) the sport fish is treated as a migratory species through the St. Clair River Lake system. Two WASTOX submodels are calibrated with 1985 field measurements. The exposure concentration model
indicates that the plume of contaminated water from the multiple sources in the Sarnia area travels along the Canadian shoreline and empties into Lake St. Clair via the Channel Ecarte and the South Channel. For both contaminants, about 20% of total loading is lost in the River due to various processes effecting the toxic pollutant. The food chain component of WASTOX predicts a too rapid response in fish concentration adjustment, caused by the change in the water exposure level. Food chain bioaccumulation of a toxicant due to consumption of contaminated food is greater for OCS than HCB in Lake St. Clair.
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Chapter I

SCOPE AND OBJECTIVES OF THE STUDY

1.1 Background of Reasons for the Study

The release of toxic organic contaminants into the Great Lakes environment is a well recognized problem. There are about 60,000 chemical compounds in commerce and this number is increasing at a rate of 500 - 1,000 per year. Almost all chemicals have access (at least to some extent) to all environmental compartments and can migrate throughout the ecosystem e.g. air, water and soil.

Typically, aquatic pollutants are classified as a "toxicants" and "conventional". The main four features of toxic substances that separate such substances from "conventional" pollutants are:

a) the tendency to sorb to particulates in the water body;
b) the tendency to be concentrated by aquatic organisms;
c) the tendency to be toxic at relatively low concentrations of the ug/L or ng/L level;
d) the tendency to be invisible and odorless in the water.

Over 400 toxic contaminants have been identified within the Great Lakes ecosystem, and the hazards for most of these are poorly understood.
The extent of toxic pollution in the Great Lakes was not realized until the early 1970's. High concentrations of DDT in Great Lakes fish severely impacted the herring gull population in the late 1960's and early 1970's (J.Struquer, 1983). PCB's levels in Lake Michigan sport fish have been significantly above the recommended level of 1 ppm (J.Camanzero, 1987). In 1971, the commercial fishery in the Lake St. Clair was halted due to high mercury levels. In late 1970's, in New York State, as a result of mirex leakage to the Lake Ontario a ban on commercial fish sales was imposed (Kaiser, 1978). Increased incidents of tumorous lesions have been found in the fishes of the Great Lakes and attributed to high concentrations of aromatic hydrocarbons. High levels of other pollutants have been measured, indicating other environmental problems.

There are many factors which contribute to the high sensitivity of the Great Lakes to chemical concentration problem. The major population centers and largest industrial complexes are located along the Lakes and their connecting channels. Contaminants from these sources have been accumulating over a long period of time. Atmospheric pollution is significant to the Great Lakes as a result of their vast surface areas. Due to the large volume of the lakes, contaminants are subject to long hydraulic detention times, allowing, in some cases, the build-up of low-level inputs.
Lake St. Clair, the smallest and the shallowest of the Great Lakes is located downstream from the highly industrialized chemical valley south of Sarnia. The bottom sediments in the Lake St. Clair are contaminated by a variety of toxic metals and organic chemicals. Because of the shallowness of the lake, wind generated sediment resuspension recycles contaminants and prolongs the recovery rates of the Lake and downstream sites.

St. Clair-Detroit River system supplies drinking water to more than five million people. It supports an extensive sport fishery and a variety of water related activities such as boating, swimming and waterskiing.

1.2 Objectives

Almost all parts of the aquatic ecosystem are contaminated to some extent. The issue is not the presence of the pollutant but rather whether its presence is at an "acceptable" or "unacceptable" level. This difficult assessment can be made based on information on toxic chemical sources, pathways and the effects on aquatic biota and human population.

The primary objectives of the fate and transport modelling study are:

a) to provide a quantitative description of chemical transport from its source through the water system as a function of chemical properties and ecosystem characteristics:
b) to prepare a management strategy relating the impact of control procedures on toxic levels in aquatic systems (e.g. to predict the input reduction that is necessary to achieve a target concentration);

c) to predict the chemical concentration for various trophic levels in the simplified food chain.

This study is limited to the St. Clair River - Lake system. The major contaminants of interest are: hexachlorobenzene (HCB) and octachlorostyrene (OCS).

1.3 General Approach

There are four general steps in the water quality simulation:

a) Hydrodynamics - describing where the water goes;

b) Mass transport - which addresses where pollutants go;

c) Water quality kinetics - which describe dynamics of the contaminant in the water and between sediment and water;

d) Environmental toxicology - which addresses to what extent chemical exposure concentrations affect the health of fish and/or people.

1.3.1 Description of Numerical Models

In the exposure assessment for the St. Clair River - Lake system two hydrodynamics models are used:

a) The University of Windsor - Ministry of Environment (MOE) k-E model. This model provides cross-sectional velocity profiles, location of river flow streamlines and lateral
dispersion characteristics:

b) The Finite Element Circulation Model for Lake St. Clair -
developed by Ibrahim and McCorquodale, (1965).

Two kinetic - transport models are implemented in the
study:

a) The Exposure component of WASTOX - Water Quality Analysis
Simulation for Toxics, created by J. P. Connolly of the
Manhattan College, New York;

b) TOXIWASP - the chemical transport and fate model develope
do by U.S. Environmental Protection Agency, Athens, Georgia.

The food chain component of WASTOX represents the post-
processor model for TOXIWASP. Both the food chain and the
exposure components of WASTOX are set up in this study. Both
models are calibrated by tuning them to available field data
sets.

1.3.2 Modelling Scheme

Since the modelling of toxic contaminants is carried out
in two different water bodies, - the river and the small,
shallow lake -, the study is divided into two components:
river simulation and lake simulation.

1.3.2.1 St. Clair River Simulation

The k - E model is implemented to provide the necessary
hydrodynamic and dispersion input for the unsteady fate and
transport model of the river. The transport of the toxic
chemical, its transfer among the air, water and solid phases, transformation (biodegradation, photolysis, hydrolysis) are modelled by the modified version of WASTOX program.

1.3.2.2 Lake St. Clair Simulation

The finite element circulation model is the first step in predictive modelling of the pollutant. It establishes hydrodynamic data and the time functions for the long term simulation by the EPA TOXIWASP model. The main mechanisms (transport, transfer, reaction) which determine the fate of the pollutant in the water system are handled similarly to WASTOX. The concentrations of the chemical modelled by the WASTOX model for the river simulation, are introduced as input (forcing functions) to TOXIWASP.

The environmental impact of predicted concentrations in the lake on individual species and communities of organisms, is estimated by the food chain model - the second component of the WASTOX model.
Chapter II

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction to Toxic Substances Modelling

In the recent years, a number of reliable models describing the behaviour of chemicals in aquatic systems has emerged. Numerous frameworks are available for modelling toxic chemicals in surface waters e.g. WASP (Di Toro et al., 1981), TOXIWASP (Ambrose et al., 1983), WASP4 (Ambrose et al., 1987). There are mass balance models describing the behaviour of the pollutant in the aquatic system as a function of the individual chemical properties and specific features of the system.

The main principle of the water quality analysis simulation program is the conservation of mass. The mass balance equation is generated for the specific water quality variable (e.g. toxicant, sediment) in any system (e.g. water, bed, biota), considering the sum of all processes and their interactions in the specific environmental compartment.

The general mass balance equation for the mass of pollutant in a well mixed water segment can be expressed:

\[ v \frac{dc}{dt} = \pm T \pm TR + L \]  \hspace{1cm} [2.01]

in which:
\[ v \left( \frac{dc}{dt} \right) = \text{change in the mass flux of the chemical} \]

\[ T \quad \text{- transport (advection, dispersion, volatilization, sediment transport, settling (-) and resuspension (+))} \]

\[ TR \quad \text{- transformations (biodegradation, photolysis, hydrolysis)} \]

\[ L \quad \text{- loadings (sinks (-) or sources (+))} \]

In Equation 2.01, contaminant removal by settling is treated as negative transport from the water cell. Resuspension of the material from the bed to the water is treated as positive transport. Therefore, the introduction of inplace pollutants to the water column is considered to be a transport process.

For a completely vertically and horizontally mixed water segment, the mass balance equation for the suspended solids is given as:

\[ v \left( \frac{dm}{dt} \right) = \pm T + L - ST + R \quad \text{(2.02)} \]

where:

\[ v \left( \frac{dm}{dt} \right) \quad \text{- rate of change of the solids mass} \]

\[ T \quad \text{- transport (advection, dispersion); positive into cell;} \]

\[ L \quad \text{- external loadings} \]

\[ ST \quad \text{- settling} \]

\[ R \quad \text{- resuspension} \]
The mass balance equation of a toxic substance in a single ecological compartment (e.g., fish) may be written as:

\[ \frac{dγ}{dt} = UP_w + UP_r - EX - GR \]  \hspace{1cm} (2.03)

where:

- \( \frac{dγ}{dt} \) - rate of change of toxicant mass in the species
- \( UP_w \) - chemical uptake from water
- \( UP_r \) - chemical uptake from food
- \( EX \) - chemical excretion rate
- \( GR \) - growth rate

The complexity of transport and transformation processes which influence the fate of a toxicant in aquatic systems call for some simplifications and assumptions. Not all chemicals require consideration of all physio-chemical interactions. It's up to a modeler to decide what processes are significant for the specific pollutant and the specific water body. Modelling the fate of toxic substances involves both scientific knowledge and engineering judgment.

2.2 Physio-Chemical Processes

Prediction of the fate of toxic chemicals involves estimation of all mechanisms acting on the toxicant (see Fig. 1). The processes fall into five categories as follows:

- **Loading Processes**
- **Speciation Processes** - sorption on sediment
- **Transport Processes**
advection
- dispersion
- volatilization
- sediment transport
- sedimentation

Transformation Processes
- biodegradation
- photolysis
- hydrolysis

Bioconcentration
- bioaccumulation

2.2.1 Loading Processes

One of the most important steps in predicting the aquatic fate of pollutants is the determination of a realistic input mass loading entering the specific water body. In general, considering the location of a source, inputs can be divided into two groups: point sources and non-point sources. The point sources have a well-defined point of discharge, usually with continuous mass inputs. Municipal and industrial discharges are considered as point sources. The mass of the chemical for a point source with continuous flow can be estimated by:

\[ W(t) = Q(t) c(t) \]  \[ 2.04 \]

where:

\[ W(t) \] - mass rate of input \[ M / T \]
$Q(t)$ - input flow \hspace{1cm} \left[ \frac{L^3}{T} \right] \\
$c(t)$ - concentration of chemical in the input \hspace{1cm} \left[ \frac{M}{L^3} \right] \\

Some examples of non-point sources are: agricultural runoff, urban and suburban runoff, atmospheric deposition and groundwater seepage. For this category of inputs, it is not possible to relate the discharge to a specific location and their mass loading tend to be transient (e.g. due to precipitation events).

2.2.2 Speciation Processes

2.2.2.1 Sorption on sediment

As mentioned before, one of the most significant properties of toxics is their tendency to sorb to particulates in the water body. Thus, the toxicant can exist in two forms: the dissolved phase and the toxicant on the solids. In the particulate phase, the chemical may be physically associated or chemically bound through attachment to the surface of the solid. The rate of adsorption is much more rapid than any other transport or transformation mechanism (order of minutes to hours), so that on a time scale of all other mechanisms sorption appears to be an equilibrium process (Thomann and Mueller, 1987). Assuming that the sorption is reversible (desorption) and that the sorption — desorption kinetics are linear, the partition coefficient or distribution of the chemical at equilibrium between the particulate and dissolved form can be expressed:

$$K_p = \frac{r}{c_d} \hspace{1cm} \left[ 2.05 \right]$$
where:

\[ K_p - \text{partition coefficient} \quad \text{[L/kg]} \]
\[ r - \text{adsorbed chemical} \quad \text{[ug/kg]} \]
\[ c_d - \text{dissolved chemical} \quad \text{[ug/L]} \]

Theoretical models of sorption consider adsorption to be a completely reversible process (Thomann and Mueller, 1987). However, Di Toro (1985) questioned the complete pollutant reversibility between the liquid and solid phases. It was found that for some organic chemicals there is a fraction of the sorbed chemical which is resistant to desorption.

The total chemical is a sum of the particulate chemical, \( c_p \), and the dissolved phase \( c_d \), both in \([\text{ug/L}]\):

\[ c_T = \sum_{i=1}^{n} c_{p_i} + \theta c_d \quad \text{[2.06]} \]

where:

\[ c_{p_i} = r_i m_i \quad \text{[2.07]} \]

\( m \) - concentration of solids type \( i \) \([\text{kg/L}]\)
\( n \) - number of solids type
\( \theta \) - porosity (liquid volume/total volume)

The dissolved and particulate toxicant concentrations may be represented as fractions of the total concentration:

\[ c_d = f_d c_T \quad \text{[2.08]} \]

\[ c_{p_i} = f_{p_i} c_T \quad \text{[2.09]} \]
where:

\[
f_d = \frac{1}{\left( \Theta + \sum_{i=1}^{n} m_i K_{p_i} \right)} \tag{2.10}
\]

\[
f_p = \frac{m_i K_{p_i}}{\left( \Theta + \sum_{i=1}^{n} m_i K_{p_i} \right)} \tag{2.11}
\]

The distribution of the chemical between the two phases depends on the partition coefficient and the solids concentration. Partitioning of organic chemicals depends mainly on two factors:

a) characteristics of the solid

- organic carbon content
- grain size

b) characteristics of the chemical

- \( K_{ow} \) – octanol-water partition coefficient (concentration of the chemical in octanol divided by the concentration of the chemical in water, at equilibrium)

Karickhoff et al. (1979) related the solids partition coefficient \( K_{ow} \) to organic content of the sediments and an organic carbon partition coefficient \( K_{oc} \) as well as the organic carbon coefficient \( f_{oc} \) to \( K_{ow} \) of the chemical by equations:

\[
K_p = K_{oc} f_{oc} \tag{2.12}
\]

\[
K_{oc} = 0.63 K_{ow} \tag{2.13}
\]
where:

$f_{oc}$ - mass fraction of organic carbon in sediment

Therefore, the very useful relationship to estimate the partition coefficient is obtained:

$$K_p = 0.53 f_{oc} K_{ow}$$  \[2.14\]

The magnitude of the octanol - water partitioning coefficient ($K_{ow}$) for the chemical describes its sorption - desorption mechanism in an aquatic environment. $K_{ow}$ values range from about zero for chemicals that do not partition into octanol, to $10^6$ to $10^7$ for chemicals that partition very strongly. According to Ambrose (1987), organic chemicals with a low octanol - water partitioning coefficient (i.e., $\log K_{ow} < 3$) for a normal range of solids in natural waters, exist mainly in the dissolved phase. Interaction with solids can be neglected (see Fig. 2). Figure 3 (Thomann and Mueller, 1987) presents the relationship between fraction dissolved of organic chemicals and log suspended solids concentration. Chemicals with low partition coefficient ($< 100 \text{ L/kg}$) exist principally in the dissolved form. For the higher partition coefficients, the particulate and dissolved forms must be included in the analysis. At $K_p$ greater than $10^3 \text{ L/kg}$ and solids concentration $> 10 \text{ mg/L}$, the fraction of dissolved pollutant is approximately a constant at about 0.3 to 0.4 over the entire range of solids.
The partition coefficient to the bed sediment, due to lack of appropriate relationships, is estimated using the theory developed for partitioning to solids in the water column.

2.2.3 Transport Processes

2.2.3.1 Advection

Advection represents the main component of transport in the water system. It accounts for three dimensional transport of any water quality variables - suspended sediment, dissolved or particulate contaminant - with bulk water. Advection is considered to be an important mechanism for all water bodies.

2.2.3.2 Dispersion

Mixing or dispersion occurs in natural water systems due to temporal and spatial velocity gradients, density differences, shear, turbulence and geometry changes (coves, deep holes). The significance of this process has been proven for such water systems as ponds, lakes and reservoirs. In streams, large rivers this mechanism is not very important. The mixing phenomenon can be considered in three dimensions and it's called longitudinal, lateral and vertical dispersion. The general computational form of dispersion between segment $i$ and segment $j$ is:

$$\frac{dM}{dt} = \left(\frac{E_{ij}}{A_{ij}}\right)\left(\frac{c_i - c_j}{L_{ij}}\right) \quad [2.15]$$
in which:

\[ M_i \] - mass of chemical in segment \( i \)  
\[ E_{ij} \] - dispersion coefficient  
\[ A_{ij} \] - cross sectional area between segments  
\[ L_{ij} \] - distance from centroid of segment \( i \) to centroid of segment \( j \)  
\[ I = \frac{(L_1 + L_2)}{2} \]

\[ L_{1,2} \] - length of segment in the direction of dispersion  
\[ c_i \] - total chemical concentration in segment \( i \)  
\[ \frac{M}{L} \] -  

The magnitude of the dispersion coefficient for the specific water body can be estimated by dye studies, various empirical relationships or hydrodynamic models (McCorquodale and Yuen, 1937).

2.2.3.3 Sediment Transport

Particulate material enters the water body in one of four ways: shore erosion, river discharge, atmospheric deposition or bottom erosion. Its transport, because of chemical sorbed to it, plays the great role in fate of toxic organic compounds. Transport of contaminants between their source and final burial is complex and involves a number of vertical transport processes: settling, deposition, resuspension, sedimentation. The coarse fractions of sediment - sand and
gravel — are moved mostly as bedload by the currents, although occasionally storms can resuspend this material. Transport of the fine material occurs almost totally in suspension. If the particle reaches the bottom, it may be consolidated with the bed or be resuspended and mixed into the water column. The process is repeated until the material is finally incorporated into the bottom sediment.

The correct evaluation of all mechanisms effecting the sediment transport can predict either the release of contaminants from the sediment into the water or burial of toxic substances into the bottom sediment. Thus, the natural sediment in the environment can represent a sink or a source of toxic chemicals.

2.2.3.4 Volatilization

Volatilization is the transfer of matter from the dissolved to the gaseous phase. As reviewed by Ambrose (1987), the mass exchange of the chemical across the air-water interface can be defined as:

\[ v(\text{dc}_w/\text{dt}) = k_L/D \left( \text{c}_g / H_o - \text{c}_w \right) \quad [2.16] \]

in which:
- \(v(\text{dc}_w/\text{dt})\) — exchange rate \( [M / L^3 T] \)
- \(c_w \) — dissolved concentration \( [M / L^3] \)
- \(c_g \) — concentration of the chemical in the gas phase \( [M / L] \)
- \(k_L \) — overall exchange rate (conductivity) \( [L / T] \)
D - average depth of the water body \([ \text{L} ] \)

\(H_0^*\) - Henry's Law constant \([ \text{dimensionless} ]\)

The Henry's constant represents a partitioning of the toxicant between the water and atmospheric phases and is given by:

\[
H_0^* = \frac{P}{c_w^*} \quad \text{[ 2.17 ]}
\]

where:

\(H_0^*\) - Henry's Law constant \([ \text{atm m}^3 / \text{mole} ]\)

\(P\) - equilibrium partial pressure of pollutant in atmosphere \([ \text{atm} ]\)

\(c_w^*\) - equilibrium concentration of pollutant in water \([ \text{mole / m} ]\)

In dimensionless form, the Henry's law constant is:

\[
H_0 = \frac{c_g^*}{c_w^*} = H_0^*/R T \quad \text{[ 2.18 ]}
\]

For \(R\), the universal gas constant is equal \(6.206 \times 10^{-5} \text{ atm m}^3 / \text{°K mole} \) and \(T\) (temperature of water, °K) equal 20 °C, the above relationship has the form (Mills et al., 1962):

\[
H_0^* = 4.5 H_0 \quad \text{[ 2.19 ]}
\]

The Equation 2.16 shows that the flux of the chemical can be from the air to the water \((c_g^* / H_0 > c_w^*)\) or from the water to the air \((c_w^* > c_g^* / H_0^*)\). In most cases, the concentration of toxicants in the atmosphere can be assumed zero and the chemical is lost to the air.
The "two film" theory is used to determine the overall exchange rate, $k_e(L/T)$. As suggested by Mackay (1981):

$$\frac{1}{k_e} = \frac{1}{k_L} + \frac{1}{k_G H} \quad [2.20]$$

where:

- $k_L$ - the liquid film coefficient [L/T]
- $k_G$ - the gas film coefficient [L/T]

The rate of volatilization of a substance from the water body will be determined by properties of the substance (H) and the environment (wind, water turbulence and temperature). As can be seen from the Equation 2.20, for large values of the Henry's coefficient (> 10) the resistance to transfer is located in the aqueous film. If the Henry's constant is "small" (< 10), then the resistance to transfer is in the gas phase and the system is said to be gas phase limited. When both $k_L$ and $(k_G H)$ are of the same magnitude, both phases contribute to the overall transfer. To evaluate the transfer rate $k_L$, values of $k_L$, $k_G$ and $H$ (Eq. 2.20) are required. Following the work of Smith et al. (1981), Mills et al. (1982), the liquid film coefficient $K_L$ [L/T] is given by:

$$K_L = \left(\frac{32}{M}\right)^{1/4} k^* \quad [2.21]$$

where:

- $M$ - molecular weight of the chemical [g/mole]
- $k^*$ - oxygen transfer rate at ambient water temperature [L/T]
The liquid mass transfer coefficient $K_L$ and the gas film transfer coefficient $K_g$ can be estimated from O'Connor's (1981) equations:

$$K_L = \left( \frac{D_w}{\gamma_w} \right) \left( \frac{c_p \rho_s}{\rho_w} \right) \frac{U_{10}}{\lambda_w} \quad [2.22]$$

$$K_g = \left( \frac{D_g}{\gamma_a} \right) \left( \frac{c_p \rho_s}{\rho_w} \right) \frac{U_{10}}{\lambda_g} \quad [2.23]$$

where:

$D_w / D_g$ — diffusion coefficient of the chemical in water / atmosphere

$\gamma_w / \gamma_a$ — viscosity of water / air

$c_d$ — drag coefficient

$\rho_w / \rho_a$ — density of water / air

$U_{10}$ — wind velocity at 10 meters above the water surface

$\lambda_w / \lambda_g$ — coefficient related to the thickness of the water / gas viscous sublayer

Volatilization is an important process not only for "highly volatile" chemicals. Even though for many toxic substances the volatilization rates might be slow, volatilization will influence the fate of the toxicant.

2.2.4 Transformation Processes

2.2.4.1 Biodegradation

Organic chemicals are degraded in the aquatic environment by bacteria or fungi by two types of biodegradation: growth metabolism and cometabolism. The chemical that is metabolized by a microorganism serves as food source which provide energy and carbon for growth. Two stages of metabolic activity can be distinguished: microbial adaptation time and real degradation. The adaptation time (2 to 50 days) is influenced by prior exposure to the pollutant and the initial number of the community. The acclimation time is shorter for chronic exposure and higher microbial population. It's longer in presence of easily degradable carbon sources and in very low chemical concentrations. After adaptation to the chemical, the utilization of the compound begins. The reduced Monod equation is used to describe the degradation rate of the compound:

\[ \frac{dc}{dt} = - K_{b2} B c \]  

[2.24]

in which:

- \( K_{b2} \) - second order biodegradation rate constant \( \left[ \frac{1}{(\text{cells} / \text{L}^3 \text{T})} \right] \)
- \( B \) - bacterial concentration \( \left[ \text{cells} / \text{L}^3 \right] \)
- \( c \) - pollutant concentration \( \left[ \text{M} / \text{L}^3 \right] \)

In cometabolism, microorganisms degrade organic compounds that cannot be used as a food source. There is usually no adaptation time and the degradation rates are much slower.
2.2.4.2 Photolysis

Substances which absorb sunlight in the ultraviolet and visible portion of the spectrum may gain sufficient energy to initiate a chemical reaction. The chemical degrades or is decomposed by the change in molecular structure. However, the product of the photochemical decomposition of the toxic compound may still be toxic. Thus, even that photolysis is treated as irreversibly decay process it should be remembered that the decomposition of the toxic compound does not imply the detoxification of the environment. The rate at which the chemical photolyses depends on numerous pollutant and environmental factors:

a) the light absorption properties and reactivity of the compound;

b) the intensity of solar radiation which depends on the meteorological and geographical conditions;

c) the light transmission characteristics of natural waters which is a function of the suspended solids, phytoplankton and dissolved organic carbon.

Photolysis is classified into two types that are defined by the mechanism of energy absorption. Direct photolysis is the result of direct absorption of photons by the compound. Indirect or sensitized photolysis is a result of energy transfer to the compound from some other molecule that has absorbed radiation.
The estimation of the rate of photolysis is through the approximate first-order reaction:

\[
\frac{dc_d}{dt} = -K_h c_d \tag{2.25}
\]

where:

\(K_h\) - the overall photolysis rate \([\text{1/day}]\), is given by:

\[K_h = K_{h_d} + K_{h_s}\tag{2.26}\]

where:

\(K_{h_d}\) - the direct photolysis rate \([\text{1/day}]\)

\(K_{h_s}\) - the sensitized/indirect photolysis rate \([\text{1/day}]\)

Due to lack of reliable theory for sensitized photolysis, only direct photolysis is considered in modelling studies.

2.2.4.3 Hydrolysis

In hydrolysis, the toxic compound reacts with the water and the cleavage of the chemical bond occurs. Typically hydroxide replaces another chemical group. The subsequent product of the reaction may not be less toxic than the original compound. In general, the hydrolysis is a second order because of dependence on the molar concentration of \([H^+]\), \([OH^-]\), or other mediators (enzymes).

The hydrolysis rate equation is:

\[
\frac{dc_d}{dt} = -K_h c_d \tag{2.27}
\]

where:

\(K_h = K_h + K_A [H^+] + K_B [OH^-]\)
for $K^H$ - overall hydrolysis rate  \[ \text{[1/day]} \]

$K^N$ - neutral hydrolysis rate  \[ \text{[1/day]} \]

$K_A$ - acid catalyzed hydrolysis rate constant  \[ \text{[1/mole day]} \]

$K_B$ - base catalyzed hydrolysis rate constant  \[ \text{[1/mole day]} \]

$[H^+]$ - molar concentration of hydrogen ions

$[OH^-]$ - molar concentration of hydroxide ions

2.2.5 Bioconcentration

Bioconcentration is the increase in the aquatic organism chemical concentration due to pollutant exposure in the water phase only.

A direct uptake of the substance from water is one of the two principal routes of accumulation of the toxic chemical by aquatic organisms. The dissolved phase of the pollutant is sorbed into the fish mainly through its gills to phytoplankton through surface sorption. The bioconcentration factor (BCF) can be introduced assuming the equilibrium steady state pollutant concentration in the organism to the dissolved water concentration:

\[ BCF = \gamma_w / c_d \]

(2.28)

where:

$\gamma_w$ - organism concentration of the toxicant resulting from exposure to the chemical in the water only  \[ \text{[ug/g (wet wt)]} \]
c - dissolved concentration in the water (ug / L)

The bioconcentration factor represents the partition coefficient for the biological system and is in typical units (ug / g(wet wt) - ug / L), similarly to the solids partition coefficient. Partitioning of the lipid soluble chemical under exposure to the water may be related to a specific property of that chemical (octanol - water partitioning coefficient, water solubility) and the fraction of lipid content of the organism. R. Thomann (1987), presents the equation that expresses the BCF as a function of K_{ow} and lipid content (f):

\[ BCF = K_{ow} f \]  \[ 2.29 \]

The mechanism of accumulation of the dissolved chemical over time is described by a mass balance equation:

\[ \frac{d\gamma}{dt} = k_u c - K'\gamma \]  \[ 2.30 \]

in which:

- \( k_u \) - rate of chemical uptake or sorption rate \[ L / g (wet wt) \text{ day} \]
- \( K' \) - loss rate \[ 1 / \text{day} \]
- \( K' = K + G \)
- \( K \) - excretion rate of the chemical \[ 1 / \text{day} \]
- \( G \) - growth rate of the organism \[ 1 / \text{day} \]
- \( \gamma * c \) - as in Eq. 2.28
At equilibrium or steady state \((d\gamma/dt = 0)\), the concentration of the pollutant \( [uq / q] \) in the organism may be written as:

\[
\gamma = k_u c_d / K^* \tag{2.31}
\]

Substitution of Eq. 2.31 to Eq. 2.26 yields:

\[
BCF = k_u / K^* = k_u / (G + K) \tag{2.32}
\]

Thus, the bioconcentration factor is defined as the ratio of the uptake rate, \( k_u \), to the sum of the depuration and growth rates and defines the amount of toxicant that will reside in the aquatic organism for a given amount of the chemical in the water.

For phytoplankton, the base level of the food chain, the accumulation of toxic substances is controlled by sorption-desorption processes. Since the sorption rates are very fast, the equilibrium may be assumed and the concentration in phytoplankton is obtained by Eq. 2.28:

\[
\gamma = BCF c_d \tag{2.33}
\]

For the higher trophic levels, fish, the primary process for uptake directly from water is through transfer of the chemical across the gill surface (Connolly and Winfield, 1984). A diffusive transport mechanism analogous to oxygen transport is assumed. The uptake rate constant, \( k_u \) [L/
\( q(\text{wet wt day}) \) for the toxicant is related to the respiration rate of the organism by:

\[
k_u = B R / c_{o_2}
\]  \[2.34\]

where:

- \( B \) - ratio of the diffusivity of the chemical to the diffusivity of oxygen
- \( R \) - respiration rate \( \left[ \frac{q(O_2)}{q(\text{wet wt day})} \right] \)
- \( c_{o_2} \) - dissolved oxygen concentration

The respiration rate is a function of temperature, organism weight \( q \) and swimming speed and may be specified as:

\[
R = \beta w T e^{\rho T - \nu u}
\]  \[2.35\]

where:

- \( T \) - temperature \( \left[ ^{\circ}C \right] \)
- \( u \) - swimming speed \( \left[ \text{cm/s} \right] \)
- \( \beta, \gamma, \rho, \nu \) - parameters for the specific organism obtained from laboratory experiments, implemented after Steward (1980).

The rate of loss of the chemical from the organism is a sum of the organism growth rate and the excretion rate of the pollutant (see Eq. 2.30). Assuming exposure of the species to the toxicant in water only and no significant weight change, the loss rate, \( K^* \), may be written as:

\[
K^* = k_u / BCF
\]  \[2.36\]
The growth rates for aquatic organisms are determined by laboratory tests.

2.2.5.1 Bioaccumulation

In the aquatic food chain pathways for intake to any level include direct uptake from the water and ingestion via a contaminated food source. Bioaccumulation is the increase in the organism chemical concentration over that which would be expected from exposure to the chemical in the water phase only. The bioaccumulation factor (BAF) is the equilibrium ratio of the organism toxicant concentration resulting from the water and food routes to the water concentration:

\[
BAF = \frac{\tau_{w,f}}{c_d} \quad \text{[2.47]}
\]

where:

- **BAF** - lipid based bioaccumulation factor \(\text{[ug / kg(lp)} - \text{ug / L]}\)
- \(\tau_{w,f}\) - organism concentration of the substance on a lipid basis resulting from the water and food routes \(\text{[ug / kg(lp)}\)
- \(c_d\) - dissolved water concentration \(\text{[ug / L]}\)

The ratio of bioaccumulation factor (BAF) to bioconcentration factor (BCF) is a measure of the tendency of the chemical to accumulate in the organism from both food and water exposure over the concentration expected from the water only. If an equilibrium has been reached, then \(\text{BAF/BCF} > 1\) indicates that food chain accumulation has occurred.
The food ingestion rate, which controls the uptake of the chemical from food, depends on metabolism and growth. It is computed as the intake necessary to produce the weight change observed in the environment. The rate of consumption of food can be expressed as:

\[
C = \frac{R + G}{a} \tag{2.38}
\]

where:

- \(C\) = rate of consumption \[\text{[g (wet wt prey) / g (wet wt predator) day]}\]
- \(a\) = fraction of ingested food that is assimilated
- \(R\) = as in Eq. 2.35

The uptake of the toxicant due to consumption of contaminated food depends on:

a) the chemical concentration in the prey;

b) the rate of food ingestion;

c) the degree of pollutant assimilation into the tissue.
Chapter III

DESCRIPTION OF THE WASTOX MODEL

3.1 Introduction

Water Quality Analysis Simulation for TOXics - WASTOX (Connolly and Winfield, 1984) is a dynamic model simulating the transport and fate of toxic chemicals in water bodies and aquatic food chains. WASTOX was developed from the general water quality model WASP (Di Toro et al., 1981), transfer and transformation processes are modifications of those included in EXAMS (Burns et al., 1982).

The WASTOX framework consists of two stand-alone computer programs, which may be termed the exposure concentration and food chain components, respectively. The exposure concentration model simulates loading, speciation, transport and transformation processes of toxic chemicals in water bodies. The food chain model determines the effect of toxic pollutants on individual species and communities of organisms. The two above components can be run either as separate models or the food chain may be executed as a post-processor to the exposure model.

The basic principle of both submodels is the conservation of mass. Masses of contaminant being studied in any environmental medium (water, sediment, biota) are tracked and
accounted for over time and space using a series of mass balance equations.

The following assumptions are made to generate the WASTOX model:

a) all segments are well mixed (laterally and vertically);

b) sorption - desorption kinetics are rapid compared to other processes;

c) all the first order kinetic rates can be combined linearly.

The principle advantages of WASTOX over other exposure concentration models are:

a) it introduces the "moving sediment" layer;

b) it calculates the time variable concentrations up to three solids type.

WASTOX is a general model and can be applied to all types of natural water systems. The water quality variables modelled by the program include:

a) total toxicant in the water/bed [ ug / l ]

b) dissolved toxicant in the water/bed [ ug / l ]

c) adsorbed toxicant in the water/bed [ ug / q ]

d) solids concentration in the water/bed [ mg / l ]

e) toxicant concentration in an aquatic organism [ ug / g (wet wt) ]
3.2 Exposure-Concentration Model

The model is a set of segments that represent the physical configuration of the water body. Lateral, vertical and longitudinal subdivision of the water body and the bed is permitted. Segmentation scheme is very important in achieving the expected goal of the model. The spatial scale of the problem, temporal variability of inputs and the degree of spatial concentration gradients reproduction should be considered.

Segment volumes and the simulation time step are directly related. In order to maintain stability for the numerical solution, the integration time step is limited by:

\[
\Delta t \leq \min \left( \frac{v_i}{L Q_{i,j} + L R_{i,j} + K_i V_i} \right) \tag{3.01}
\]

where:

- \( v_i \) - volume of segment \( I \) \( [L^3] \)
- \( Q_{i,j} \) - advective flow between segments \( I \) and \( J \) \( [L^3/T] \)
- \( R_{i,j} \) - dispersive flow between segments \( I \) and \( J \) \( [L^3/T] \)
- \( B_{i,j} = (Z_{i,j} A_{i,j}) \) \( [L^3/T] \) see Eq. 2.15
- \( K \) - transformation rate of chemical in segment \( i \) \( [1/T] \).

Usually, \( \Delta t \) is controlled by advective or dispersive flows.
3.2.1 **Governing Equations**

The analysis of toxicant distribution in the water/bed segments involves the solution of at least three simultaneous mass balance equations: for dissolved chemical, particulate chemical and solids. However, since the distribution of the dissolved and particulate components can be determined directly from the distribution of total chemical and solids concentration, the number of equations can be reduced.

The available version of WASTOX generates only the time variable solution.

### 3.2.1.1 Water Column

The three dimensional, differential equation describing the distribution of the total chemical is:

\[
\frac{\partial c_T}{\partial t} = \frac{2}{\partial x} \left( E_x \frac{\partial c_T}{\partial x} \right) + \frac{2}{\partial y} \left( E_y \frac{\partial c_T}{\partial y} \right) + \frac{2}{\partial z} \left( E_z \frac{\partial c_T}{\partial z} \right) + \frac{\partial u_x c_T}{\partial x} + \frac{\partial u_y c_T}{\partial y} + \frac{\partial u_z c_T}{\partial z} + \frac{2}{\partial z} w_s (c_{T1} c_T) = S
\]

(3.02)

where:

- \( c_T \) - concentration of total chemical \[ \text{M} / \text{L}^3 \]
- \( E \) - dispersion coefficient \[ \text{L}^2 / \text{T} \]
- \( u \) - velocity \[ \text{L} / \text{T} \]
- \( w_s \) - settling velocity of the particulates \[ \text{L} / \text{T} \]
- \( c_{T1} \) - fraction of total chemical adsorbed to solids type \( i \)
- \( S \) - sources / sinks due to reactions and transfers or direct addition - removal of the chemical
$x,y,z$ - coordinate directions.

The first three terms in Eq. 3.02 account for dispersion or mixing of the chemical. The next three terms account for longitudinal, lateral and vertical advection, respectively. The next term represents the vertical advection of the particulate component due to settling. The last term in the relationship considers the chemical load or loss in the system due to volatilization (Eq. 2.16), biodegradation (Eq. 2.24), photolysis (Eq. 2.25), hydrolysis (Eq. 2.27).

The distribution of the solids is written:

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x} \left( E \frac{\partial m}{\partial x} \right) + \frac{\partial}{\partial y} \left( E \frac{\partial m}{\partial y} \right) + \frac{\partial}{\partial z} \left( E \frac{\partial m}{\partial z} \right) - \frac{3}{\partial x} u_x m$$

$$- \frac{3}{\partial y} u_y m - \frac{3}{\partial z} u_z m + \frac{3}{\partial z} u_z m$$

in which:

$m$ - concentration of solids \( \left[ \frac{M}{L^3} \right] \)

$E, u_x, u_y, u_z$ - as in Eq. 3.02

3.2.1.2 Sediment Bed

The mass balance equation with the advective component defining the solids distribution is:

$$\frac{\partial m_b}{\partial t} = \frac{v_x m_w}{h} - \frac{m_b}{h} (u_x + v_x) + \frac{u_x}{B} \frac{\partial}{\partial x} (B m_b)$$

where:

$m_b/m_w$ - concentration of solids in the bed/water \( \left[ \frac{M}{L^3} \right] \)
3 - width of the bed layer  [ L ]
h - depth of the bed layer  [ L ]
u - horizontal velocity  [ L / T ]
w_s - settling velocity  [ L / T ]
w_r - resuspension velocity  [ L / T ]
w_d - sedimentation velocity  [ L / T ]

The equation describing the distribution of the total chemical is:

\[
\frac{\partial c_{TB}}{\partial t} = \frac{v_s}{h} f_p c_{TB} - \frac{f_p}{h} (v_u + v_d) c_{TB} + ubc_{TB} - \frac{EA}{I} (f_{d_b} c_{TB} - f_{d_w} c_{Tw})
\]

where:

\(c_{TB} / c_{Tw}\) - total chemical in the bed/water  [ M / L^3 ]

I - mixing depth, see Eq. 2.15

\(f_p\) - fraction of total chemical adsorbed to solids

\(f_{d_b} / f_{d_w}\) - fraction of dissolved chemical in the bed/water

h, \(v_s\), \(v_u\), \(v_d\) - as in Eq. 3.04

The fluxes contributing to Eq. 3.05 are presented in Fig. 4.

3.2.1.3 Finite Difference Approximation

The central difference approximation of space derivatives in the mass balance equations is applied. Assuming the completely mixed finite segments, the distribution of the total chemical for water segment 1 is expressed:
\[
\frac{dc_i}{dt} = v_i \left( \sum_{i=1}^{k} Q_{i,k} \sqrt{c_i} - \sum_{j=1}^{L_i} E_{i,j} A_{i,j} \left( c_j - c_i \right) \right) + \sum_{j=1}^{L_i} \left( \frac{E_{i,j}}{L_i} \right) A_{i,j} \left( f_{i,j} - f_{i,j} \sqrt{c_i} \right) + S
\]

where:

- \( v_i \) - volume of segment \( i \) [L\(^3\)]
- \( c_i \) - total chemical concentration in segment \( i \) [M/L\(^3\)]
- \( Q_{ij} \) - hydrodynamic flow from segment \( j \) to segment \( i \) [L\(^3\)/T]
- \( Q_{ik} \) - hydrodynamic flow from segment \( i \) to segment \( k \) [L\(^3\)/T]
- \( E_{ij} \) - dispersion coefficient between segment \( i \) and \( j \) [L\(^2\)/T]
- \( L_{ij} \) - mixing length of segments \( i \) and \( j \) [L] (see Eq. 2.15)
- \( w_{ij} \) - settling velocity of particulates from segment \( i \) to segment \( j \) [L/T]
- \( w_{ii} \) - resuspension velocity from segment \( i \) to segment \( i \) [L/T]
- \( f_d/f_p \) - fraction of dissolved/particulate contaminant
- \( S \) - as in Eq. 3.02
For the time derivative in the above equation, a forward difference approximation (Euler scheme) is used:

\[ C_i^{n+1} = C_i^n + \left( \frac{dC_i^n}{dt} \right) \Delta t \]  \[ 3.07 \]

The relationship states that the concentration at time \( n+1 \) is equal to the concentration at time \( n \) plus the derivative evaluated in time \( n \) times the time step, \( \Delta t \).

3.3 Food Chain Model

The food chain model is a generalized model of the uptake and elimination of toxicant by aquatic organisms. A mass balance equation written for each species in the food chain represents the flow of the chemical into and out of the organism. The following mechanisms effecting the toxicant are considered in the model:

a) sorption and direct uptake of the pollutant from the water
b) desorption and excretion of the chemical to the water
c) consumption of contaminated food through predation
d) respiration and growth rate of the organism

The mass balance equation for the base of the food chain has a form of a single reversible sorption - desorption linear relationship:

\[ \frac{d\gamma}{dt} = k_v c_o - k^r \gamma \]  \[ 3.33 \]
where:

\( \gamma \) - chemical concentration in the organism
\[ \text{uq} / \text{g(wet wt)} \]

\( k_s \) - sorption rate
\[ \text{L} / \text{g(wet wt) day} \]

\( c_d \) - concentration of dissolved toxicant
\[ \text{uq} / \text{L} \]

\( K' \) - loss rate, see Eq. 2.30
\[ \text{1/day} \]

For any higher food chain level that may accumulate toxicant via the food route as well as the water, the mass balance equation is obtained as:

\[ \frac{d\gamma}{dt} = k_s c_d + \alpha C \gamma_p - K' \gamma \]
\[ \text{(3.33)} \]

where:

\( k_s \) - rate of chemical uptake
\[ \text{L} / \text{g(wet wt) day} \]

see Eq. 2.30, Eq. 2.33

\( \alpha \) - toxicant assimilation efficiency

\( C \) - consumption rate
\[ \text{g(wet wt prey) / g(wet wt predator) day} \]

\( \gamma_p \) - toxicant concentration in a prey
\[ \text{uq} / \text{g(wet wt)} \]

The steady state solution for the lower end of the food chain is assumed (Eq. 2.33). The time variable simulation is performed for other levels.

Each species at the higher food chain level is separated into discrete age classes. The bioenergetic parameters (growth and respiration rates, food and pollutant assimilation efficiencies, predator - prey relationships, feeding
habits and migration patterns) are specified in relation to age and are assumed to be constant within any age class.

The water body to which the food chain is exposed is separated into compartments in which the toxic chemical concentration is assumed to be constant. The chemical concentrations may be specified or taken directly from the exposure part of WAS TOX.
Chapter IV

DEVELOPMENT OF THE WASTOX MODEL

The St. Clair Lake - River system is a part of the waterway connecting Lake Huron with Lake Erie. A map of the studied water bodies is given in Figure 5.

4.1 The Exposure-Concentration Model for the St. Clair River

4.1.1 Hydrodynamics

The St. Clair River is a 64 km - long waterway with a normal flow of 5240 m³/s (185,600 cfs).

For the purpose of this study, the river has been divided into two reaches. The upper reach extends downstream from Huron Lake to the head of Stag Island for a total length of 13.4 km (44,000 ft). Except for the river division by Stag Island, the upper reach forms a well-defined channel which is about 600 m wide. The flow splits around Stag Island and it is assumed that 30.3% of the total flow is distributed into the channel along the Canadian shore.

The lower reach of the river up to Lake St. Clair consists of a mainly uniform channel and a Delta. The St. Clair River Delta is divided into three channels with the follow-
ing flow distribution: 4.7% into the Channel Scarte, 42.6%
% into the South Channel, 52.7% into the North Channel. The
Delta flow distribution implemented in the model is present-
ed in Figure 6.

The exposure concentration model simulates summer condi-
tions. The water temperature is set at 20°C with a wind
speed 3 m/s.

4.1.2 Segmentation

Due to the highly industrialized and urbanized "chemical
valley" of Sarnia and the necessity to model higher concen-
tration gradients in this area, the exposure concentration
model is set up for two reaches of the St. Clair River:

a) the "fine grid" from Sarnia to Stag Island (22,000 ft
- 44,000 ft), for the upper part of the river. To
account for a difference in concentration gradients,
fine segments are used.

b) the "coarse grid" from Stag Island (44,000 ft)
to Lake St. Clair. Since this reach contains only a few
load inputs, long segments are implemented.

Longitudinal subdivision of the river into the "fine" and
"coarse" grids is presented in Figure 7.

The lateral segmentation of the St. Clair River follows
the location of river flow streamlines. For both reaches,
the river flow is divided into four segments: 5%, 21%, 24%
%, and 50% of the total flow starting from the Canadian
side of the river.
Because the major pollutant sources exist along the Canadian shoreline and the WASTOX cannot handle more than 75 segments, all segments are not identical. The four segment model is developed for the 5% flow segments along the Ontario shore, representing two water cells and two bed layers (the upper is a "moving" bed, the lower is a "stationary" layer). The two segment model, containing a single water and a bed layer, is assumed for all other segments. The vertical cross section through these two types of segments is given in Figure 12.

Figure 8 shows the physical segmentation of the "fine grid", Figure 9 its schematic representation. Since the "coarse grid" follows the same pattern in the longitudinal and lateral division through the whole reach and the spatial segmentation is drawn in Figure 7, only the schematic view of this grid is given (Figure 11).

4.1.3 Physico-Chemical Processes

According to Mills et al. (1982), the most significant process determining the fate of HCB in an aquatic system is sorption.

For both contaminants, HCB and OCS, WASTOX simulates the time variable concentrations for coarse, medium and fine sediment. The same partitioning coefficient for each type of solids is used for water and bed segments. Its magnitude is determined by Eq. 2.14.
The main contaminant sources are identified on the Canadian side in the Sarnia - Corunna area. Two types of steady load point sources are present: municipal discharges and wastes received from petroleum refining and petrochemical industries. The continuous 1985 input mass loading, for HCB and OCS, are estimated by Eq. 2.04 from data given in Tables 1 and 2. The mass loading rates and location of point sources are given in Figure 3 and Figure 11 for HCB, and Figure 10 for OCS.

All transport mechanisms described in Chapter 2.2.3 are included in the study. Two transformation processes - photolysis and hydrolysis - are considered to be unimportant for the two modelled contaminants, and are not simulated in this analysis. The chemical parameters required by the exposure concentration component are presented in Table 3.

4.2 The Food Chain Model for Lake St. Clair

The purpose of this study is to analyze a chemical accumulation by the food chain leading to the top trophic predator in the lake (sport fish). The food chain modelled in this project is similar to the system that was generated for the Lake Michigan and Lake Ontario by Connolly and Di Toro (J. Connolly, 1987). At this stage the model is generic in nature. The consensus of the 1987 Food Chain Modelling Workshop, Ontario Ministry of the Environment 1987, was that there was insufficient field data to develop a species specific food chain model for the St. Clair System.
4.2.1 Spatial Compartment

The food chain component of WASTOX is run as a post-processor to the TOXIWASP model. The same lake segmentation is used for these two models. A total of nine compartments are introduced. Eight of them are in Lake St. Clair and one is located in the St. Clair River Delta to account for the migratory nature of sport fish. The segment layout for the modelled system is shown in Figure 13. All segments are vertically similar, consisting of one water and one active bed segment.

It is assumed that dissolved and particulate chemical introduced into the two layers are completely mixed. Predicted values for the total-average HCB and OC3 concentration in water columns are presented respectively in Figure 14 and 15, for circa 1985.

4.2.2 Steady State and Age Dependent Species

The species used to define the food chain are chosen to represent the major trophic levels as well as the significant pathways of contaminant transfer. The trophic levels introduced in this model are:

- phytoplankton
- benthic invertebrates
- zooplankton
- small fish
- sport fish
Phytoplankton and benthic invertebrates, because of their ability to rapidly achieve equilibrium with the ambient chemical concentrations, are treated as steady-state species. Benthic invertebrates are assumed to consume sediment (detritus) and thus provide a vector for transferring sediment—attached contaminant to the upper levels of the food chain. Phytoplankton represents living organic material and remains in dynamic equilibrium with the dissolved chemical.

Two eight-month age classes (after Connolly, 1987) are considered for zooplankton. Detritus is considered to be the diet of this trophic level.

Small fish are represented by two three-year classes: juvenile and adult small fish. According to stomach content data, they feed mainly on zooplankton. Three age classes of sport fish are presented in the model. Two of these are single-year classes for juvenile sport fish and one is a ten-year class for adult fish. An analysis of the stomach content data set indicates that the diet of the adult sport fish consists mainly of the juvenile fish and zooplankton (MacGregor, R.B., 1987; Knight, R.L., Margraf J.P., 1964; Timmerman A.J., 1987).

Figure 16 presents the food chain structure implemented in the model and indicates the assumed predator—prey relationships among the various trophic levels.
4.2.3 Species Migration Pattern

It is assumed that the adult sport fish is a migratory species that spawns in the spring in the St. Clair River Delta. The following migratory pattern through the St. Clair Lake-River system is utilized by the model:

January - Cell No. 3 (7% of the year)
February - Cell No. 5 (7%)
March or April - Cell No. 9 (3%)
April to November - Cell No. 6 (70%)
December - Cell No. 7 (7%)

The migratory adult sport fish is exposed sequentially to various concentrations in the lake and in the spring to the high concentrations in the river (Cell No. 9).

The assumed seasonal movement of the fish is shown in Figure 17. All other levels of food chain below the top predator are assumed to permanently reside in the specific St. Clair Lake compartments.

4.2.4 Parameters

A number of input parameters are required to describe the interaction of the pollutant and each species.

Bioenergetic Related Parameters

The majority of growth rates, respiration rates and assimilation efficiencies of food are taken from the model developed by Connolly and Di Toro (1987). Lipid content of the small fish and sport fish is estimated from 1982 MOE data set for Lake St. Clair. For the lower trophic levels,
the magnitude of lipid content is determined by the calibration process.

**Toxic Chemical Related Parameters**

The bioconcentration factor (BCF) is obtained as a product of the lipid fraction of the species and the $K_{ow}$ of the compound (see Eq. 2.29). The molecular diffusivity of the toxicant in water ($D_t \text{ [ m}^2 \text{ / day ]}$) can be related to its molecular weight ($M \text{ [ g / mole ]}$) and the oxygen diffusivity by the relationship (Thomann, 1987):

$$D_t = (32 / M)^{0.5} D_L$$

where:

$$D_L = 1.81 \times 10^{-4} \text{ m}^2 \text{ / day (oxygen diffusivity)}$$

The molecular weight for OCS and HCB respectively are: 380 g / mole and 285 g / mole. Calibration of the food chain component for these two contaminants adjusts the assimilation efficiency of the pollutant at each trophic level. The values for species specific bioenergetic and toxic chemical parameters are summarized in Table 4 for HCB and in Table 5 for OCS.
Chapter V

CALIBRATION AND VERIFICATION OF THE MODEL

5.1 The Exposure Concentration Model

Since the most of the Ontario Ministry of the Environment (MOE) field measurements were taken in the Sarnia area, calibration and verification of the exposure component of WASTOX is performed for the "fine grid" of the river. Calibration of parameters effecting distribution of the contaminant or solids in a water/bed segment is executed for HCB simulation. The process of validation of the calibrated model is performed by OCS simulation. An additional verification of the model is made using the field data generated by the 1996 St. Clair River MISA pilot site investigation. The project is designed to check the effect of discharges from Sarnia chemical plants on the aquatic environment in the St. Clair River, particularly in the vicinity of the Ontario shoreline. The effluent and ambient samples at half-hour intervals were collected for period of seven hours in May, July and October of 1986. In a separate study WASTOX is implemented to model six contaminants: octachlorostyrene (OCS), hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), hexachloroethane (HCE), carbon tetrachloride (CTC) and perchloroethylene (PCE). The results for the HCB spring simulation are presented in this study.
5.1.1 Data Analysis

Solids

Suspended solids concentration is estimated from St. Clair River field measurements (1986 St. Clair River MOE study). The concentration of 9.0 mg/L is defined for upper water cells in the 5% streamline along the Canadian shore. The initial concentration for all other upper water segments is equal 6.3 mg/L. Analysis of grain size distribution determines the following solids composition: 70% consists of fine fraction and 22% of medium particle sizes. Due to lack of measurements, the suspended solids concentration in lower water layers is assumed to be 15 mg/L (10% coarse fraction, 20% medium, 70% fine).

The solids concentrations in the bed are assigned similar to those values introduced by Connolly, 1987, for Lake Ontario. The following concentrations are used in the model: 260,000 and 500,000 mg/L for the "moving" and "stationary" bed, respectively. The same size distribution is assumed for both bed layers: 15% coarse material, 60% medium and 5% fine. Estimated thickness of the upper and lower layers is 10 cm. Several factors were considered in determining these depths:

a) where bedload is present, the observed ripple or dune highs are in the range 5 to 15 cm;

b) bioturbation, where it exists, can extend to 15 cm;

c) alluvial sediment depths vary from less than 1 cm to more than 30 cm.
To model the response of the bed to the contaminant loading, the bed layer depths in the centre of the river are reduced to 2 cm; a decrease in the layer volume lowers the toxicant "dilution" in the segment.

**Contaminant**

A non-contamination condition for the whole river is assumed at the beginning of each simulation. The continuous boundary concentrations matching field measurements are introduced to the system at the upstream boundary. For both pollutants, these concentrations vary laterally and are in range of $0.077 - 0.011 \text{ng/L}$ for HCB and $0.01 - 0.005 \text{ng/L}$ for OCS.

5a1.2 Calibration Procedure

The first step in the calibration process is verification of settling, resuspension and sedimentation velocities. The estimate of the sedimentation velocity ($1 \text{mm/year}$) and approximate values for settling and resuspension velocities are obtained from work by Ibrahim (1986). With the assigned sedimentation velocity, both the settling and resuspension velocities are fixed to match observed solids concentration in the water and bed segments. From this procedure the settling velocity of $9.3 \text{ m/day}$ for the fine and coarse material ($18.6 \text{ m/day}$ for coarse sediment) and the resuspension velocity of $20 \text{ cm/year}$ are generated. Simultaneously at this stage, the horizontal transport is considered. Calibration process defines the coarse sediment transport rate of $0.5 \text{ t/day/m}$ for the St. Clair River.
In the next step, the fraction of organic carbon for each type of sediment is obtained. This is done by matching the computed adsorbed and total HCB concentrations to measured concentrations in the river. The following organic carbon fractions are assumed in the calibration of the model:

- fine sediment - 7%
- medium sediment - 5%
- coarse sediment - 3%

The lateral dispersion coefficient is the last important parameter defined by the calibration process. The approximate values of this coefficient were obtained following the k-E model (McCorquodale and Yuen, 1987). The modified values are determined for each lateral segment interface by comparison of predicted pollutant concentrations to the survey data, focusing on the lateral variation of contaminant distribution.

5.1.3 Simulation Results

Figures 18 and 19 show the predicted total HCB concentration (ng/L), adsorbed chemical concentrations (µg/kg) in water segments and solids adsorbed concentration in bed layers for the "fine grid" and "coarse grid", respectively. Figures 20 and 21 present the same results for the OCS simulation.

The modelled by WASTOX and measured (MOE) HCB total longitudinal concentrations in water segments, along the Canadian shoreline for the "fine grid", are shown in Figure 22.
for the entire river in Figure 23 (see Fig. 24 and Fig. 25 for OCS concentrations).

Due to availability of survey data along the Ontario side of the St. Clair River, the comparison of modelled and observed pollutant concentrations in the bed is also given for near-shore segments. Figure 26 and Figure 27 show sediment adsorbed concentrations in the upper bed layer of the entire river for HCB and OCS, respectively. The predicted by TOXIWASP HCB concentrations (McCorquodale, Ibrahim, 1986) are superimposed on Figure 23 and 26. The cross sectional HCB concentrations in water segments are plotted in Fig. 23. The figure indicates a steep lateral gradient near the Canadian shore.

The response of the river to HCB discharges is assessed by the 1986 MISA investigation. The predicted by WASTOIA water concentrations in segments along the Canadian shore-line show good agreement with the ambient concentrations obtained by sequential sampling. Figures 29, 30 and 31 illustrate these comparisons for segment No. 5, No. 10, and No. 12, respectively. It should be mentioned, that in order to model the contaminant plume in the river, the lower water segment is treated as a near-shore water cell with decreased dispersion.
5.2 The Food Chain Model

5.2.1 Calibration Procedure

Calibration of the food chain component of WASTOX involves defining the following parameters: assimilation efficiency of food, assimilation efficiency of chemical in food and fraction of lipid content of the organism. Adjustment of the lipid content is performed for species below the sport fish trophic level. It should be pointed out, that modification of lipid percentage in species is equivalent to changing the bioconcentration factor (BCF) and consequently the excretion rate of the organism K (see Eq. 2.29 and Eq. 2.32). Since the concentration for phytoplankton is obtained by a simple sorption - desorption equation (Eq. 2.32), adjustment of the BCF value is essential for this trophic level. For the higher levels of the food chain, the uptake rate is calculated from the respiration rate of the organism (independently of BCF); therefore an increase in the bioconcentration factor causes decrease in the excretion rate (Eq. 2.32).

The lipid content fraction for benthic invertebrates is determined by the best fit with the observed clam concentrations in the lake.

Due to severe field data limitations, calibration of the food and chemical assimilation coefficients is carried out simultaneously matching the measured pollutant concentration in the top predator.
The calibration process of the food chain model is performed by predicting the response of the specific levels of food chain exposed to HCB concentration in a water body (Figures 32 and 44). For OCS simulation, the magnitudes of the food and contaminant assimilation efficiencies are modified to get a good agreement with the observed data (Figures 33 and 43). The values assigned to the calibrated coefficients are presented in Table 4 for HCB and Table 5 for OCS simulation.

5.2.2 Simulation Results

The available field data on species in Lake St. Clair have a number of limitations:
- measured toxicant concentrations are obtainable only for two species: clams and adult sport fish;
- monitoring of fish concentrations is mainly restricted to eastern basin of the lake (Mitchell Bay);
- lack of information on sport fish migratory patterns.

Due to these data set limitations and the fact that the study is focused on toxicant accumulation in the higher trophic levels, the food chain model considers two possibilities:

a) the top predator — adult sport fish — is assumed to be a migratory species that moves through the lake and spawns in the St. Clair River or its Delta;

b) the top predator is a non-migratory species; it remains in a specific compartment of the lake or river.
All other food chain levels in the above submodels are identical. Several scenarios are implemented for each submodel.

5.2.2.1 Scenarios for the Stationary Sport Fish

The main interest of the modelling effort is to predict fish concentrations in two cells of the St. Clair River - Lake system: cell No. 5 and cell No. 9 (Figure 13). The compartment No. 5 represents the location of sampling stations. The river cell No. 9, has the highest exposure concentrations in the system.

Long Term Exposure

The effect of long contaminant exposure is modelled by applying the constant 1985 - level load for the period of five years. Predicted concentrations for the adult sport fish are presented in Figure 32 for HCB and in Figure 33 for OCS. Irregularities in the shape of curves may reflect changes in food habits as the fish graduates to a new "age" class. Adult sport fish concentrations, averaged over a year, for all compartments used in the study are shown in Figure 34 and Figure 35. The bar graph (Figure 35) presents predicted OCS and HCB concentrations for all trophic levels of the food chain.

Decline in HCB Load in 1986

In 1986, the HCB load declines to about 77 lb./day or by 78% compared to 3.5 lb./day in 1985. The simulation is started with the previously modelled HCB concentration in
the fish for December 1985. It is carried out for a year assuming the constant load. To demonstrate the relationship between predicted and measured fish concentrations, as well as to show the scatter in the field data set, the mean measured concentration and standard deviation are plotted in Figure 37.

**OCS Load Decline**

Concentrations in adult sport fish are predicted assuming two conditions:

a) the bed of the system remains contaminated;

b) there is no toxicant in the bed.

The above two cases are presented for cell No. 3 in Figure 38 and for cell No. 5 in Figure 39. These two plots show the significance of benthic animals in transferring the pollutant to the higher trophic level.

5.2.2.2 Migratory Sport Fish

The adult sport fish are free to relocate throughout the St. Clair Lake - River system as described in Section 4.2.3 "Species Migration Pattern". Figure 40 presents the comparison of HCB simulation results for the migratory / stationary fish (see Figure 41 for OCS). The migratory species is "followed" through the specific compartments of the model. The pollutant concentration in the stationary fish is shown for the same cells.
5.2.2.3 Benthic Organisms

To illustrate the acceptable agreement of modelled and measured pollutant concentrations at lower levels of the food chain model, the Great Lakes Institute data on clams is used. The location of sampling stations is given in Figure 42. Figure 43 and Figure 44 compare concentrations in "free" clams (Muncaster B., 1987) with predicted benthic invertebrate concentrations for OCS and HCB respectively.
Chapter VI

DISCUSSION

6.1 The Exposure Concentration Model

The fine and coarse grid versions of the modified WASTOX model were implemented to model the temporal and spatial variations in HCB and OCS concentrations in the St. Clair River.

The predicted water concentrations in the "fine grid" show very good agreement with observed values for both contaminants (Fig. 22 and Fig. 24). Due to the averaging effect of the model, the very high concentrations existing in outfall areas cannot be simulated. Analysis of the pollutant concentration in water segments for the "coarse grid" (Fig. 23 for HCB and Fig. 25 for OCS simulation) indicate an overestimation of WASTOX modelled values compared to MOE measurements; however, only three sampling stations are available for the whole "coarse" reach of the river.

Figures 26 and 27 show the longitudinal variation of adsorbed chemical concentrations in bed segments for the entire St. Clair River. Again, the peak concentrations cannot be reproduced by the model: the main WASTOX assumption of the well mixed segments is a poor one in the vicinity of pollutant point-sources. These plots demonstrate a very
good agreement of predicted mean concentrations with the field observations.

The graphical presentation of HCB and OCS WASTOX simulation results for two reaches for the St. Clair River (Figures 18, 19, 20, 21 and Fig. 28) indicates that plume from the multiple sources in the Sarnia area is mainly confined to a narrow band along the Canadian shoreline and empties via the Channel Écarte and the South Channel into Lake St. Clair.

Estimation of the HCB mass entering and leaving the St. Clair River shows that 20% of the total HCB load is lost in the river due to various processes affecting the pollutant in this water body. Volatilization is the most significant loss mechanism for HCB. A mass balance calculation for OCS indicates that 25% of the total loading is lost, mainly due to toxicant accumulation to the sediment.

4.2 The Food Chain Model

The developed food chain component of WASTOX generates results comparable with the observed data, as shown in Figures 32, 33, 43 and 44. Due to limitations in available field data, the comparison of monitored and predicted concentrations is mainly restricted to two trophic levels: adult sport fish and benthic invertebrates.

According to 1985 MOE measurements (Mitchell Bay), the mean HCB and OCS concentrations in adult sport fish respectively are: 7.4 ng/g wet wt and 15.9 ng/g wet wt. The
model shows good agreement with modelled body burdens for two introduced submodels in which a) the top predator is treated as stationary fish; b) the sport fish is considered to be migratory species. For the first case the averaged over the year HCB and OCS concentrations are presented in Fig. 34 and Fig. 35, respectively. The mean concentrations in cell No. 5 (representing the sampling area) are: 7 ng/q wet wt for HCB and 19.3 ng/q wet wt for OCS. Results of the five year HCB and OCS simulations, for the same water segment, are demonstrated in Fig. 32 and Fig. 33. For both contaminants, assuming constant chemical exposure in a water column, the highest concentrations in non-migratory fish occur in the winter. The seasonal OCS concentration variations in adult sport fish are about ±40% compared to the mean OCS concentration level. For the HCB simulation temporal variations are in range of ±10%. The elevated mean concentrations in migrating fish reflect its exposure to high water concentration in the St. Clair River segment. For migratory species, the mean HCB concentration is in order of 8 ng/q wet wt. for OCS in order of 25 ng/q wet wt.

Water temperature is one of important factors affecting the body burdens of HCB and OCS in adult sport fish. Therefore, the fish chemical concentrations should be monitored on seasonal bases.

The model predicts very rapid response in sport fish concentration adjustment due to change in water exposure level.
Both, concentration increase and decrease, occur very fast particularly for HCB simulation (see Fig. 40; two plots are nearly identical). 78% reduction in HCB load into the lake causes 75% decline in fish body burden within the three month period (Fig. 37). Analysis of Fig. 32 suggests that HCB concentration at the beginning of simulation reaches about 80% of its mean value. For OCS simulation, the species concentration variation due to change in exposure level is more gradual (Figures 33 and 41). However, introducing the sport fish with average OCS concentration into uncontaminated water produces 63% concentration reduction over 30 days (Fig. 38, Fig. 39). The effect of too rapid adaptation to changed exposure conditions can be caused by overestimation of excretion/uptake rates for the top predator. Also the diffusion coefficient may be too high. The uptake rate of toxicant from water is estimated by the rate of transfer of chemical across the gills. Its magnitude is assumed to be proportional to the pollutant diffusion coefficient in water. However, the water is not the only barrier in the toxicant transfer process. A greater resistance to the pollutant transfer is expected in gills than in water. To obtain more realistic uptake rates, an overall (for water and gills) transfer coefficient should be generated, similarly to the overall transport parameter in the "two film" theory for volatilization. The more reasonable concentration increase and decrease rates for CCS are a result of the low-
er OCS diffusivity coefficient. Since the respiration rate is expressed as a function of this coefficient, the estimated pollutant uptake and excretion rates are slower than for HCB. The food chain model is very sensitive to the contaminant diffusivity coefficient.

Benthic invertebrates show good agreement with reported field values for OCS and HCB simulations (Fig. 43 and Fig. 44 respectively). The averaged over a year HCB and OCS concentrations in all food chain trophic levels are presented in Fig. 36. The bioaccumulation rate in a predator due to pollutant uptake via food routes is greater for OCS than HCB.

The bottom sediment represents a significant source of contaminant for adult sport fish. With decreased loads to the system, it accounts for approximately 30% of the body burden for OCS (Fig. 38 and Fig. 39).

In the food chain model a distinction can be made between the fish that feed on the bottom of the water body and those that feed on its surface. Thus, the chemical concentrations can be modelled for aquatic bottom and surface feeders.
Chapter VII

CONCLUSIONS

The exposure concentration component of WASTOX is a general, flexible water quality modelling framework for toxic pollutants and can be applied to many types of natural water systems. The model predicts longitudinal and lateral variations in depth averaged concentrations in the St. Clair River. It represents average but not highly localized conditions in water and bed segments. The model indicates a good agreement between the predicted toxic chemical concentrations and the averaged field measurements. For the fine water cells along the Canadian shoreline, modelled HCB and OCS concentrations are in the range 57.7 ng / L to 55.3 ng / L and 2.56 ng / L to 3.24 ng / L, respectively. The corresponding mean measured concentrations in these segments are: 66 ng / L and 5.5 ng / L. Due to high concentration gradients reported by the field data, the estimated magnitudes of standard deviation are high. The standard deviation for the HCB simulation is 48.7 ng / L (73 % of the average concentration), for OCS simulation 4.1 ng / L (75 %). The predicted HCB and OCS contamination levels for the downstream water cells of the “fine grid” correspond well to the mean observed values of 37 ng / L and 1.2 ng / L, respectively.
The modelled dCB concentrations vary from 50.7 ng/L to 32.9 ng/L while OCS concentrations from 2.98 ng/L to 1.97 ng/L.

The comparison of model predictions with the bed measurements indicate that WASTOX gives a good indication of the bed contamination in the river. For the HCB simulation, an acceptable agreement with TOXIWASP generated concentrations in water and bed segments was found.

Due to the averaging effect of the model, high concentration gradients cannot be reproduced by WASTOX. This exposure concentration model limitation is usually insignificant for food chain simulations. Since the biota rate of concentration change is slow (in order of weeks), the localized or instantaneous exposure concentration variation in a water column doesn't affect a species toxicant accumulation. However, peak contaminant concentrations can be important in assessing the lethality of the exposure for aquatic organisms.

The exposure concentration component has a few disadvantages that limit its application. Restricted number of segments and the cell averaging effect in modelled concentrations means that the model cannot accurately represent the conditions near an outfall. In this area of high concentration gradients, predicted concentrations are underestimated. An attempt to overcome this difficulty by representing a water body by fine segments increases significantly the computation time and makes the model less efficient.
The WASTOX model does not make a distinction between the solids partition coefficient in a water and a bed column. The available version of the exposure concentration component is set up as a time-variable model which makes obtaining a steady-state solution computationally inefficient.

The developed food chain component of WASTOX reproduces magnitude of HCB and OCS contamination reported in Lake St. Clair clams and sport fish. The mean measured HCB and OCS concentrations in sport fish respectively are: 7.4 ng/g wet wt and 15 ng/g wet wt. The estimation of the standard deviations (6.4 ng/g wet wt for HCB, 9.6 ng/g wet wt for OCS simulation) indicates the greater dispersion of OCS field measurements than HCB field data. The monitored concentrations correspond well with model generated body burden levels for both contaminants assuming that the top predator is migratory and/or stationary fish. The HCB and OCS mean concentrations for stationary sport fish are: 7 ng/g wet wt and 19.3 ng/g wet wt, and for the migratory species: 3 ng/g wet wt and 25 ng/g wet wt.

The model produces OCS body burdens in benthic invertebrates in the range 0.7 ng/g wet wt to 4.1 ng/g wet wt (field data ranges from 1 ng/g wet wt to 3.3 ng/g wet wt). For the HCB simulation predicted concentrations are: 0.6 ng/g wet wt to 3.3 ng/g wet wt (field measurements vary from 1.2 ng/g wet wt to 4.3 ng/g wet wt).
However, at this stage the food chain component cannot be considered as a verified, reliable framework for toxic pollutant modelling in aquatic species. This is mainly due to lack of bioenergetic and toxicant related parameters that are estimated from approximate relationships in the literature. The calibration process in this case is uncertain considering limitations in available field measurements and information on species characteristics (e.g. migratory patterns). Implementation of the more complete field data set including species bioenergetic characteristics (respiration and excretion rates, bioconcentration factor) would verify the organism intake and loss rates as well as check accuracy of the model formulations. The model predicted concentrations for intermediate food chain levels should be confirmed by field data. Monitoring data is required to test seasonal concentration variation throughout a year. If the significant temporal concentration variations in sport fish are confirmed by the field measurements, they should be indicated in fish consumption health guidelines.

The available version of the food chain model limits to three the number of prey of species in a prey-predator relationship. Benthic invertebrates must be considered as steady-state species.
**Figure 1:** Processes influencing the toxicant in aquatic environment. (After McCorquodale and Ibrahim, 1986)
Figure 2: Sediment sorption – desorption mechanism. Fraction of dissolved chemical in function of $K_{ow}$ and organic carbon content of sediment (after Ambrose and Connolly, 1987).
Figure 3: Sediment sorption - desorption mechanism. Relationship between fraction dissolved of organic chemical and log suspended solids concentration. Numbers on curves in figure are equal to $\log K_p$ [L/kg] (after Thomann and Mueller, 1987).
PROCESS

1) DEPOSITION OF SOLIDS
2) SCOURING OF SOLIDS
3) NET SEDIMENTATION
4) HORIZONTAL BED MOVEMENT
5) DIFFUSION OF DISSOLVED CHEMICAL

MASS FLUX TERM

\[
\begin{align*}
\frac{W_s}{h} & f_p C_{Tw} \\
\frac{W_u}{h} & f_p C_{Tb} \\
\frac{W_d}{h} & f_p C_{Tb} \\
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\frac{EA}{l} & (f_{db} C_{Tb} - f_{dw} C_{Tw})
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Figure 4: Fluxes of toxic chemical associated with bed.
**Figure 5:** St. Clair River - Lake study area.
Figure 6: Flow distribution in St. Clair River Delta.
Figure 7: Definition of reaches in St. Clair River.
Figure 8: Segmentation of "fine grid" of St. Clair River.
Figure 9: "Fine grid" flow pattern (showing locations of HCB loads).
Figure 10: "Fine grid" flow pattern (showing locations of OCS loads).
Figure 11: "Coarse grid" flow pattern (showing locations of MC3 loads).
Figure 12: Vertical arrangement of segments.
Figure 13: cell layout for food chain model.
Figure 14: Predicted total HCs concentrations in water segments. Concentrations (ng/l) are based on 1985 loads (MOE).
Figure 15: Predicted total OCS concentrations in water sediments. Concentrations (ng/l) are based on 1965 loads (MO2).
NOTE: DECIMAL FRACTIONS INDICATE DISTRIBUTION OF PREDATOR DIET.

Figure 16: Food chain structure and prey-predator relationships.
Figure 17: Assumed migratory pattern of adult sport fish.
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**Figure 18:** Predicted HCB concentrations — "fine" grid. Concentrations are based on typical loads in 1983 (MOE).
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**Figure 19:** Predicted HC3 concentrations - "coarse grid". Concentrations are based on typical loads in 1985 (MOE).
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### Water and Bed Concentrations

- \( C_{TOT} \) [ug/hr]
- \( C_{SS} \) [ug/kg]
- \( C_{BED} \) [ug/kg]

**Figure 20**: Predicted CCS concentrations - "fine grid". Concentrations are based on typical loads in 1965 (MOE).
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**Figure 21:** Predicted OCS concentrations - "coarse grid". Concentrations are based on typical loads in 1985 (MOE).
HCB longitudinal water concentrations - "line grid". Comparison of predicted and measured HCB longitudinal concentrations in water segments (1985 loads, MOE).

- WASTOX
- FIELD DATA
St. Clair RIVER - WASTOX - HCB
HCB Concentration in WATER

HCB longitudinal concentrations - "fine grid" and "coarse grid". Comparison of predicted and measured HCB longitudinal concentrations in water segments (1985 loads, KOE).

- WASTOX
- FIELD DATA
- TOXIWASP

Figure 23: THOUSAND FEET
CHEMICAL CONC. IN NANOGRAM/LITRE
OCS longitudinal water concentrations - "fine grid". Comparison of predicted and measured OCS longitudinal concentrations in water segments (1985 loads, MO2).

- WASTOX
- FIELD DATA

Figure 24:

THOUSAND FEET
St. Clair RIVER - WASTOX - OCS
OCS Concentration in WATER

OCS longitudinal concentrations - "fine grid" and "coarse grid". Comparison of predicted and measured OCS longitudinal concentrations in water segments (1985 loads, NUE).

- WASTOX
- FIELD DATA

Figure 25:
HCB longitudinal bed concentrations. Comparison of predicted and measured HCB longitudinal concentrations in bed segments in St. Clair River (1985 loads, MOE).

- WASTOX
- FIELD DATA
- TOXIWASP
St. Clair RIVER - WASTOX - OCS
OCS Concentration in BED

OCS longitudinal bed concentrations: Comparison of predicted and measured OCS longitudinal concentrations in bed segments in St. Clair River (1985 loads, MOE).

- WASTOX
- FIELD DATA

Figure 27: Thousand Feet
St. Clair RIVER - WASTOX - HCB

HCB Concentration in WATER

HCB lateral water concentrations. Comparison of predicted and measured HCB lateral concentrations in water segments (1985 loads, MOE).

Water segments No. 17, 19, 20 and 21.

- WASTOX
- FIELD DATA

Figure 2b: DIST. FROM CAN. SHORE (M)
St. Clair River - WASTOX - Fine Grid
HCB Concentration in Spring

SEGMENT 5
WASTOX □
MOE ▲

HCB water concentrations in cell 130.5
1986 sequential sampling.

Figure 22:
Time in Hours
HCB water concentrations in cell No. 19 - 1986 sequential sampling.
St. Clair River - WASTOX - Fine Grid
- HCB Concentration in Spring

SEGMENT 12
WASTOX ■
MOE ▲

HCB water concentrations in cell No. 12 - 1995 sequential sampling.
OCS concentrations in adult sport fish (cell No. 5). 1985 loads (HDE).
Figure 34: Modelled HCB concentrations in stationary adult fish. 1965 loads (MOE).
Figure 25: Modelled OCS concentrations in stationary adult fish. 1985 loads (MOE).
**Figure 36:** HCB and OCS concentrations in species included in food chain. 1985 loads (MOE).
LAKE St. Clair - WASTOX - HCB
HCB Conc. in ADULT SPORT FISH - 1986

HCB concentrations in adult sport fish - 1986.

- WASTOX
- FIELD AVERAGE
- STANDARD DEVIATION

Figure 2:
CHEMICAL CONC. IN NANOGRAM/GRAM
TIME IN DAYS
0 100 200 300 400
OCS concentrations in adult sport fish - cell No. 3, 1985 loads (MOE).

- CHEMICAL IN BED
- NO CHEMICAL IN BED

**Figure 36:**

**Time in Days**

**Chemical Conc. in Nanogram/gram**
OCS concentrations in adult sport fish - cell No. 5, 1985 loads (405).

- CHEMICAL IN BED
- NO CHEMICAL IN BED
LAKE St. Clair - WASTOX - OCS
OCS Conc. in ADULT MIGR./STAT. SPORT FISH

- MIGRATORY FISH
- STATIONARY FISH

Figure 41:
TIME IN DAYS
Figure 42: Location of sampling stations for clams analysis.
OCS concentrations in benthic invertebrates and "free" clams. 1985 loads (MOE).

Figure 43: OCS Concentration in 'FREE' CLAMS/BENTHICS

- WASTOX
- FIELD DATA
LAKE St. Clair - WASTOX - HCB
HCB Concentration in 'FREE' CLAMS/BENTHICS

HCB concentrations in benthic invertebrates and "free" clams. 1985 loads (MOE).

- WASTOX
- FIELD DATA

Figure 22:

STATION NUMBER
Table 1: HCB Industrial Point Sources into St. Clair River

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(Reference: McCorquodale and Ibrahim, 1965)
Table 2: OCS Industrial Point Sources into St. Clair River

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### Toxic chemical parameters required by Exposure Concentration Model

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Parameter values for HCB food chain simulation.

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$\log K_{OW} = 5.5$

Diffusivity = $7.03 \times 10^{-6}$ cm$^2$/s
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meter values for OCS food chain simulation.

| \( \rho \) \( s/cm \)
| \( \nu \) \( s/cm \)
| \( \omega \) \( s/cm \)
| \( \delta \) \( s/cm \)
| \( \phi \) \( s/cm \)
| Lipid content
| BCF
| BCF
| Food assim. effic.
| Toxicant assim. effic.
| Fraction dry weight
| IA | RHO | OMGA | DLTA | PHI | 1. | 15.8 | --- | --- | .1 |
| 0. | 0. | --- | ----- | 0. | 1. | 15.8 | .3 | .35 | .2 |
| 0. | 0. | 0. | 0. | 0. | 1. | 15.8 | .8 | .35 | .25 |
| 0. | 0. | 0. | 0. | 0. | 1. | 15.8 | .8 | .25 |
| 0. | 0. | 0. | 0. | 0. | 1. | 15.8 | .8 | .25 |

\( \log K_{\text{OW}} = 6.2 \)

Diffusivity = \( 6.08 \times 10^{-6} \ \text{cm}^2/\text{s} \)
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